22. *An X-Ray and Thermal Examination of the Glycerides. Part IV. Symmetrical Mixed Triglycerides,* $CH(O{\cdot}COR')(CH_2{\cdot}O{\cdot}COR)_2$.

By Thomas Malkin and Melville L. Meara.

The two following groups of symmetrical mixed triglycerides have been examined and their m. p. and *X*-ray data determined: (*a*) Glycerides in which the group R′ is shorter than R, *viz.*, β-decodilaurin, β-laurodimyristin, β-myristodipalmitin, β-palmitodistearin; (*b*) those in which R′ is longer than R, *viz.*, β-laurodidecoin, β-myristodilaurin, β-palmitodimyristin, β-stearodipalmitin. These are found to exist in four solid modifications, *viz.*, vitreous, α, β′, and β, in order of increasing m. p., transition from lower- to higher-melting forms being more rapid than with simple triglycerides.

X-Ray data support the tuning fork structure of glycerides () proposed in Part I, and also distinguish between glycerides of the two types mentioned above.

THE natural extension of our recent investigation of αα′-diglycerides (Part III, J., 1937, 1409) is to the derived symmetrical mixed triglycerides, $CH(O{\cdot}CO{\cdot}R')(CH_2{\cdot}O{\cdot}CO{\cdot}R)_2$, and we have now examined all the possible mixed triglycerides derived from the even-membered acids decoic to stearic. These fall into certain related groups, and for convenience in the presentation of our results, we confine the present account to the two following series,* in which the β-acyl radicals are respectively (*a*) two carbon atoms shorter or (*b*) two carbon atoms longer than the corresponding pair of α-acyl radicals, *viz.*,

(*a*)	β-Decodilaurin.	β-Laurodimyristin.	β-Myristodipalmitin.	β-Palmitodistearin.
	$(\beta)C_{10}\begin{cases}C_{12}(\alpha')\\C_{12}(\alpha)\end{cases}$	$C_{12}\begin{cases}C_{14}\\C_{14}\end{cases}$	$C_{14}\begin{cases}C_{16}\\C_{16}\end{cases}$	$C_{16}\begin{cases}C_{18}\\C_{18}\end{cases}$
(*b*)	β-*I.aurodidecoin*.	β-Myristodilaurin.	β-Palmitodimyristin.	β-Stearodipalmitin.
	$C_{12}\begin{cases}C_{10}\\C_{10}\end{cases}$	$C_{14}\begin{cases}C_{12}\\C_{12}\end{cases}$	$C_{16}\begin{cases}C_{14}\\C_{14}\end{cases}$	$C_{18}\begin{cases}C_{16}\\C_{16}\end{cases}$

This selection is such that, for each group independently, the irregularity in the crystal packing due to the different lengths of chains in the molecule is the same for each member, and since there is a regular increase in the length of chain from member to member, simple relationships in both *X*-ray and m. p. data would be expected.

We find that mixed triglycerides exist in four solid modifications, *viz.* (in order of increasing m. p.), vitreous, α, β′, and β, the last being the stable modification and the one normally obtained from solvents. Except for the existence of the β′-form, the polymorphism is similar in its main features to that of the simple triglycerides (Part I; J., 1934, 666), and the same conditions hold for the formation and stability of the various forms.

Each modification yields a characteristic *X*-ray spectrum, and the "side spacings" of the stable forms of the group (*a*) series are strikingly different from those of group (*b*) (Plate I).

Like the simple triglycerides and αα′-diglycerides, mixed triglycerides show spherulite formation (Plate I, Figs. 4, 5, 6). Figs. 4 and 5, taken from the same specimen, are interesting in that parts of the field show the ripple effect characteristic of αα′-diglycerides (Part III, *loc. cit.*). The latter are, however, distinguished by the absence of the sharp spherulite nucleus.

EXPERIMENTAL.

Preparation of Mixed Triglycerides.—Our triglycerides were prepared by the acylation of αα′-diglycerides, the method being a slight modification of that used by King and his co-workers (*J. Amer. Chem. Soc.*, **1929**, **51**, 866; **1932**, **54**, 705; **1934**, **56**, 1191). The acylation proceeds smoothly and quantitatively, but it is important that the αα′-diglycerides conform with the standards of purity given in Part III (*loc. cit.*), since the presence of small amounts of triglyceride in the starting material makes the final purification almost impossible.

The following preparation of β-laurodimyristin is typical. 1·2 G. (1·5 mols.) of lauryl chloride (b. p. 155°/28 mm.), followed by 2·5 c.c. of pyridine (good excess), are added to a cold solution of 2 g. (1 mol.) of αα′-dimyristin in 30 c.c. of benzene (dried over sodium), and the reaction vessel is corked and kept overnight. The reaction mixture is then decanted into a separating funnel, the precipitated pyridine salt being washed with benzene and ether, and the benzene–ether solution is washed with dilute sulphuric acid and water and dried (sodium sulphate). After removal of the solvent, two crystallisations from alcohol (2 × 40 c.c.) yield 2·7 g. of crystalline product, m. p. 50°.

Only slight modifications of the above procedure are required for other members of the series. If the acid chains are longer, slightly more benzene is required for the reaction and for washing, and the final crystallisation is preferably from benzene–alcohol; with shorter acid chains, less alcohol is required in the final crystallisations. All the mixed glycerides now described crystallise in felted masses of needles reminiscent of the finer grades of asbestos.

* An account of the corresponding unsymmetrical triglycerides,

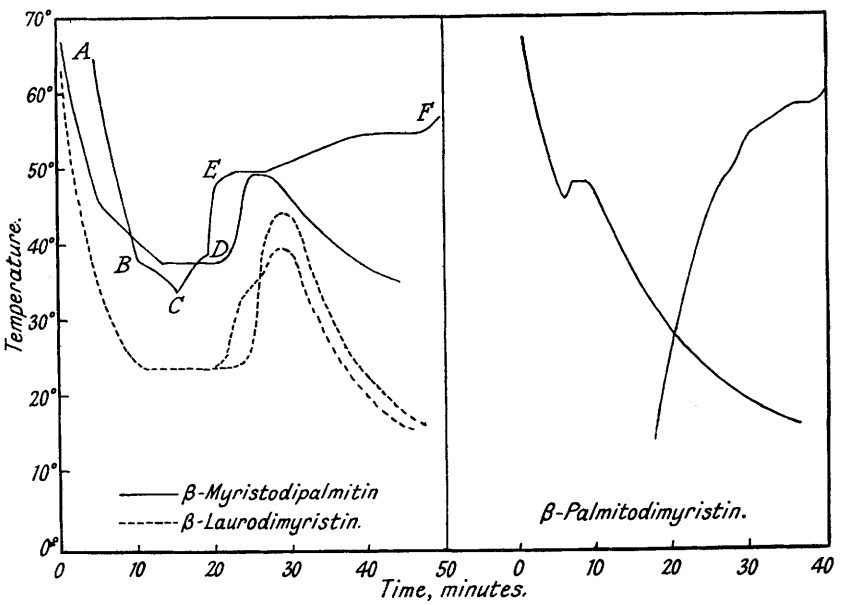
$$CH_2(O{\cdot}CO{\cdot}R){\cdot}CH(O{\cdot}CO{\cdot}R){\cdot}CH_2(O{\cdot}CO{\cdot}R'),$$

is in preparation in collaboration with Dr. M. G. R. Carter.—T. M.

β-*Laurodidecoin* has not hitherto been prepared (Found: C, 72·3; H, 11·4. $C_{35}H_{66}O_6$ requires C, 72·1; H, 11·4%).

Thermal Investigation.—This was carried out as described in Part I and Part II (*locc. cit.*), by means of cooling and heating curves and capillary m. p. determinations. In general, transitions from lower- to higher-melting modifications were more rapid than was the case with simple triglycerides (Part I, *loc. cit.*), but by varying the cooling and heating gradients, evidence of the existence of four modifications was found. A preliminary curve, cooling to room temperature, followed by a heating curve, usually gives sufficient information to suggest the required modification in gradient; *e. g.*, in Fig. 1, *AC* is the cooling curve for β-myristodipalmitin (room temperature). The arrest *B* represents separation of the vitreous modification, since on warming (curve *CF*), there is a corresponding arrest (*D*) followed by a sharp rise in temperature (*i.e.*, liquefaction and crystallisation of vitreous form; Part I, p. 669). A smaller cooling gradient is therefore required for solidification in the α-form. Fig. 1 (cooling bath at 30°) shows formation of both the α and the vitreous forms, and also indicates the rapidity of the transitions in group (*a*). After a steady period of vitreous separation, the transitions

FIG. 1.



vitreous → α → β′ set in, with a rise in temperature to the m. p. of the β′-form. The same transitions occur when β-laurodimyristin is cooled to room temperature (Fig. 1), and here evidence of the α-form is occasionally found in the rising part of the curve.

With room-temperature cooling, members of group (*a*), except β-decodilaurin (α-solidification), solidify in the vitreous modification, but in group (*b*) only β-stearodipalmitin solidifies in this form, the other members solidifying in the α-modification (Fig. 1). Heating curves for both groups are similar with regard to β′- and β-forms. The β′-arrest is often quite short owing to the rapid transition β′ → β at this temperature, a transition diminishing in velocity with increasing length of hydrocarbon chains. Heating curves for the two groups are, however, dissimilar in that indication of the melting of the α-form is usually present on the curves for group (*b*).

The data obtained from the curves were checked against capillary determinations, but owing to the rapidity of the transitions, capillary m. p. data for vitreous and α-forms are not regarded as being so accurate as those obtained from the curves, although differences are not great. True " double melting," *i.e.*, complete melting followed by resolidification, is usually observed only with the higher members, for the transition vitreous → α. Small amounts of impurity stabilise the lower-melting forms and retard the transition speeds noticeably for the β′ → β transitions; rapid transitions are therefore a good indication of purity.

The m. p.'s obtained in the present investigation are given in Table I and plotted in Fig. 2.

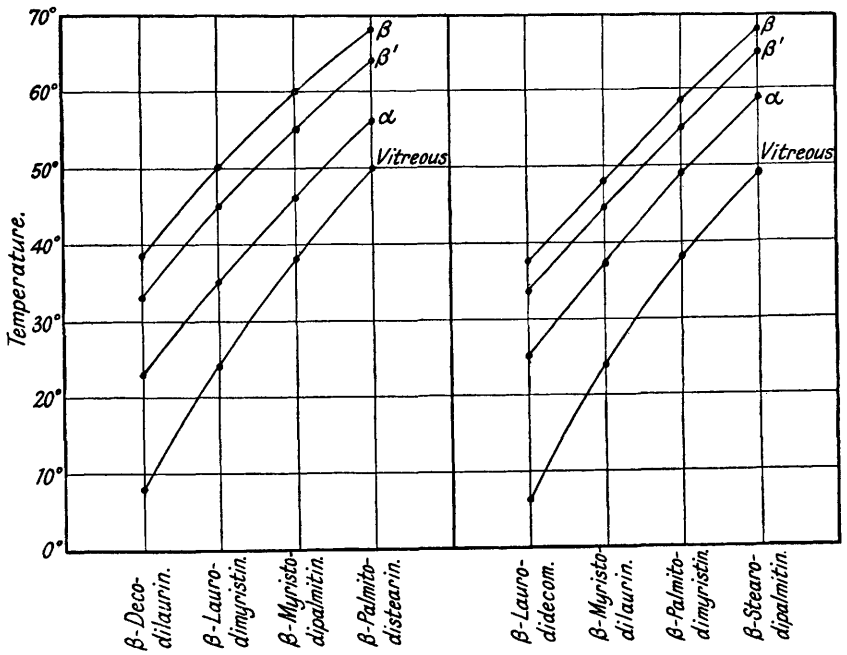
TABLE I.

	Vitreous.	α.	β.	β′.	Other workers' data.
		Group (*a*).			
β-Decodilaurin	8°	23°	33°	38·5°	38·8° [1]
β-Laurodimyristin	24	35	45	50	49·5 [2]; 46·5 [3]
β-Myristodipalmitin	37	46	55	60	58·5—59 [2]
β-Palmitodistearin	50	56	64	68	68 [4]; 52·5, 62, 63 [5]; 67·9 [6]
		Group (*b*).			
β-Laurodidecoin	6	25	34	37·5	—
β-Myristodilaurin	24	37	44	48	50·2 [1]; 32, 36·5, 39·5 [3]
β-Palmitodimyristin	38	49	55	58·5	59·8—60 [2]
β-Stearodipalmitin	49	59	65	68	64·8 [2]; 60 [7]; 59·1 [6]

[1] McElroy and King, *J. Amer. Chem. Soc.*, 1934, **56**, 1191. [2] Averill, Roche, and King, *ibid.*, 1929, **51**, 866. [3] Grün, *Ber.*, 1907, **40**, 1787. [4] Robinson, Roche, and King, *J. Amer. Chem. Soc.*, 1932, **54**, 705. [5] Kreis and Hafner, *Ber.*, 1903, **36**, 2767. [6] Amberger and Bromig, *Biochem. Z.*, 1922, **130**, 263. [7] Guth, *Z. Biol.*, 1902, **44**, 98.

FIG. 2.

M.p.'s of symmetrical mixed triglycerides.



X-*Ray Investigation.*—This was carried out as described in Parts I and II, pressed and melted layers and rods being examined. The Philips Metalix tube (copper anticathode) being run at 10 ma., exposures of 1—2 hours and 3 hours each side were required for pressed and melted layers respectively. Rods required an exposure of ½—1 hour.

Long spacings of the stable β-form were obtained from pressed layers, and those of α- and β′-modifications from melted layers, either by cooling the molten specimen at the required rate, or by first cooling it rapidly to the vitreous form, and then, by suitable warming, converting it into the α- and the β′-form. Considerable difficulty was experienced owing to the rapidity of the transitions, but with a certain amount of repetition and a choice of cool days for examination of the lower members, measurements of metastable forms were obtained for all the glycerides except β-decodilaurin and β-laurodidecoin. Side spacings of the various modifications were obtained from rods in a similar manner.

Table II gives the complete *X*-ray data, long spacings being plotted in Fig. 3 against the " effective length " of the acyl groups in the glyceride molecule in carbon atoms; *i.e.*, the effective length of decodilaurin is 22, $\overline{C_{10}\!<\!C_{12}}$.

β-Decodilaurin.

β-Laurodidecoin.

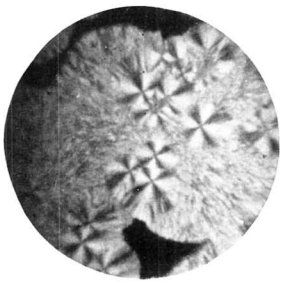


FIG. 4.

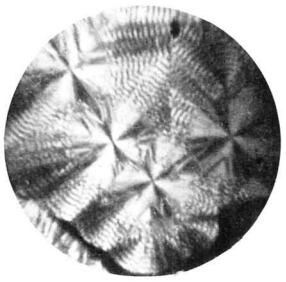


FIG. 5.

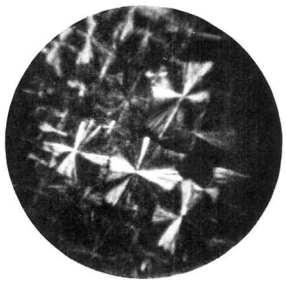


FIG. 6.

FIG. 7.—*Side spacings.*

,, 8.— ,,

,, 9.— ,,

,, 10.— ,,

,, 11.— ,,

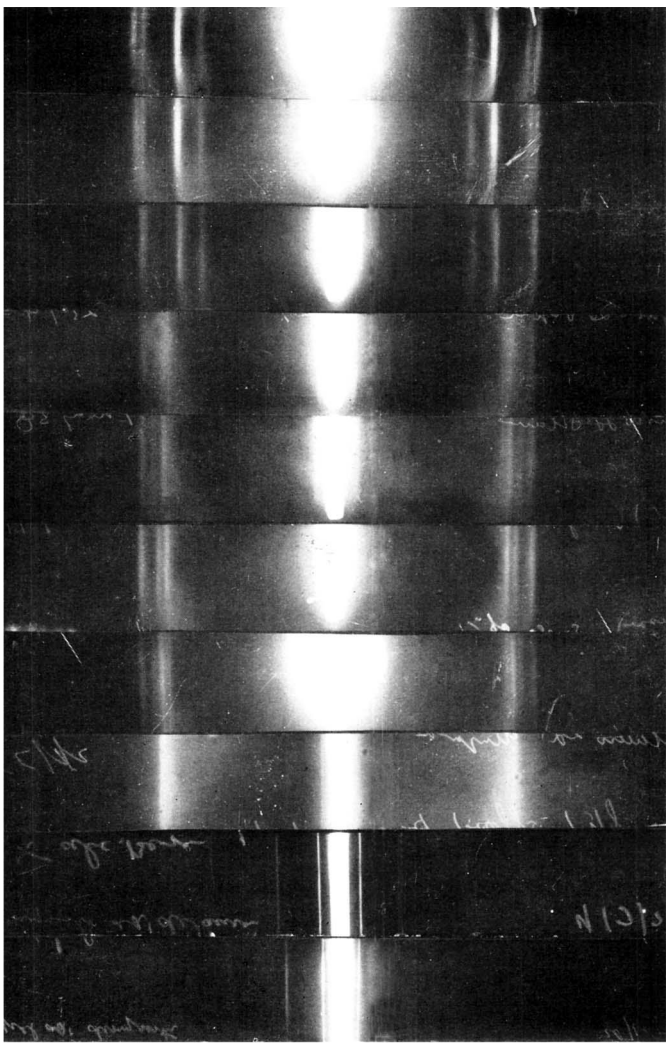
,, 12.— ,,

,, 13.— ,,

,, 14.— ,,

,, 15.—*Long spacings.*

,, 16.— ,,



Tripalmitin β.

Myristodipalmitin β.

Decodilaurin β.

Myristodipalmitin β′.

Myristodilaurin β.

Palmitodimyristin β.

Stearodipalmitin β.

Laurodimyristin α.

Myristodilaurin.

Palmitodimyristin.

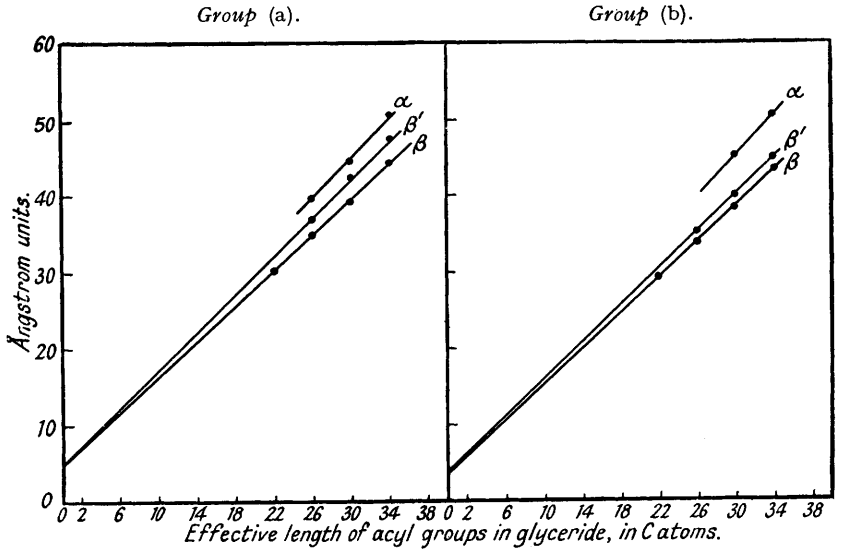
[*To face p.* 107.

TABLE II.

	Long spacings, A.			Side spacings, A.								
	α.	β′.	β.	β.				β′.				α.
Group (*a*).												
β-Decodilaurin	—	—	30·0	3·79	4·06*, 4·35*, 4·62, 5·33							—
β-Laurodimyristin	39·6	36·7	34·7	3·84, 3·89			4·61, 5·34	3·82, 4·05*, 4·16, 4·35*				4·19
β-Myristodipalmitin ...	44·4	42·4	39·0	3·74, 3·86,			4·61, 5·34	,,	,,	,,	,,	,,
β-Palmitodistearin	50·5	47·5	44·2	3·68, 3·86,			4·61, 5·34	,,	,,	,,	,,	,,
Tripalmitin (for comparison of side-spacings)				3·7, 3·9			4·6, 5·3					—
Group (*b*).												
β-Laurodidecoin	—	—	29	3·87,	4·17,	4·39						—
β-Myristodilaurin	—	34·5	33·6	3·85, 4·06*, 4·26, 4·45*				3·85, 4·35†				—
β-Palmitodimyristin ...	45·0	39·7	38·1	3·81, 4·13, 4·31				3·88, 4·13, 4·31				4·19
β-Stearodipalmitin	50·2	44·7	43·2	3·81, 4·03*, 4·2, 4·48				3·81, 4·35†				,,

* Denotes weak lines. † Denotes diffuse lines.
Vitreous forms yield only a diffuse side spacing of ≃ 4·2 A.

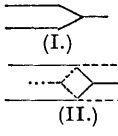
FIG. 3.



Typical *X*-ray photographs are given in Plate I, Figs. 7—16. These show the close relationship in structure between the stable forms of group (*a*) and the simple triglycerides, both giving " broad band " side spacings, compared with the " narrow band " of group (*b*) and β′-forms.

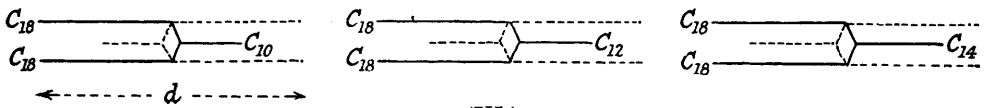
From the curves in Fig. 3, the increase in length of spacing per carbon atom for the stable forms of groups (*a*) and (*b*) respectively are 1·18 and 1·147 A., corresponding with tilts of chain of 69° 33′ and 65° 30′. Approximate tilts for other forms are: Group (*a*), α- and β′-modifications, vertical; group (*b*), α, vertical; β′, 70° 55′.

The intercepts on the ordinates, *viz.*, 4·5 and 4·0 A. for groups (*a*) and (*b*) respectively, support the tuning fork structure (I), advanced in Part I (*loc. cit.*), adjacent molecules lying in reversed positions (II). Consideration of this structure makes clear the necessity for the selection of mixed glycerides in appropriate family groups, if simple relationships between physical properties and constitution are to be sought.


(I.)

(II.)

If, for example, the β-distearins are taken, where the β-substituent is decoyl, lauroyl, myristoyl, etc., a linear relationship between length of molecule and *X*-ray data



(III.)

would not be expected, as the increasing length of the shorter acyl chain would not bring about a corresponding increase in the distance between the reflecting planes (*d*) (see III). In the final paper of the series, it is hoped to discuss these relationships in greater detail.

Grants from the Royal Society and the Colston Society are gratefully acknowledged.

THE UNIVERSITY, BRISTOL. [*Received, November 19th,* 1938.]