92. *Migration of Acyl Groups during Hydrogenation of Triglycerides.*

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It is shown that during hydrogenation of mixtures of glycerides at 180° in presence of nickel on kieselguhr interchange of acyl groups between the molecules of the triglycerides present proceeds at a comparatively slow rate, about 5% of the total glycerides present possibly being involved per hour of exposure to the hydrogenation conditions. Difficulties in the separation and analysis of the products render the results more qualitative than quantitative in character, but it is shown that, under the experimental conditions, the interchange of acyl groups proceeds between completely saturated glycerides, *i.e.*, is not dependent on concurrent hydrogenation. The change appears to take place more readily between mixtures of simple triglycerides (tristearin, tripalmitin, etc.) than in the case of mixed triglycerides (*e.g.*, oleodipalmitin, palmitodiolein).

The results are considered in their bearing on procedure employed in the determination of the proportion of tri-C_{18} glycerides in fats by hydrogenation, followed by estimation of tristearin in the products, and on analytical difficulties encountered in the latter method. It is recommended, when use of this procedure is essential, that the hydrogenation should be effected at low temperatures (65—70°) by means of Raney nickel, platinum or palladium catalysts, and as rapidly as possible.

The possible effect of time of hydrogenation, involving variations in the degree of acyl interchange, on the texture or other properties of technically hydrogenated fats is indicated.

It is well known that at temperatures above 250°, in presence of a suitable catalyst (alkali hydroxide or ethoxide, certain salts of tin, cadmium, zinc, etc.), the acyl groups of a mixture of triglycerides may migrate and a new mixture of mixed triglycerides will be produced (" inter-esterification "). Acyl migration may take place between molecules of different triglycerides or of the same triglyceride. For example, a mixture of tripalmitin and tristearin may undergo partial intermolecular change such as that represented by $G(P_3) + G(S_3) \longrightarrow G(P_2S) + G(PS_2)$,* whilst a mixed triglyceride such as palmitodistearin may suffer rearrangement of acyl groups of the nature : $2G(PS_2) \longrightarrow G(P_2S) + G(S_3)$. Oda (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 331) studied the effect of heating various mixtures of fats in hydrogen at 200° in presence of small proportions of potassium carbonate; with mixtures of olive or linseed oil with a hydrogenated fat he found no evidence of interesterification, but when mixtures of either olive or linseed oil with coconut oil were similarly treated as much as 30% of the coconut oil glycerides appeared to have undergone intermolecular change with acyl groups from the more unsaturated component of the mixture. Steger and van Loon (privately communicated) have informed us that they found that after heating a mixture of triolein and tristearin at about 200° in an inert atmosphere in presence of nickel catalyst the proportion of tristearin in the product was considerably less than that in the original mixture.

It has therefore been desirable to ascertain to what extent migration of acyl groups

* $G = C_3H_5\leqslant$; $P = C_{15}H_{31}\cdot CO\cdot O\cdot$; $S = C_{17}H_{35}\cdot CO\cdot O\cdot$.

occurs during hydrogenation of triglyceride mixtures at 180° in presence of nickel–kieselguhr catalyst, especially since this procedure has in some instances been used in former work in this laboratory in order to ascertain the proportion of tri-C_{18} glycerides in a natural fat (or fraction thereof), this being estimated from the amount of tristearin observed in the hydrogenated product. To this end mixtures of synthetically prepared triolein and tripalmitin, oleodipalmitin, palmitodiolein or trilaurin have been hydrogenated at 180° and the triglycerides present in the products have been examined.

The analysis of mixtures of tristearin with palmitodistearin, dipalmitostearin and tripalmitin presents considerable difficulty. The procedure adopted (cf. Hilditch and Jones, *J. Soc. Chem. Ind.*, 1934, **53**, 13T; Hilditch and Stainsby, *ibid.*, 1936, **55**, 95T) has been to separate the almost completely hydrogenated glycerides by systematic crystallisation from anhydrous ether into a number of fractions and to calculate the composition of each fraction (as a binary mixture of tristearin and palmitodistearin, or of palmitodistearin and dipalmitostearin, etc.) from its saponification equivalent or its component fatty acids. Great accuracy in the determination of the saponification equivalents of the fractions is essential, since the difference between those of successive members in the series (*e.g.*, tristearin 296·7, palmitodistearin 287·4) is but small. Latterly, when the quantity of material permits, it has been preferred to determine the proportion of the component acids present by means of ester-fractionation.

Apart from the comparatively large influence of possible small errors in the determined saponification equivalents, however, the validity of the assumption that only binary mixtures of the triglycerides have been obtained by the crystallisation procedure employed requires careful consideration. The solubilities of, for example, tristearin, palmitodistearin, dipalmitostearin and tripalmitin in ether are not widely dissimilar, and complete separation into binary mixtures, although probably possible in many instances, is not by any means certain to be attained. A fraction of triglycerides with a mean equivalent somewhat above that of palmitodistearin (287·4) might still contain some dipalmitostearin, but from calculation on the basis of a mixture of tristearin and palmitodistearin would appear to contain no dipalmitostearin, with more palmitodistearin and less tristearin than is actually present. Similarly, a fraction of somewhat lower equivalent than 287·4 would thus appear to contain less dipalmitostearin and again more palmitodistearin than the truth, whilst small quantities of tristearin possibly present would be overlooked. Any error due to imperfect separation by the crystallisation procedure followed may therefore lead, in many instances, to a calculated composition in which less tristearin is found than is actually present in the hydrogenated fat, and thus suggest more " inter-esterification " than may actually have taken place. (In one special case, namely, the possible resolution of two molecules of palmitodistearin into tristearin and dipalmitostearin by " inter-esterification," the error due to any incomplete separation into binary mixtures, leading as above to an apparent content of palmitodistearin greater than that actually present, may lead to the conclusion that less acyl migration has occurred than in fact is the case.)

Control experiments in which approximately equal amounts, respectively, of tristearin and tripalmitin, or of tristearin and dipalmitostearin, were merely melted together, and the respective binary mixtures then submitted to fractional crystallisation from ether (followed by ester-fractionation analyses on the glyceride fractions obtained) have indeed indicated that the results are far from satisfactory :

Binary mixture of glycerides.	Tristearin (% mol.). Actual.	Observed.
Tristearin and tripalmitin	48·1	36·4
Tristearin and dipalmitostearin	52·1	34·1

On the other hand, Hilditch and Jones (*loc. cit.*) tested the crystallisation procedure somewhat differently by determining the tristearin content of (i) a hydrogenated cottonseed oil and (ii) a mixture of 79·6% of this hydrogenated oil with 20·4% of added tristearin : the observed content of tristearin in the mixture (39·6%) was close to the calculated figure (40·0%, the observed tristearin content of the hydrogenated cottonseed oil being 24·6%). Similarly, they found that addition of 20% of tripalmitin to hydrogenated olive oil did not interfere with the determination of tristearin by this method. The results quoted

above, therefore, may have some connection with the conclusion arrived at on other grounds by Hilditch and Thompson (*J. Soc. Chem. Ind.*, 1937, **56**, 434T), namely, that the analytical method used cannot be regarded as trustworthy for mixtures of saturated triglycerides which contain between about 50% and 70% of tristearin, but that it gives satisfactory results with mixtures containing below 40% or above 75% of tristearin.

In the present work, accordingly, we have not relied solely on the results of crystallisation of completely hydrogenated mixtures of triolein with tripalmitin, oleodipalmitin or palmitodiolein, but have also studied the hydrogenation of mixtures of triolein and trilaurin (leading to a mixture of tristearin and trilaurin, the latter glyceride being comparatively easily separated by repeated crystallisations from ether). Finally, we have obtained conclusive proof of the occurrence in a minor degree of acyl migration during hydrogenation at 180° by experiments in which (i) the hydrogenation of a mixture of triolein and tripalmitin was interrupted prior to completion, (ii) a similar mixture was heated at 180° in presence of catalytic nickel but in an atmosphere of carbon dioxide; in each of these experiments it was found that the product contained a small, but definite, proportion of mixed glycerides in which both palmitic and oleic groups were present.

I. *Mixtures of Triolein (Tristearin) and Tripalmitin.*—These include the analytical control test mentioned above, and two experiments in which approximately equimolecular quantities of (*a*) triolein and tripalmitin, and (*b*) tristearin and tripalmitin, were agitated in presence of catalytic nickel–kieselguhr with hydrogen at 180°. The products were intensively crystallised from ether, and the crystal fractions analysed, their compositions being calculated from the results on the assumption that binary mixtures had been obtained. The data are in Table I.

TABLE I.

Conditions of experiment.	Duration of expt.	Original mixture, % (mol.).	Found by analysis in product. Tristearin, % (mol.).	Tripalmitin, % (mol.).
Analytical control-mixture	—	48·1% tristearin, 51·9% tripalmitin	36·4	35·1
Hydrogenation conditions at 180°	9 hours	48·7% tristearin, 51·3% tripalmitin	15·3	25·3
Hydrogenation conditions at 180°	9 hours	49·7% triolein, 50·3% tripalmitin	25·2	

In spite of the unsatisfactory nature of the analytical methods avail[illegible] these figures indicate that appreciable inter-migration of acyl groups takes place at [illegible] in presence of nickel catalyst, and that this process is effected between tristearin and tripalmitin molecules, irrespective of whether the tristearin is being concurrently produced in the system as the result of hydrogenation of triolein. (The triolein in the actual hydrogenation experiment had been practically completely converted into tristearin, the iodine value of the product being 0·9.)

II. *Mixtures of Triolein and Oleodipalmitin, or of Tristearin and Dipalmitostearin.*—Similar experiments to the foregoing were carried out with the following results:

TABLE II.

Conditions of experiment.	Duration of expt.	Original mixture, % (mol.).	Tristearin found in product, % (mol.).
Analytical control-mixture	—	52·1% tristearin, 47·9% dipalmitostearin	34·1
Hydrogenation at 180°	10·5 hours	25·3% triolein, 74·7% oleodipalmitin	21·0

In this hydrogenation experiment (iodine value of product 2·3) the proportions were chosen so that the total amounts of oleic and palmitic groups present in the mixture were approximately equimolecular. This brings the original content of tri-C_{18} glycerides within the range in which it has previously been found that the method of analysis is fairly trustworthy, and it therefore appears that some acyl interchange takes place, but apparently less than in the case of mixtures of the simple triglycerides triolein (tristearin) and tripalmitin. The probability of some acyl migration was confirmed by the observation

that the more soluble crystal-fractions obtained from ether possessed equivalents lower than that of dipalmitostearin, suggesting the presence of about 2% of tripalmitin in the product.

III. *Mixture of Triolein and Palmitodiolein.*—A mixture of 40% of triolein and 60% of palmitodiolein was hydrogenated with nickel at 180° for 9 hours, its iodine value being reduced to 2·5. After crystallisation of the product from ether and analysis as described above, it appeared to contain 37·2% (mol.) of tristearin and to contain a very small proportion of dipalmitostearin. Acyl migration (in this case, conversion of palmitodistearin into dipalmitostearin + tristearin) had thus only taken place to a very slight extent.

From the foregoing data it is permissible to draw the following conclusions. At 180° in presence of nickel on kieselguhr, appreciable interchange of acyl groups takes place between tripalmitin and triolein (or tristearin), but this phenomenon is much less evident in mixtures of oleo- or of stearo-dipalmitin with triolein (or tristearin), and appears to occur only to a small extent during the hydrogenation of mixtures of palmitodiolein and triolein. For the reasons already discussed, conclusions from the analytical data in these experiments cannot be accepted as having more than qualitative significance, but confirmatory results of a more positive character were obtained from the subsequent experiments next to be described.

IV. *Hydrogenation of Mixtures of Triolein and Trilaurin.*—Two experiments were made in which the time of treatment of mixtures of triolein and trilaurin was widely different; hydrogenation in presence of nickel on kieselguhr was effected in each case at 180° and the products were almost completely hydrogenated (iodine values 1·5 and 1·0). The analytical results obtained were as follows:

TABLE III.

Time of	Original mixture.		Found by analysis in product.	
hydrogenation.	Triolein, % (mol.).	Trilaurin, % (mol.).	Tristearin, % (mol.).	Trilaurin, % (mol.).
200 minutes	40·7	59·3	35·0	50·9
755 minutes	44·8	55·2	35·5	27·1

The relatively great difference in solubility in ether between trilaurin and tristearin renders less likely the presence of unresolved ternary mixtures in the final crystal fractions obtained, and the observed amounts of tristearin and trilaurin should accordingly be not far from the true values. It therefore appears that, in the experiment lasting for 3 hours 20 minutes, about 14% of the glycerides have undergone acyl interchange (although this may still be an over-estimate if the product was incompletely resolved into binary mixtures by crystallisation). The second experiment, which occupied over 12½ hours, indicates a much larger amount of interesterification (about 37%); since, as in the previous experiment, the actual hydrogenation was complete in about 3 hours, this confirms the earlier results with a mixture of tristearin and tripalmitin, and shows that acyl interchange slowly proceeds between fully saturated glycerides when subjected to the conditions of hydrogenation. It may also be concluded from these experiments, however, that at 180° and in presence of nickel on kieselguhr the rate of acyl interchange between triglycerides, even in those cases in which the process appears to be most favoured (mixtures of simple triglycerides), is comparatively slow (in the two experiments with trilaurin the proportion of the total glycerides present affected was of the order of 3—4% per hour of exposure to the conditions of hydrogenation). The analytical data in both these experiments suggested that the mixed triglycerides produced by inter-esterification were almost wholly dilaurostearin, laurodistearin being apparently only formed in small quantities; but this may be no more than an accidental circumstance due to the proportions of the reactants employed, or to some other unperceived cause.

V. *Examination of the Products of Partial Hydrogenation of Mixtures of Triolein and Tripalmitin.*—(*a*) A mixture of triolein (49·8% mol.) and tripalmitin (50·2% mol.) was hydrogenated at 180° in presence of nickel on kieselguhr until, after 105 minutes, its iodine value had been reduced from 49·4 to 18·3; at this point most of the unsaturated glycerides present would be mono-oleo-derivatives (Hilditch and Jones, J., 1932, 805; Bushell and Hilditch, J., 1937, 1767). The product was submitted to oxidation in acetone solution with powdered permanganate, and the fully saturated glycerides present were then separated

from the acidic products of oxidation (azelao-glycerides either from triolein or from any palmito-oleins produced by acyl migration). It was found that the semi-hydrogenated product contained 52·0% (mol.) of fully saturated glycerides, the component acids of which (from ester-fractionation) were made up of 82·7% of palmitic and 17·3% of stearic (mol.). The higher fatty acids present in the acidic products of oxidation were separated from azelaic and nonoic acids and analysed by ester-fractionation, palmitic acid being identified; the amount of palmitic acid detected in the acidic oxidation products (*i.e.*, present with oleic acid in mixed glycerides) corresponded to 5·6% (wt.) or about 6% (mol.) of the total fatty acids in the original fat, and thus connotes the presence of about 9% (mol.) of oleodipalmitin or 18% of palmitodiolein in the hydrogenated product (or mixtures of these triglycerides equivalent to the 6% of palmitic acid observed). This experiment affords further definite proof of the occurrence of acyl migration, and suggests in the present instance that the rate of acyl interchange was at least 5% of the original fat mixture per hour of exposure to the conditions of hydrogenation.

(*b*) A similar mixture of triolein (47·6% mol.) and tripalmitin (52·4% mol.) was agitated at 180° with nickel on kieselguhr in an atmosphere of carbon dioxide for 9 hours, and the product oxidised as above in order to examine the fully saturated glycerides and the higher fatty acids present in the acidic products of oxidation. It contained 47·1% (mol.) of fully saturated glycerides (in this instance, of course, wholly tripalmitin). From the acidic products of oxidation, palmitic acid was identified (m. p. 62·5°, unchanged when mixed with an authentic specimen); the quantity present corresponded to 4·0—4·9% (mol.) of the total fatty acids in the original mixture. This is equivalent to the presence in the product of 6% (mol.) of oleodipalmitin or about 15% (mol.) of palmitodiolein, and therefore proves that acyl interchange had occurred at a rate of about 1—2% of the original fat mixture per hour of exposure to the experimental conditions.

The foregoing results establish that in presence of nickel on kieselguhr at 180° acyl interchange between triglycerides takes place, but at a much slower rate than at 250° and above, or in presence of certain other catalysts. The extent of the change is mainly dependent on the time of exposure to the conditions favouring interchange of acyl groups, and this proceeds independently of whether hydrogenation is actually in progress: mixtures of completely saturated glycerides also undergo the change. Experiments with mixtures of saturated glycerides in hydrogen suggest, indeed, that the rate of change is of the same order as during hydrogenation of a mixture of saturated and unsaturated glycerides: the definitely slower rate observed when a mixture of triolein and tripalmitin was exposed to nickel on kieselguhr at 180° may be due to some side effect caused by the substitution of carbon dioxide for hydrogen as the gaseous constituent.

Although the difficulties of analytical separation and estimation of the components of the mixtures produced render the data in this communication more qualitative than quantitative in character, it seems that the process of acyl interchange takes place more rapidly between mixtures of simple triglycerides than when one component is already a mixed triglyceride (*e.g.*, oleodipalmitin or palmitodiolein). With mixtures of palmitodiolein and triolein the rate of interchange appears to be small at 180° under hydrogenation conditions.

Nevertheless, the determination of tri-C_{18} glycerides in a natural fat by hydrogenation and subsequent estimation of tristearin is not satisfactory, firstly because of the inherent difficulties of analytical separation, and secondly because of the tendency towards acyl migration during the hydrogenation. Fortunately, however, any error due to acyl interchange is likely to have been minimised, when this procedure has been followed, by two factors. In the first place, hydrogenation is normally effected rapidly and has not involved treatment at 180° with nickel on kieselguhr for more than $1\frac{1}{2}$—2 hours at most. Secondly, the natural fats rarely contain any appreciable proportion of a simple triglyceride; whilst in most cases in which the method has been used the fats concerned (or the fraction of the original fats to which it has been applied) consist for the most part of mixed tri-C_{18} glycerides (usually mainly oleolinoleins) with monosaturated-diunsaturated glycerides (usually palmitodioleins) and, to a smaller extent, disaturated-monounsaturated glycerides (*e.g.*, oleodipalmitin). With the already known proviso that the method is

only trustworthy, for analytical reasons, for tristearin contents of below 40% or over 75% (in most instances the actual content involved has been less than 40% of tristearin), it seems probable that no serious inaccuracy may have hitherto been involved in those cases in which recourse has been had to this procedure.

At the same time, in consequence of the results now communicated, it may be recommended that, for estimation of the proportion of tri-C_{18} glycerides in a fat, the fat should be hydrogenated at low temperatures (65—70°) in presence of Raney nickel or of platinum or palladium catalysts, and that the time of hydrogenation should be made as short as possible.

It may be pointed out, in conclusion, that the operation of this comparatively slow isomeric rearrangement of mixed glycerides under hydrogenation conditions has a certain technical importance, since wide variations in the time occupied in hydrogenation of a given fat will be accompanied by corresponding differences in the extent to which acyl interchange progresses, and consequent possible variations in the consistency, texture, or similar properties of the hydrogenated material.

Experimental.

Synthetical Preparation of Triglycerides.—The lauric, palmitic, and oleic acids required were obtained from stocks of the corresponding methyl esters which had been accumulated in the laboratory during ester-fractionation analyses of a number of fats. These esters were redistilled in a vacuum through an electrically-heated and packed fractionating column, and fractions of the individual esters thus obtained. The " oleic " esters contained small proportions of linoleic esters, which, from the point of view of hydrogenation experiments, could have no influence on the final results; the tedious and wasteful separation of pure oleic acid was therefore unnecessary for the present purpose (cf. Bushell and Hilditch, J., 1937, 1767). Stearic acid was prepared from the product of complete hydrogenation of methyl oleate–linoleate fractions which had been purified by fractional distillation.

Preparation of Simple Triglycerides.—These were obtained by direct condensation of the requisite fatty acid with glycerol in presence of 0·2% of camphor-β-sulphonic acid as catalyst at 160° and 15 mm. pressure. A slight excess of fatty acid was used in order to avoid the presence of any mono- or di-glycerides in the products. In this way stocks of trilaurin (m. p. 46°, sap. equiv. 212·0. Calc.: sap. equiv. 212·7), tripalmitin (m. p. 65°, sap. equiv. 268·6. Calc.: sap. equiv. 268·7), and tri-" olein " (from " oleic " acid of iod. val. 99·0. Found: sap. equiv. 294·6, iod. val. 94·8. Calc.: sap. equiv. 294·7, iod. val. 94·7) were prepared, whilst a quantity of tristearin (m. p. 70°) was available from earlier experiments.

Preparation of Mixed Palmito-glycerides.—The appropriate α-monoglycerides were first prepared and then directly esterified with the second fatty acid in order to produce the desired mixed triglycerides (Bushell and Hilditch, *loc. cit.*). α-Monostearin was prepared from αβ-*iso*-propylideneglycerol and stearic acid as described by Malkin and Shurbagy (J., 1936, 1628). α-Monopalmitin and α-mono-olein were obtained by direct esterification of the respective acids with excess of glycerol in phenol solution at 160° in presence of a small amount of camphor-β-sulphonic acid (Hilditch and Rigg, J., 1935, 1774).

The following mixed triglycerides were then prepared by direct esterification with a second fatty acid: palmitodiolein (Found: sap. equiv., 286·0; iod. val. 63·9. Calc.: sap. equiv., 286·0; iod. val., 65·1), oleodipalmitin (Found: sap. equiv., 280·3; iod. val., 35·0. Calc.: sap. equiv., 277·3; iod. val., 33·4), dipalmitostearin (Found: sap. equiv., 278·1. Calc., 278·0).

The relevant data from the analyses of the final hydrogenated and other mixtures are summarised below.

I. *Mixtures of Triolein (Tristearin) and Tripalmitin.*—(i) *Mixture of tristearin* (48·1% *mol.*) *and tripalmitin* (51·9% *mol.*) *crystallised from ether.* The mixture (49·5 g.) after being melted and well shaken, was systematically crystallised from ether and resolved finally into three fractions: *A*, 22·9 g. (44·2% mol.), *B*, 19·3 g. (40·4% mol.), and *C*, 7·3 g. (15·4% mol.). The equivalent of *C* (269·9) showed that it was substantially tripalmitin. Fractions *A* and *B* were converted into methyl esters, and the latter fractionated in a vacuum; it was then found that the acids in *A* consisted of palmitic 6·0, and stearic 94·0% (mol.), whilst those in *B* were palmitic 82·8, and stearic 17·2% (mol.). This corresponds to 82·0% of tristearin in fraction *A*, or 36·4% on the whole mixture.

(ii) *Tristearin* (48·7% *mol.*) *and tripalmitin* (51·3% *mol.*) *heated under hydrogenation conditions at* 180° *for* 9 *hours.* The product (54·9 g.) was resolved by systematic crystallisation

from ether into four fractions, of which the proportions and component acids (determined by ester-fractionation) were as follows :

Fraction.	G.	% (mol.).	Sap. equiv.	Component acids (% mol.). Palmitic.	Stearic.
A	26·2	46·2	290·5	22·3	77·7
B	10·2	19·2	272·5	86·7	13·3
C	8·2	15·4	274·0	80·9	19·1
D	10·3	19·2	274·5	79·2	20·8

The calculated tristearin content of fraction *A* (33·1%) corresponds to 15·3% on the whole mixture.

(iii) *Triolein* (49·7% *mol.*) *and tripalmitin* (50·3% *mol.*) *hydrogenated at* 180° *for* 9 *hours.* The product (71·0 g., iod. val. 0·9) was resolved by systematic crystallisation from ether into six fractions, the composition of each of which (in terms of binary mixtures) was estimated from their saponification equivalents :*

	A.	*B.*	*C.*	*D.*	*E.*	*F.*
Wt. (g.)	29·5	5·1	3·2	7·0	13·4	12·8
Sap. equiv.	295·1	272·3	276·9	276·6	285·6	286·4
,, ,, †	292·6	272·1	272·7	274·8	278·6	281·7
Iod. val.	—	—	—	—	0·7	3·3

Tristearin only appeared to be present in fraction *A* (16·7 g.), whilst unsaturated glycerides, reckoned as oleodistearin, were present in small amounts in the most soluble fractions *E* and *F* (1·8 g.); the original product therefore appeared to contain 18·5 g., or 25·2% (mol.), of tri-C_{18} glycerides.

II. *Mixtures of Triolein and Oleodipalmitin, or of Tristearin and Dipalmitostearin.*—(i) *Mixture of tristearin* (52·1% *mol.*) *and dipalmitostearin* (47·9% *mol.*) *crystallised from ether.* The mixture (46·9 g.) after being melted and well shaken, was resolved by systematic crystallisation from ether into four fractions, of which the proportions and component acids (determined by ester-fractionation) were as follows :

Fraction.	G.	% (mol.).	Sap. equiv.	Component acids (% mol.). Palmitic.	Stearic.
A	15·7	32·7	292·7	13·9	86·1
B	10·6	22·1	293·8	10·4	89·6
C	2·5	5·5	277·7	(not estimated)	
D	18·1	39·7	278·1	66·2	33·8

From these data it was calculated that the tristearin content (% mol.) of fractions *A* and *B* was respectively 58·3% and 68·8%, whence the observed tristearin content of the original mixture is 34·1%.

(ii) *Triolein* (25·3%) *and oleodipalmitin* (74·7%) *hydrogenated at* 180° *for* 10·5 *hours.* The product (75·9 g., iod. val. 2·3) was resolved by systematic crystallisation from ether into seven fractions, the composition of each of which (in terms of binary mixtures) was estimated directly from their saponification equivalents :

	A.	*B.*	*C.*	*D.*	*D.*	*E.*	*G.*
Wt. (g.)	16·3	3·2	8·6	6·2	9·3	9·5	22·8
Sap. equiv.	292·7	286·5	281·5	279·3	279·7	280·6	289·7
,, ,, †	292·7	285·6	280·0	277·5	278·0	280·6	287·1
Iod. val.	—	—	—	—	2·0	1·7	7·5

In fraction *A* there appeared to be 9·45 g. of tristearin, whilst the unsaturation in fractions *E*, *F*, and *G*, reckoned as oleodistearin, amounted to 7·05 g. The tri-C_{18} glycerides present in the whole product thus amounted to 16·5 g., or 21·0% (mol.).

III. *Mixture of Triolein* (39·9%) *and Palmitodiolein* (60·1%) *hydrogenated at* 180° *for* 9 *hours.*—The product (71·6 g., iod. val. 2·5) was resolved by systematic crystallisation from ether into six fractions, the composition of each of which (in terms of binary mixtures) was estimated directly from their saponification equivalents :

	A.	*B.*	*C.*	*D.*	*E.*	*F.*
Wt. (g.)	39·5	7·1	4·9	8·2	6·3	5·6
Sap. equiv.	293·0	286·3	286·1	290·7	294·2	300·5
,, ,, †	292·7	286·0	284·8	287·7	287·1	288·9
Iod. val.	—	—	—	0·5	5·2	13·9

* In employing this method, any traces of unsaponifiable matter present were determined and allowed for in the subsequent calculations.

† Corrected for unsaponifiable matter.

In fraction *A* there appeared to be 23·0 g. of tristearin, whilst a small amount (0·3 g.) was also present in fraction *D*; the unsaturation in fractions *D*, *E*, and *F*, calculated to oleodistearin, represented 3·7 g. of the latter. The tri-C_{18} glycerides thus amounted to 27·0 g., or 37·2% (mol.), of the whole hydrogenated product.

IV. *Hydrogenation of Mixtures of Triolein and Trilaurin.*—(i) *Mixture of triolein* (40·7%) *and trilaurin* (59·3%) *hydrogenated at* 180° *for* 200 *minutes.* The product (48·7 g., iod. val. 1·5) was resolved by systematic crystallisation from ether into six fractions, the composition of each being estimated as above from their saponification equivalents :

	A.	*B*.	*C*.	*D*.	*E*.	*F*.
Wt. (g.)	15·7	3·0	2·4	4·9	15·3	7·4
Sap. equiv.	294·4	293·2	275·0	212·7	218·7	244·5
,, ,, †	294·4	292·8	273·2	212·7	216·2	238·6
Iod. val.	—	—	—	—	0·8	4·9

In fractions *A*, *B*, and *C* there appeared to be respectively 15·3, 2·9, and 0·4 g. of tristearin, whilst the unsaturation of fractions *E* and *F* corresponded with the presence therein of 0·4 and 1·3 g. of oleodistearin. The tri-C_{18} glycerides in the whole product thus amounted to 20·3 g., or 35·0% (mol.). Trilaurin (mainly in *D*, *E*, *F*, with minor quantities in *A* and *B*) amounted to 21·2 g., or 50·9% (mol.).

(ii) *Mixture of triolein* (44·8%) *and trilaurin* (55·2%) *hydrogenated at* 180° *for* 755 *minutes.* As in the previous experiment, the hydrogenation was completed in about 3 hours, but treatment under the hydrogenation conditions was prolonged for a further 9½ hours. The product (22·0 g., iod. val. 1·0) was resolved into five fractions by systematic crystallisation from ether :

	A.	*B*.	*C*.	*D*.	*E*.
Wt. (g.)	8·2	2·1	2·4	2·3	7·0
Sap. equiv.	296·8	274·0	225·3	225·2	232·7
,, ,, †	296·8	273·8	225·0	225·2	232·7
Iod. val.	—	—	—	0·9	1·8

Fractions *A* and *B* appeared to contain respectively 8·2 and 0·4 g. of tristearin; the unsaturation of fractions *D* and *E* corresponded with the presence therein of 0·1 and 0·4 g. of oleodistearin. The tri-C_{18} glycerides in the whole hydrogenated product thus amounted to 9·1 g., or 35·5% (mol.). Trilaurin (in fractions *C*, *D*, *E*) amounted to 5·0 g., or 27·1% (mol.).

V. *Products of Partial Hydrogenation of Mixtures of Triolein and Tripalmitin.*—(i) *Mixture of triolein* (49·8%) *and tripalmitin* (50·2%) *hydrogenated at* 180° *for* 105 *minutes to iod. val.* 18·3. The product (44·0 g.) was oxidised in acetone solution with powdered potassium permanganate, giving a mixture of neutral and acidic products, which were separated. The neutral portion consisted substantially of fully saturated glycerides (24·6 g., iod. val. 0·7), which were resolved into two fractions by crystallisation from ether : *A*, 13·7 g. and *B*, 10·9 g. The component acids in each fraction were determined with the following results :

	A, % (mol.).	*B*, % (mol.).
Palmitic acid	87·9	74·8
Stearic acid	11·6	24·1
Oleic acid	0·5	1·1

The data indicate the presence of 52·0% (mol.) of fully saturated glycerides in the partly hydrogenated product, the acids present being palmitic 82·7% and stearic 17·3% (mol.). Most of the stearic acid was doubtless tristearin produced by the hydrogenation of triolein; it was not possible to ascertain whether any mixed palmitostearins were present in this fully saturated part of the product. Proof of acyl migration, on the other hand, lay in this experiment in the isolation of palmitic acid from the acidic products of oxidation, *i.e.*, from unsaturated glycerides in which some palmitic groups must also have been present.

The acidic products of oxidation were completely saponified and any higher fatty acids present were separated as far as possible from accompanying nonoic and azelaic acids by repeated boiling with water. The residual water-insoluble acids (8·7 g.) were converted into methyl esters, and the latter fractionally distilled; it was then found that their composition was palmitic 30·0% and stearic 70·0% (wt.). This amount of palmitic acid corresponds with 5·6% (wt.) or about 6% (mol.) of the total fatty acids in the original hydrogenated product.

(ii) *Mixture of triolein* (47·6%) *and tripalmitin* (52·4%) *heated at* 180° *in presence of nickel catalyst in a current of carbon dioxide for* 9 *hours.* The product (50·2 g.) was oxidised in acetone

† Corrected for unsaponifiable matter.

solution with potassium permanganate, and gave 22·8 g. of unchanged fully saturated glycerides (iod. val. 0·6, equiv. of acids present 255·7; palmitic acid, equiv. 256); it thus contained 47·1% (mol.) of tripalmitin (original mixture 52·4%). The acidic products of oxidation, separated from the fully saturated glycerides by solution in aqueous alkali, were completely hydrolysed, and the acids liberated and boiled with water repeatedly to remove as much nonoic and azelaic acids as possible. 2·9 G. of water-insoluble acids were recovered, the equivalent of which (225·4) indicated that some nonoic and/or azelaic acid was still present. Crystallisation of these acids from ethyl acetate gave an acid, m. p. 62·5° (unchanged when mixed with authentic palmitic acid). The amount of palmitic acid present in the impure acid of equivalent 225·4 corresponds to between 4·0 and 4·9% (mol.) of the total acids in the original fat-mixture (according to whether the accompanying acid was azelaic or nonoic). It was thus established that, under the particular experimental conditions employed, between 4 and 5% of the palmitic acid originally combined in the mixture had been transferred from tripalmitin to a mixed glyceride containing both palmitic and oleic acids.

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