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

By M. G. R. CARTER and T. MALKIN.

The following two groups of unsymmetrical mixed triglycerides have been examined and their m. p. and *X*-ray data determined : (*a*) glycerides in which the radical R′ is shorter than R, *viz.*, α-decodilaurin, α-laurodimyristin, α-myristodipalmitin, α-palmitodistearin ; (*b*) those in which the radical R′ is longer than R, *viz.*, α-laurodidecoin, α-myristodilaurin, α-palmitodimyristin, α-stearodipalmitin. These are found to exist in four solid modifications, *viz.*, vitreous, α, β′, and β, in order of increasing m. p., transitions from lower- to higher-melting forms being less rapid than those of symmetrical mixed triglycerides (Part IV; this vol., p. 103). Comparison of m. p.'s of corresponding symmetrical and unsymmetrical mixed glycerides shows that the former melt at the higher temperature.

THE present investigation is complementary to that of the symmetrical mixed triglycerides described in Part IV (*loc. cit.*), and deals with the corresponding unsymmetrical isomers. For the reasons given in Part IV, these have been arranged in the same manner, *viz.*, groups (*a*) and (*b*), in which the single acyl radicals (α) are respectively (*a*) two carbon atoms shorter or (*b*) two carbon atoms longer than the corresponding pair of acyl radicals (α′, β), *viz.*,

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

All the above are found to exist in four solid modifications, *viz.* (in order of increasing m. p.), vitreous, α, β′, and β, the polymorphism being similar to that of the symmetrical mixed triglycerides, except that the transitions from lower- to higher-melting forms are slower. The transition β′ ⟶ β, in particular, is exceptionally slow, and even from solvents the stable β-form separates only on very slow cooling in a Dewar flask.

In agreement with King and his co-workers (*J. Amer. Chem. Soc.*, 1929, **51**, 866; 1930, **52**, 365; 1932, **54**, 705; 1934, **56**, 1191), we find that the unsymmetrical glycerides melt a few degrees lower than the corresponding symmetrical compounds.

The *X*-ray examination revealed no unusual features. Long spacings exhibit normal linear relationships, and side spacings of the stable β-forms are almost identical with those of simple triglycerides. In contrast to the symmetrical glycerides (Part IV), no marked differences in the side spacings of groups (*a*) and (*b*) were found.

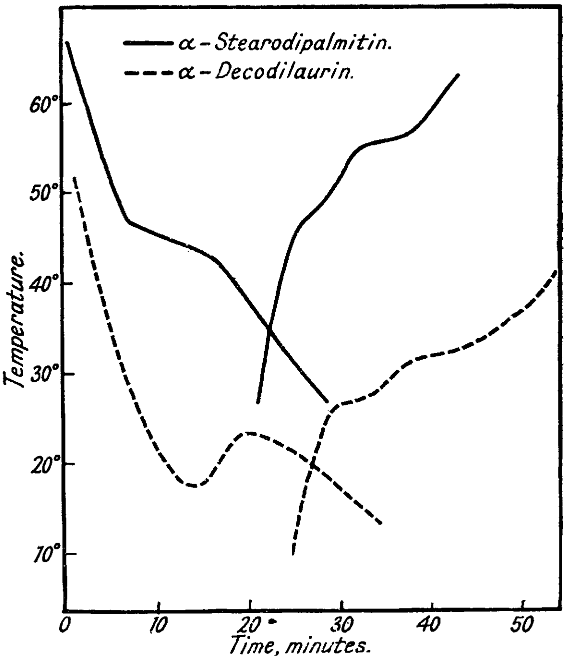
Spherulite formation, similar to that displayed by simple triglycerides, is general, α-laurodidecoin being characterised by slow formation of brilliant isolated spherulites showing the ripple effect mentioned in Part IV.

EXPERIMENTAL.

Preparation of Unsymmetrical Mixed Triglycerides.—These were prepared by the acylation of α-monoglycerides (Part II; J., 1936, 1628) in dry benzene in the presence of pyridine. The following preparation is typical:

α-Palmitodistearin. 2·1 G. (2·3 mols.) of stearoyl chloride (b. p. 180°/5 mm.), followed by 5 c.c. of pyridine, are added to a solution of 1 g. of α-monopalmitin in 60 c.c. of benzene (dried over sodium) at room temperature, and the reaction vessel is stoppered and kept overnight.

FIG. 1.



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 × 60 c.c.) yield 2·4 g.

The product at this stage, although pure, has the appearance of precipitated chalk and is mainly in the β′-form (m. p. 61°). Conversion into the stable β-form (m. p. 65°) can be brought about by slowly cooling a solution in benzene or xylene in a Dewar flask initially filled with hot water. Glycerides with shorter chains were crystallised from slightly less solvent, and α-decodilaurin and α-laurodidecoin, which are very soluble in benzene, were crystallised finally from benzene–alcohol (2 : 1).

Unsymmetrical glycerides are easily distinguished, by their less crystalline appearance, from the symmetrical compounds (Part IV), which form masses of felted needles. Under the microscope, the former appear as short, thickish prisms, and the latter as long, slender, thin prisms.

α-Laurodidecoin has not hitherto been prepared (Found: C, 71·8; H, 11·3. $C_{35}H_{66}O_6$ requires C, 72·1; H, 11·4%).

Thermal Investigation.—This was carried out as described in Part I (J., 1934, 66) and Part II (*loc. cit.*), by means of cooling and heating curves, and capillary m. p. determinations. Curves

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* The higher saturated glycerides are almost insoluble in ether, which should be used sparingly. Addition of small amounts assists the benzene–water separation.

obtained by cooling the molten glycerides to room temperature show a single arrest, due to separation of either the vitreous form (α-stearodipalmitin, α-palmitodimyristin, α-palmitodistearin, α-myristodipalmitin) or the α-form (α-myristodilaurin, α-laurodidecoin, α-laurodimyristin, α-decodilaurin), curves for the latter group being characterised by supercooling (Fig. 1).

The sudden rise in temperature due to the transition α ⟶ β′, which is so marked a feature of the cooling curves of group (*a*) of the symmetrical mixed glycerides, was not observed for any of the unsymmetrical glycerides.

Heating curves for the first of the above groups show arrests at the m. p.'s of the vitreous and α-forms, and those for the two lowest members may also show a slight arrest at the m. p. of the β′-form. This is absent, however, if the heating gradient is excessive.

Heating curves for the second of the above groups show arrests at the m. p.'s of the α- and β′-forms, and those of α-laurodidecoin and α-decodilaurin may show a slight arrest at the m. p. of the β-form. This is more pronounced if the curve is taken some hours after solidification, but under these conditions, the transition α ⟶ β′ has meanwhile proceeded at room temperature and the arrest due to melting of the α-form no longer appears. Apart from the last two cases, heating curves give no indication of the presence of the stable β-form. The transition β′ ⟶ β can, however, be brought about by maintaining the specimen in the neighbourhood

FIG. 2.

M. p.'s of unsymmetrical mixed triglycerides.

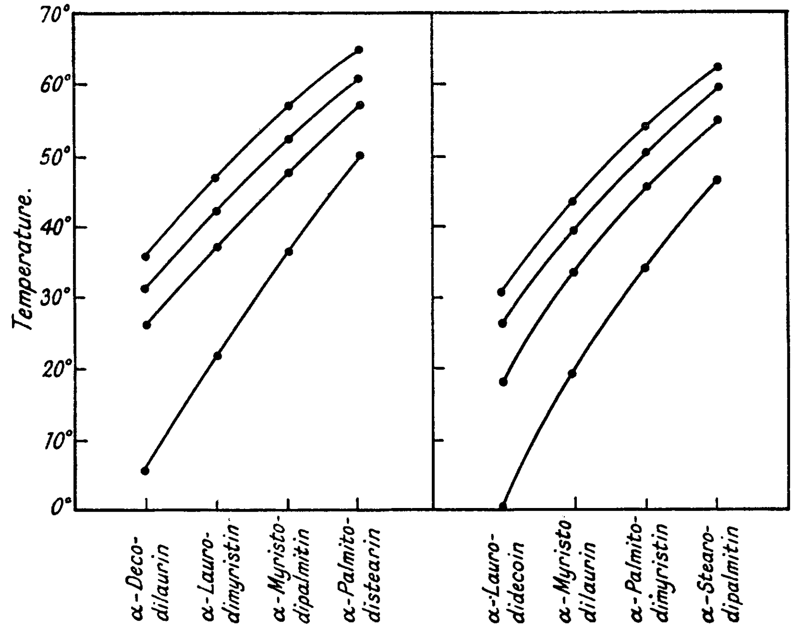


TABLE I.

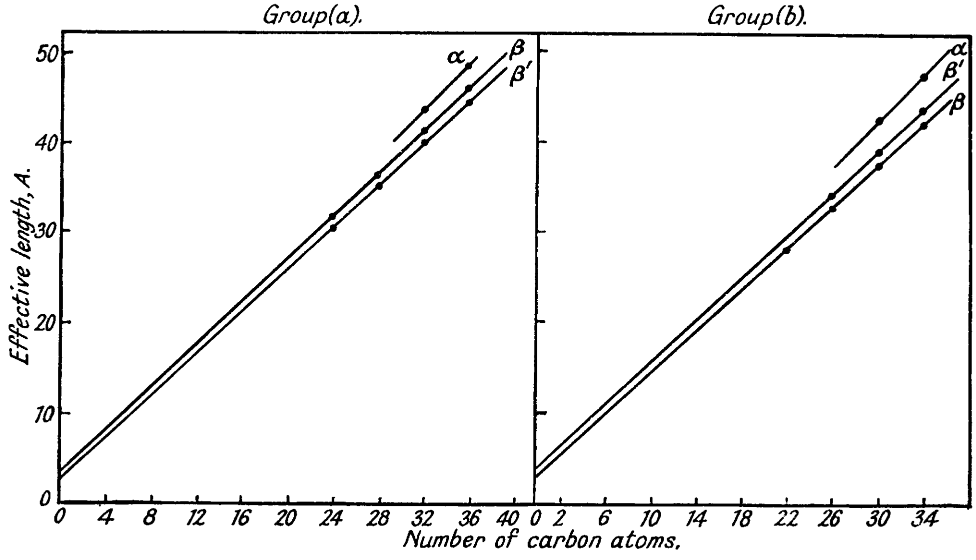
	Vitreous.	*α*.	*β′*.	*β*.	Other workers' data.
α-Decodilaurin	5°	26°	31°	35·5°	32·6° [1]
α-Laurodimyristin	22	37	42	46·5	48·5 [2]
α-Myristodipalmitin	36	47·5	52	57	55·5 [2]
α-Palmitodistearin	50	57	61	65	63·2,[3] 62·6 [4]
α-Laurodidecoin	0	17·5	26	30	— [5]
α-Myristodilaurin	19	33·5	39	43·5	42·8,[1] 41, 36·5 [5]
α-Palmitodimyristin	34	45·5	50·5	54	53,[2] 47·8 [6]
α-Stearodipalmitin	46·5	55	59·5	62·5	63·5,[3] 62·6,[2] 60 [7]

[1] McElroy and King, *J. Amer. Chem Soc.*, 1934, **56**, 1191. [2] Averill, Roche, and King, *ibid.*, 1929, **51**, 866. [3] Amberger and Bromig, *Biochem. Z.*, 1922, **130**, 252. [4] Robinson, Roche, and King, *J. Amer. Chem. Soc.*, 1932, **54**, 705. [5] Grün, *Ber.*, 1907, **40**, 1792. [6] Heiduschka and Schuster, *J. pr. Chem.*, 1928, **120**, 145. [7] Guth, *Z. Biol.*, 1902, **44**, 98.

of the m. p. of the β′-form for periods varying from 12 hours to several days, according to the lengths of the acyl groups. As work on the symmetrical mixed glycerides showed that the velocity of the transition β′ ⟶ β is greatly retarded by impurities, we have thoroughly examined this possibility, and we are satisfied that the present slow transitions are not due to the presence of impurities.

Good agreement was found between m. p.'s obtained from the above curves and by the capillary method. The latter are easy to determine owing to the fact that all the glycerides exhibit true " double melting " phenomena. The m. p. of the stable β-form is first obtained in the usual manner, the solvent-crystallised glyceride being used. The molten specimen is then cooled sufficiently to cause solidification in the vitreous form, and immersed in a bath at a temperature (found by trial) just sufficient to cause melting and resolidification (vitreous m. p.). The process is then repeated at higher temperatures to give the m. p. of the α- and β′-forms. Approximate bath temperatures are known from the heating curves. M. p.'s of the various forms are given in Table I and plotted in Fig. 2.

FIG. 3.



Effective length of acyl chains in glycerides.

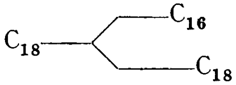
X-Ray Investigation:—This was carried out as described in Parts I, II, and IV, pressed and melted layers and rods being used. Long and side spacings were obtained for most of the forms mentioned in the previous section, except for certain of the metastable forms of the lower

TABLE II.

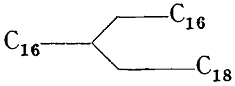
	Long spacings, A.			Side spacings, A.		
	α.	β′.	β.	α.	β′.	β.
α-Decodilaurin	—	30·4	31·8	4·19	3·83, 4·18, 4·35*	3·67, 3·86, 4·6, 5·35
α-Laurodimyristin	—	35·3	36·5	—	3·83, 4·18, 4·35*	3·67, 3·86, 4·6, 5·35
α-Myristodipalmitin	43·9	40·3	41·5	—	3·83, 4·18, 4·35	3·67, 3·86, 4·6, 5·35
α-Palmitodistearin	48·8	44·7	46·5	—	3·83, 4·18, 4·35*	3·67, 3·86, 4·6, 5·35
α-Laurodidecoin	—	—	28·4	—	3·83, 4·18, 4·35	3·75, 3·86, 4·6, 5·35
α-Myristodilaurin	—	34·5	33·0	—	3·83, 4·18, 4·35	3·75, 3·86, 4·6, 5·35
α-Palmitodimyristin	42·8	39·5	37·7	—	3·83, 4·22, 4·35*	3·67, 3·86, 4·6, 5·35
α-Stearodipalmitin	47·8	43·9	42·5	—	3·83, 4·18, 4·35*	3·67, 3·86, 4·6, 5·35

* Weak line.

members, which could not be obtained owing to transitions taking place during the somewhat lengthy *X*-ray exposure. Spacings are given in Table II. In Fig. 3, long spacings are plotted against the "effective length" of the acyl chains (cf. Part IV), *i.e.*,



effective length C_{36}



effective length C_{34}

Tilts of the hydrocarbon chains for the various forms are: Group (*a*), β-form, 73°; β′-form, 68° 6′: Group (*b*), β-form, 62°; β′-form, 63° 30′. (Increase in length per carbon atom respectively, 1·21, 1·17, 1·11, 1·125 A.)

The intercepts on the ordinates at C = 0 (Fig. 3) are 3·0 and 2·5 A. [β-form, groups (*a*) and (*b*)] compared with 4·5 A. for simple triglycerides. This difference is greater than the experimental error, and may be due to slight overlapping of the terminal methyl groups, owing to the unequal lengths of the acyl chains.

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