XII. THE BODY FATS OF THE PIG.

IV. PROGRESSIVE HYDROGENATION AS AN AID IN THE STUDY OF GLYCERIDE STRUCTURE.

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It was pointed out in an earlier communication in this series [Banks and Hilditch, 1932] that the relationship between the content of fully-saturated glycerides and the degree of saturation as a whole of pig, ox and sheep depot fats and also cow milk fats (a group in which the saturated fatty acids ranged from 34 to 72.5 mols. % of the total fatty acids in each fat) was closely similar to that of a series of progressively hydrogenated cottonseed oils. Cottonseed oil resembles the most unsaturated type of pig body fat in so far as it contains about 25 % of saturated (almost all palmitic) and 75 % of unsaturated acids, all the saturated acids being present in the form of mixed, saturated-unsaturated glycerides. In the present paper the glyceride structure of a similar group of hydrogenated pig fats is described, since it was considered of some interest to compare the increase in fully-saturated glycerides, in fats produced by progressive hydrogenation of an animal depot fat of the most unsaturated type, with that observed in the series of natural lards, tallows and butters.

The experimental material required for this purpose was also suitable for the study of other features of the glyceride structure of the original pig fat employed. We have been able to estimate, by two independent methods, the total content therein of glycerides consisting wholly of C_{18} (stearic, oleic and/or linoleic) acids, to show that the monopalmitoglycerides of the fat were almost entirely, if not wholly, β -palmito- $\alpha\alpha'$ -diacylglycerides, and finally, to give a more detailed statement than previously of the probable proportions of the chief component glycerides of the original fat.

The inner layers of the pig back fat, the component acids of which had already been examined [Dean and Hilditch, 1933] and found to be practically the same throughout the layer, served as the primary material for the present study. Owing to the large quantity of material required by the present work, it was necessary to commence from the inner back fat; the amount of the outermost layer of back fat (which would have provided a still better starting-point, owing to its somewhat greater unsaturation) was not sufficient to provide the requisite quantities of all the desired hydrogenated products.

The mixed inner back fat had a mean saponification equivalent of 286.2 and a mean iodine value of 63.0. Its mixed fatty acids (setting-point 40.7°) were analysed by the ester-fractionation method; the results, together with the corresponding figures of Dean and Hilditch [1933] for the outermost (I), middle (II) and innermost (III) layers of the inner back fat, are given in Table I.

Portions of the fat were hydrogenated to varying degrees by agitation with a small proportion of nickel on kieselguhr in hydrogen at atmospheric pressure at 175 – 180° , and products of the following iodine values were thus prepared: 48.9, 43.0, 35.8 (800 g. of each), and 28.9, 18.7, 10.0 and 0.2 (400 g. of each).

Table I. *Component acids of original inner back fat.*

Acid	Weight percentages				Molar percentages			
	I	II	III	Mixed	I	II	III	Mixed
Myristic	2.9	2.8	3.0	2.3	3.5	3.3	3.6	2.8
Palmitic	24.9	25.5	24.6	25.6	26.6	27.3	26.2	27.3
Stearic	14.5	14.5	14.5	14.9	14.0	14.0	14.0	14.4
Oleic	42.7	41.3	42.8	42.2	41.4	40.1	41.6	40.9
Linoleic*	13.9	14.5	13.7	13.8	13.6	14.2	13.4	13.5
C ₂₀₋₂₂ unsaturated	1.1	1.4	1.4	1.2	0.9	1.2	1.2	1.1

* Some of the C₁₈ unsaturated esters isolated from the original pig fat were examined qualitatively. It was found that the oleic and linoleic acids present were respectively the common forms of $\Delta^{9:10}$ -octadecenoic and $\Delta^{9:10,12:13}$ -octadecadienoic acids. Oxidation with dilute alkaline permanganate gave 9:10-dihydroxystearic acid, m.p. 131°, and two tetrahydroxystearic acids, m.p. 154° and 172°; a tetrabromostearic acid which was sparingly soluble in light petroleum and melted at 114° was also obtained. The yields of tetrabromo- and tetrahydroxy-stearic acids were of the same order as those given by the linoleic acid from a seed-fat such as cottonseed oil.

Sufficient of each fat (including the original) was oxidised with potassium permanganate in acetone to yield a suitable quantity of fully-saturated glycerides to permit of the component acids of the latter being analysed by the ester-fractionation method with the results¹ shown in Table III.

In Table III are also given the fatty acid compositions of each of the hydrogenated fats. To facilitate comparison between the various products, the latter have been calculated from the original analysis (Table I) in conjunction with the observed iodine values of the fats. This course has been adopted in order to avoid the slight variations otherwise introduced by the small but inevitable experimental errors of analysis [cf. Hilditch, 1934]. In view of the good agreement between the four analyses recorded in Table I the figures for the original fat must be considered to be a close approximation to the truth.

We have however made independent ester-fractionation analyses of the component fatty acids of the fats of iodine value 48.9, 35.8, and 10.0 (Table II). The direct analysis of the first-named fat was essential in order to ascertain the extent to which linoleic glycerides were undergoing hydrogenation. The result showed that the hydrogenation had followed the usual, mainly selective course and indicated that linoleic acid would no longer be present in the remaining, more saturated products.

 Table II. *Component fatty acids of hydrogenated pig fats (by direct analysis) (mol. %).*

	48.9	35.8	10.0
Iodine value of fat	%	%	%
Myristic	2.8	2.2	1.3
Palmitic	25.6	28.1	29.0
Stearic	18.1	28.2	56.3
Oleic (and <i>iso</i> -oleic)	50.9	40.5	11.9
Linoleic	0.9	—	—
C ₂₀₋₂₂	1.7	1.0	1.5

The complete analytical data for each hydrogenated product and its corresponding fully-saturated components may now be considered. In Table III, in which these are summarised, are included the weights of fat from which the fully-saturated glycerides were obtained, and the weights of the esters of the mixed acids of the latter which were subsequently fractionated.

¹ All percentages in Table II *et seq.* are molar, not weight.

Table III. *Fully-saturated glycerides and component fatty acids of the hydrogenated pig fats.*

Iodine value of fat	63.0*	48.9	43.0	35.8	28.7	18.7	10.0
Component fatty acids (mol. %) in whole fat:†							
Myristic	2.8	2.8	2.9	2.8	2.8	2.8	2.8
Palmitic	27.3	27.4	27.4	27.4	27.5	27.5	27.5
Stearic	14.4	15.7	21.4	29.6	36.2	47.5	57.4
Oleic (and iso-oleic)	40.9	52.1	47.3	39.2	32.5	21.2	11.3
Linoleic	13.5	1.0	—	—	—	—	—
C ₂₀₋₂₂	1.1	1.0	1.0	1.0	1.0	1.0	1.0
<i>Fully-saturated glycerides.</i>							
Weight of whole fat oxidised (g.)	401.8	404.8	308.2	302.7	103.0	100.5	100.0
Fully-saturated glycerides (mol. %)	5.6	7.1	10.9	19.6	32.0	53.2	71.1
Component acids (mol. %) in fully saturated glycerides:							
Myristic	—	1.3	0.5	—	—	—	—
Palmitic	54.0	47.3	44.7	41.2	40.4	38.9	36.7
Stearic	46.0	51.4	54.8	58.8	59.6	61.1	62.2
C ₂₀₋₂₂	—	—	—	—	—	—	1.1
(Weight of fully-saturated esters fractionated (g.))	18.8	23.0	25.1	27.5	27.0	23.0	27.0)

* Original fat.

† Calculated from iodine value of fat and analysis of acids from original fat of iodine value 63.0.

Comparison of the proportions of fully-saturated components in the partially-hydrogenated pig fats and in natural depot (and milk) fats of similar relative unsaturation.

The relation between the molar content of fully-saturated glycerides and the molar percentages of saturated acids in the total fatty acids of the various fats is shown graphically in Fig. 1. The points indicated by letters refer to the different natural fats (depot fats of pig (L), ox and sheep (T), or butter fats (B)), whilst the unbroken curve has been drawn through the values obtained from the hydrogenated pig fats (Table III). The dotted curve represents the relationship which would obtain if the amount of fully-saturated components in a fat were proportional to the cube of the proportion of saturated acids present in the mixed acids. The broken line shows the fundamentally different relations subsisting in seed-fats, in which fully-saturated glycerides are rarely found in greater amount than that necessary to leave a ratio of about 55–60 % of saturated to 45–40 % of unsaturated acids linked together as mixed saturated-unsaturated glycerides [Collin and Hilditch, 1929].

In fats hydrogenated by metallic catalysts under the conditions which we have used, the linoleic glycerides are very largely converted into oleic derivatives before the stearic content is appreciably augmented. Thus the molar percentage of linoleic acid in the component fatty acids fell from 13.5 to 1, while the increase in stearic acid was less than 2 %, and the fully-saturated glyceride content only rose from 5.6 % to 7.1 %. In this respect the artificially hydrogenated fats form a different series from the natural depot fats in which stearic acid augments mainly at the expense of oleic acid, rather than of linoleic acid. This difference does not however affect the relationships now under consideration, since these are based on the relative proportions of saturated to unsaturated acids as a whole in each fat.

It will be seen that, as in the case of hydrogenated cottonseed oils, the points given on the graph by the natural tallows and lards¹ follow the hydrogenated pig fat curve with a fair degree of consistency. The most arresting feature of the diagram is that, as with the hydrogenated fats, the series of values for the natural fats definitely tends to meet the horizontal axis at a point representing 25–30 % of saturated acids in the total fatty acids. This amount is also of course that of the approximately constant palmitic acid content which has been shown to be characteristic for animal depot fats and also butter fats. If the occurrence

Fig. 1. *L*, pig fats. *T*, tallows. *B*, butter fats. — Hydrogenated pig fat. --- Seed fats. $y \propto x^2$.

of fully-saturated glycerides in these fats were determined by the relative concentration of any one acid, or class of acid, the presence of 25–30 % of palmitic acid alone should suffice to produce 5 % or somewhat more of tripalmitin. Actually, tripalmitin has never been observed in either lards or tallows, the fully-saturated components being almost entirely mixed palmitostearins.

These facts, as well as the parallelism in general glyceride structure between the natural fats and the hydrogenated pig fats, accord with the suggestion made in an earlier paper [Banks and Hilditch, 1932] that, in the lard and tallow types of depot fats (with relatively high stearic contents), a mixture of triglycerides, formed initially from about 30 % of palmitic and about 70 % of oleic acids and containing little or no fully-saturated compounds, may undergo subsequent hydrogenation of some of the oleo-glycerides. Mere similarity of chemical structure in two series of compounds is of course no proof of the

¹ Fig. 1 shows that the milk fats fall into line with tallows and lards from the point of view of their general glyceride structure, and it has also been found [Hilditch and Sleightholme, 1931, p. 518] that in these fats the united molar contents of the characteristic lower saturated fatty (butyric-lauric) acids together with stearic and oleic acids tend towards a constant figure of about 65 % (mol.)—little different from that of the total C_{18} acids in tallows and lards. There are therefore fundamental and quantitative similarities in the general constitutions of these milk and depot fats.

mechanism by which one of the series may have been produced; nevertheless, specific features in the structure of natural products merit due consideration when hypotheses as to their biosynthesis are elaborated.

Content of tri- C_{18} -glycerides in the original pig fat.

Direct methods of determination of the triolein or triunsaturated glyceride content of a fat are still lacking, but it has recently been shown [Hilditch and Jones, 1934] that an approximate estimate of the total tri- C_{18} -glycerides present can be arrived at in suitable cases from the mean equivalents of the fractions obtained by systematic crystallisation of the fat after complete hydrogenation. An independent method, which serves as a check on the foregoing process and which has not been previously described, depends on the fact that palmitostearo-oleins are hydrogenated preferentially to distearo-oleins [Hilditch and Jones, 1932] and that, consequently, after partial hydrogenation to a point at which no dipalmito-unsaturated glycerides are left, the non-fully-saturated glycerides are composed solely of monopalmitodistearins and tri- C_{18} -glycerides. Both these methods have been applied in the present investigation.

(i) *Fractional crystallisation of the completely hydrogenated pig fat (iodine value 0.2).* The completely hydrogenated fat (102 g.) was crystallised first from 10 volumes of ether and the separated solids were then crystallised from 15 volumes of ether, the latter process being repeated three times. The fractions obtained and their analytical characteristics are summarised in Table IV.

Table IV. *Fractional crystallisation of hydrogenated pig fat*
(102 g., iodine value 0.2).

No.	g.	Glycerides			Corresponding acids (freed from unsp.)	
		M.P.	S.E.	I.V.	S.E.	I.V.
A	69.1	68°	289.2	—	—	—
B	5.5	68°	287.3	—	—	—
C	8.5	—	286.1	—	—	—
D	2.9	—	285.9	—	—	—
E	7.9	—	284.5	0.7	272.0	0.5
F	8.1	—	283.8	2.5	270.0	1.3

Assuming that fraction A is a mixture of tristearin (S.E. 296.7) and palmitodistearin (S.E. 287.3), and that the iodine values of the glycerides in fractions E and F are due to oleodistearin, it follows that the fat (102 g.) contained 14.3 g. tristearin and 0.5 g. oleodistearin, corresponding to a molar content of 14.1 % tri- C_{18} -glycerides in the whole fat¹.

(ii) *Estimation of tri- C_{18} -glycerides from some of the partially hydrogenated fats.* Before applying this method, it is necessary to ascertain, (a) whether any tristearin has already been formed and (b) at what point the absence of dipalmito-glycerides from the non-fully-saturated glycerides can be presumed. The production of tristearin can be followed by subjecting the fully-saturated glycerides

¹ This method of examination is unfortunately not sufficiently delicate to take account of the minor component acids (myristic 2.8 %, C_{20-22} 1.1 %) present in the fat. Calculated from the saponification equivalents as combinations of palmitic and C_{18} -glycerides, the molar composition of the hydrogenated fat amounted to: tristearin 13.6 %, palmitodistearin 78.4 %, dipalmitostearin 7.5 % and oleodistearin 0.5 %. This corresponds with a total molar fatty acid composition of palmitic 31 % and C_{18} -acids 69 % (calculated from original ester-fractionation analysis of the original fat: non- C_{18} -acids 31.2 %, C_{18} -acids 68.8 %).

of the fats to systematic crystallisation. Thus, the fully-saturated glycerides in the fat of iodine value 18.7 (*v. infra*) showed no tristearin content.

The second question can be answered approximately by examining the relative amounts of stearic and palmitic acids added at each stage of the hydrogenation to the fully-saturated components. This is illustrated in Table V, the (molar) data in which have been obtained from the detailed analysis made of the fully-saturated components of each of the hydrogenated fats.

Table V. *Increase in non- C_{18} and stearic acids in fully-saturated glycerides at successive stages of hydrogenation.*

Stages (Fall in i.v.)	Increase in total saturated acids	Increase in fully- saturated glycerides	Mols. (per 100 g. fat) added of		Ratio C_{18}/C_{16}
			C_{16} *	C_{18}	
63.0-43.0	7.2	5.3	1.95	3.35	1.7
43.0-35.8	8.1	8.7	3.15	5.55	1.8
35.8-28.7	7.7	12.4	4.8	7.6	1.6
28.7-18.7	11.3	21.2	7.8	13.4	1.7
18.7-10.0	9.9	17.9	6.2	11.7	1.9
10.0-nil	11.3	28.9	4.9	24.0	4.9

* Minor amounts of C_{14} or C_{20-22} acids included with C_{16} .

From Table V it appears that the remaining non-fully-saturated components of the fats of iodine values 18.7 and 10.0 both consist solely of monopalmito-di- C_{18} -glycerides and tri- C_{18} -glycerides, since the ratio of $C_{18} : C_{16}$ -glycerides added is almost exactly 2 : 1. It is also seen from Table V that, during the further hydrogenation to iodine value 10.0, there was no indication of the formation of tristearin.

Considering the fats of iodine value 18.7 and 10.0, detailed analyses reveal the data quoted in Table VI.

Table VI. *Component acids (mol. %) in the fully-saturated and non-fully-saturated part of fats of iodine value 18.7 and 10.0.*

	Fat of i.v. 18.7			Fat of i.v. 10.0		
	Whole fat	Fully- saturated	Mixed saturated- unsaturated (by diff.)	Whole fat	Fully- saturated	Mixed saturated- unsaturated (by diff.)
Mols:	100	53.2	46.8	100	71.1	28.9
Myristic	2.8	—	2.8	2.8	—	2.8
Palmitic	27.5	20.7	6.8	27.5	26.1	1.4
Stearic	47.5	32.5	15.0	57.4	44.2	13.2
C_{20-22}	1.0	—	1.0	1.0	0.8	0.2
Oleic and iso-oleic	21.2	—	21.2	11.3	—	11.3

In the non-fully-saturated portion of the fat of iodine value 18.7, therefore, there are, by difference, 10.6 mols. of non- C_{18} acids (corresponding to 31.8 mols. of "palmito-di- C_{18} -glycerides") and 36.2 mols. of C_{18} acids. Since 21.2 mols. of C_{18} acids are required in the formation of the 31.8 mols. of mixed glycerides, there remain 15.0 % (mol.) in the form of tri- C_{18} -glycerides.

A similar calculation from the results for the other fat gives 15.7 % (mol.) tri- C_{18} -glycerides.

The results of the estimations by methods (i) and (ii) are reasonably concordant and the proportion of tri- C_{18} -glycerides other than tristearin (triolein, oleodistearins, oleolinoleins or similar combinations) in the original fat is clearly about 15 % (mol.).

The occurrence of β -palmito-glycerides in the pig depot fat. Some evidence as to the configuration of the mono-palmitoglycerides of the original pig fat has been obtained from study of the fully-saturated components isolated from the fats which had been hydrogenated respectively to iodine values of 35.8 and 18.7. It has already been shown that, at these stages, no tristearin had been produced in the course of the hydrogenation. Systematic crystallisation from ether of the fully-saturated glycerides from each fat gave considerable proportions of a palmitodistearin which melted at 67–67.5° (Table VII).

Table VII. *Palmitodistearins isolated from the fully-saturated glycerides of hydrogenated pig fats.*

Hydro- genated fat I.V.	Fully- saturated glycerides crystallised g.	Palmitodistearin isolated				Composition of f.s.g. calculated from com- ponent acid analysis (Table III)	
						Palmito- distearin	Dipalmito- stearin
		g.	%	M.P.	S.P.	%	%
35.8	19.2	11.2	58.3	67.5°	287.4	77	23
18.7	22.9	15.8	69.0	67°	286.7	84	16

The melting-points of α -palmito- $\beta\alpha'$ -distearin and of β -palmito- $\alpha\alpha'$ -distearin are respectively 63.5° and 68° [Bömer *et al.*, 1907; 1909; 1913; Amberger and Wieschahn, 1923; Robinson *et al.*, 1932], and thus the data in Table VII show that the least soluble fractions isolated were β -palmito- $\alpha\alpha'$ -distearin. Moreover the quantity of β -palmitostearin amounted to 76 % and 82 % of the whole of the palmitodistearin present in the respective fully-saturated glycerides and, in the case of the fat of iodine value 18.7, the palmitostearin actually isolated corresponds to about 60 % of the whole of the monopalmito-di- C_{18} -glycerides present in the original fat, although no particular effort was made to obtain quantitative recovery of all the monopalmitodistearin. In view of the relative ease with which the compounds of melting-point 67.5° were obtained and of the well-known difficulties attending the separation of mixtures of the isomeric palmitodistearins by crystallisation, these results are considered to point definitely to the presence, in the original pig fat, of β -monopalmito-glycerides, unaccompanied by any appreciable quantities of the α -monopalmito-isomerides¹.

The exclusive occurrence of one configurational form of a mixed glyceride, as suggested for pig depot fat by these results, may be less uncommon in natural fats than would perhaps be supposed. At all events, the present observations are paralleled by the similar presence of β -oleodistearin in a group of vegetable seed fats, including those of kokum butter and *Allanblackia Stuhlmannii* [Heise, 1897; Hilditch and Saletore, 1933], cacao butter [Fritzweiler, 1902] and Borneo tallow [Klimont, 1904].

¹ Dr Banks has suggested to us that the preferential hydrogenation of palmitostearo-oleins to that of distearo-oleins may be due to relative ease of hydrogenation of oleic radicals attached to the α -glyceryl carbon atoms as compared with those attached to a β -glyceryl carbon atom. This possibility is at present being investigated in our laboratory.

The probable proportions of the chief components of the original pig depot glycerides.

The data which have now been discussed allow a somewhat fuller statement to be given than formerly as to the main components of a pig depot fat, subject to the following limitations:

(a) The methods employed are not sufficiently delicate to indicate the mode of union of the minor component acids (myristic and the C_{20-22} group) which form only 2 or 3 % of the total fatty acids. They serve however to define the chief combinations of the acids containing 18 carbon atoms with those containing other than 18 carbon atoms in the molecule; in the case of pig depot fat the latter group is very largely composed of palmitic acid, and it thus becomes possible to outline the chief combinations of palmitic and C_{18} acids which occur in the mixed glycerides.

(b) Since the methods employed involve hydrogenation, *i.e.* removal of the unsaturated group, it is impossible to discriminate, in what follows, between the linoleic and oleic radicals originally present in the fat. (For the sake of brevity the unsaturated glycerides are referred to in the paragraphs immediately following as "oleins," "oleic" derivatives *etc.*, the use of inverted commas denoting that both oleic and linoleic, and not only the monoethenoid, compounds may be concerned.)

The data now available include:

(a) The proportion (*ca.* 5 %) of fully-saturated glycerides in the original fat, these being mixtures of dipalmitostearin and palmitodistearin.

(b) The proportion (*ca.* 15 %) of tri- C_{18} -glycerides present. These might be tri-"oleins," steardi-"oleins," or distearo-"oleins"; the latter are least likely to be present, the monostearo-glycerides being probably the chief representatives of this group, but there may well be at least some triolein or mixed linoleo-oleins in the original fat (the fatty acids of which included 41 % oleic and 13.5 % linoleic acids). Estimates are given below for this group reckoned alternatively as all monostearodi-"oleins" or as all tri-"oleins."

(c) The remainder of the stearo-glycerides (corresponding to the balance of the total stearic acid unaccounted for in the form of tri- C_{18} -glycerides) must be either palmitostearo-"olein" or palmitostearins (tristearin being absent and the presence of distearo-"oleins" in significant quantities being ruled out as unlikely). The quantity of stearic acid combined as palmitostearins being known (*a*), the residue must be allotted to palmitostearo-"olein."

(d) The monopalmito-derivatives have been shown to be β -palmito-glycerides.

Alternative possible compositions of the main glycerides of the fat can therefore be given, to a rough approximation, according to whether the tri- C_{18} -glycerides contain one stearic residue or not (Table VIII).

Table VIII. *The general composition of the glycerides of pig back fat (iodine value 63.0).*

	Tri- C_{18} -glycerides estimated as	
	(a) Steardi-"oleins" % (mol.)	(b) Tri-"oleins" % (mol.)
(β -) Palmitodistearin	2	2
Dipalmitostearin	3	3
Tri-"oleins"	—	15
Steardi-"oleins"	15	—
(β -) Palmitostearo-"oleins"	21	36
(β -) Palmitodi-"oleins"	57	42
Dipalmito-"olein"	2	2

The most abundant constituents of this particular fat are the palmitodi-“oleins” (42–57 %), followed by palmitostearo-“oleins” (21–36 %) and tri- C_{18} -glycerides (15 %, mainly unsaturated).

The possible limits within which the three classes of monosaturated-di-unsaturated, disaturated-mono-unsaturated, and tri-unsaturated glycerides may be present in the fat have been considerably narrowed by the present procedure, in comparison with those which it was formerly possible to indicate by consideration only of the amount of fully-saturated glycerides present. This is shown in Table IX, which also includes the similar values indicated by the old and the present methods for the content of tri- C_{18} -glycerides other than tristearin.

Table IX. *Limiting values for certain classes of glycerides in the pig back fat.*

	(a) From f.s.g. content alone	(b) Present analysis
Mono-unsaturated-disaturated	23–59	23–38
Di-unsaturated-mono-saturated	72–0	72–42
Tri-unsaturated	0–36	0–15
Tri- C_{18} -glycerides	10–52	15

Amberger and Wiesehahn [1923], who investigated lards of iodine values 51.5 and 54.7 by fractional crystallisation of the original and of the completely hydrogenated fats, suggested that they contained dipalmitostearin (2 %), palmitodistearin (3 %), oleodistearin (2 %), oleopalmitostearin (11 %) and palmitodiolein (82 %), with possibly some triolein. These figures differ from those given above chiefly in the low proportion assigned to palmitostearo-oleins; this is perhaps to be expected in consequence of the undoubted difficulty of obtaining anything approaching a quantitative separation of these glycerides from the more abundant palmitodi-“oleins” which accompany them.

The data of Table VIII refer to a pig back fat of the more unsaturated type. A more saturated fat, such as a perinephric fat with iodine value about 55, of course must be somewhat differently constituted. Such a fat contains about 14 % of fully-saturated components and its mixed acids include about 70 % C_{18} -acids (of which about 17 % may be stearic acid). The determination of its approximate composition, which would involve the execution of another series of analyses on the lines of those described in this paper, has not been undertaken. It may be pointed out however that (if the leaf fat should contain about the same proportion of tri- C_{18} -glycerides as that in the back fat which we have examined) palmitodi-“oleins” would still be the most prominent components (35–50 %), palmitostearo-“oleins” would probably be present in proportions not differing very greatly from those given in Table IX, whilst, of course, the amount of palmitodistearin would be augmented in consequence of the increase in fully-saturated glycerides as compared with the back fat (possibly distearo-“oleins” might be present in minor quantities).

It will be perceived that the quantitative description of the component glycerides of pig depot fat is still incomplete; nevertheless the work reported above permits us to deduce with some confidence the general relative proportions of the different classes of mixed glycerides (enumerated in Table VIII) for a single specimen of the depot fat, and to indicate the probable alteration in their respective proportions in other pig depot fats of a more saturated character.

SUMMARY.

Investigation of the composition of a pig back fat after its catalytic hydrogenation to varying stages of saturation has led to the following conclusions:

1. The increase in the fully-saturated glycerides in a series of animal fats (pig, ox, sheep depot fats and cow milk fats), in which the total content of saturated acids progressively increases, is very similar to that displayed by the artificially hydrogenated pig back fats. The values for the natural fats, when plotted graphically, suggest that fully-saturated components would be absent from a fat of this group which contained only 25–30 % of saturated acids (*i.e.* palmitic but no stearic acid).

2. Estimations by two different methods showed that the fat contained 15 % (mol.) of tri- C_{18} -glycerides (other than tristearin, which was absent). The precise nature of this group (triolein, oleolinoleins, steardioleins, or oleodistearin) was not ascertainable, but it is probable that it consists mainly of steardioleins with perhaps a small proportion of tri-unsaturated glycerides.

3. The monopalmito-compounds present in the fat consist very largely, and quite probably solely, of β -palmito-glycerides (β -palmitodi-“olein” and β -palmitostearo-“olein,” with a small amount of β -palmitodistearin).

4. Palmitodi-unsaturated glycerides (chiefly palmitodiolein) are the chief components of the original fat investigated, of which they may form from 42 to 57 %; palmitostearo-“oleins” (21–36 %) and the tri- C_{18} -unsaturated (or semi-unsaturated) glycerides (15 %) are the next most abundant constituents.

The perinephric fats of the pig, which are more saturated, probably contain somewhat less of the palmitodi-“oleins” and not very different amounts of palmitostearo-“oleins,” compared with the back fat; but there is a corresponding increase in the palmitostearins present.

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REFERENCES.

- Amberger and Wieschahn (1923). *Z. Unters. Nahr. Genussm.* **46**, 276.
 Banks and Hilditch (1932). *Biochem. J.* **26**, 298.
 Bömer (1913). *Z. Unters. Nahr. Genussm.* **25**, 321.
 — and Heimsoth (1909). *Z. Unters. Nahr. Genussm.* **17**, 353.
 — Schlemm and Heimsoth (1907). *Z. Unters. Nahr. Genussm.* **14**, 90.
 Collin and Hilditch (1929). *Biochem. J.* **23**, 1273.
 Dean and Hilditch (1933). *Biochem. J.* **27**, 1950.
 Fritzweiler (1902). *Z. Unters. Nahr. Genussm.* **5**, 1164.
 Heise (1897). *Tropenpflanzer*, **1**, 10.
 Hilditch (1934). *Biochem. J.* **28**, 779.
 — and Jones (1932). *J. Chem. Soc.* 805.
 — — (1934). *J. Soc. Chem. Ind.* **53**, 13 T.
 — and Saletore (1933). *J. Soc. Chem. Ind.* **52**, 101 T.
 — and Sleightholme (1931). *Biochem. J.* **25**, 507.
 Klimont (1904). *Monatsh. Chem.* **25**, 931.
 Robinson, Roche and King (1932). *J. Amer. Chem. Soc.* **54**, 705.