

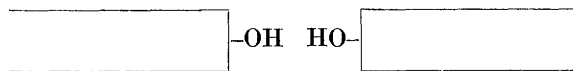
290. An X-Ray and Thermal Examination of the Glycerides.  
Part III. The  $\alpha\alpha'$ -Diglycerides.

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Continuing our study of the polymorphism of glycerides, we have now investigated a series of  $\alpha\alpha'$ -diglycerides, from  $\alpha\alpha'$ -didecoin to  $\alpha\alpha'$ -distearin, by means of X-rays and cooling and heating curves. Apart from their polymorphism, interest attaches to the  $\alpha\alpha'$ -diglycerides, as intermediates in the synthesis of the naturally occurring mixed triglycerides of the type  $\text{CH}_2(\text{OR})\cdot\text{CH}(\text{OR}')\cdot\text{CH}_2\cdot\text{OR}$ , and it is important that satisfactory criteria of purity should be established.

The polymorphism of the  $\alpha\alpha'$ -diglycerides is similar to that of the tri- and monoglycerides, but the transitions between the various forms are more rapid. An unusual discontinuity occurs at  $\alpha\alpha'$ -dipentadecoin, the lower members resembling more the  $\alpha$ -monoglycerides, and the higher members resembling the triglycerides. Thus, three modifications exist for  $\alpha\alpha'$ -didecoin to  $\alpha\alpha'$ -dipentadecoin ( $\alpha$ ,  $\beta'$ , and  $\beta$ ) and two modifications exist for  $\alpha\alpha'$ -dipalmitin to  $\alpha\alpha'$ -distearin ( $\alpha$  and  $\beta$ ).

The X-ray data favour the view that the crystals are built up of layers of double molecules, with the two hydrocarbon chains lying parallel on the same side of the glycerol molecule, *i.e.*,



$\alpha\alpha'$ -DIGLYCERIDES have frequently been prepared as intermediates in the synthesis of mixed triglycerides, but the only systematic study of them is that due to Averill, Roche, and King (*J. Amer. Chem. Soc.*, 1929, **51**, 869), who, in the course of a comprehensive investigation of glycerides, revised the earlier unsatisfactory m. p. data for  $\alpha\alpha'$ -di-laurin, -myristin, -palmitin, and -stearin. Their revision is not, however, wholly satisfactory, since the recorded m. p.'s fall on an unusually irregular curve. Moreover, no reference is made to the polymorphism ("double melting") indicated by the observations of earlier workers, *e.g.*, Grün and Theimer (*Ber.*, 1907, **40**, 1798).

We have therefore examined a series from  $\alpha\alpha'$ -di-decoin to  $\alpha\alpha'$ -distearin, in the manner previously described for the triglycerides (Part I; Clarkson and Malkin, *J.*, 1934, 666) and the  $\alpha$ -monoglycerides (Part II; Malkin and Shurbagy, 1936, 1628). We find that, like the tri- and  $\alpha$ -mono-glycerides, the  $\alpha\alpha'$ -diglycerides exhibit polymorphism. Besides the stable crystalline form obtained from solvents ( $\beta$ -form), all exist in a lower-melting metastable form (probably an  $\alpha$ -form). Further, the lower members of the series ( $\text{C}_{10}$ — $\text{C}_{15}$ ) exist in a second metastable form of intermediate m. p. ( $\beta'$ -form). When the molten  $\alpha\alpha'$ -diglyceride is cooled, the  $\alpha$ -form separates first, and rapidly changes into the  $\beta'$ -form (lower members), or the  $\beta$ -form (higher members). The  $\beta'$ -form then changes into the  $\beta$ -form. The transitions are thus very similar to those of the tri- and  $\alpha$ -mono-glycerides, but are appreciably quicker, and there is a noticeably greater tendency for the  $\alpha\alpha'$ -diglycerides to pass into their stable crystalline form.

An interesting property of the  $\alpha\alpha'$ -diglycerides, not previously recorded, is illustrated by Figs. 4 and 5, Plate I. The molten diglyceride is allowed to cool on a microscope slide under a cover slip, and viewed between crossed nicols. Typical spherulite crosses appear, distinguished from those given by triglycerides (Part I, *loc. cit.*) by the circular ripples, brought out more clearly in the higher magnification of Fig. 5. This effect is only observed when the  $\alpha\alpha'$ -diglycerides are pure, and best results are obtained with the following gradation in the rate of cooling:  $\alpha\alpha'$ -didecoin to  $\alpha\alpha'$ -ditridecoin cooled to 0—10°,  $\alpha\alpha'$ -dimyristin to  $\alpha\alpha'$ -dipentadecoin cooled to room temperature,  $\alpha\alpha'$ -dipalmitin to  $\alpha\alpha'$ -distearin cooled to between room temperature and 40°.

The  $\alpha\alpha'$ -diglycerides used in the investigation were prepared by esterifying  $\alpha$ -monoglycerides (Part II, *loc. cit.*), either with fatty acids in the presence of *p*-toluene- or camphor-sulphonic acid, or with acid chlorides in the presence of pyridine. Fischer's method (*Ber.*,

\* M. L. Meara prepared and examined  $\alpha\alpha'$ -didecoin and also elaborated the method of preparation of  $\alpha\alpha'$ -diglycerides *via* acid chlorides.

1920, 53, 1621) does not offer any advantage in yield or technique, and was not adopted on account of the expensive starting material.

*Thermal Examination.*—This was carried out as described for triglycerides and monoglycerides (*loc. cit.*). Cooling and heating curves were obtained, and the points of arrest checked against capillary m. p. determinations. The curves shown in Fig. 1 for  $\alpha\alpha'$ -dilaurin are typical for the lower members (up to  $\alpha\alpha'$ -dipentadecoin).

No special feature appears on the cooling curve, which is of a normal type, showing only one arrest ( $\alpha$ -form); but two arrests, at higher temperatures, appear on the heating curve ( $\beta'$ - and  $\beta$ -forms). Expected variations in the form of the curves occur, dependent on the rate of cooling and on the length of the hydrocarbon chains. Thus, after a small cooling gradient, the first arrest on the heating curve is much smaller than the second (*i.e.*, the transition  $\beta' \rightarrow \beta$  is more complete). Conversely, after rapid cooling, there are indications on the heating curve of a slight arrest at the m. p. of the  $\alpha$ -form, and the first upper arrest is greater than the second (*i.e.*, the transition  $\alpha \rightarrow \beta'$  is not complete and the transition  $\beta' \rightarrow \beta$  is slight). These variations, obtained by rapid cooling, are the same as those due to increasing length of hydrocarbon chain, the speed of the transitions being retarded in each case. With  $\alpha\alpha'$ -dipalmitin, -diheptadecoin, and -distearin, we found no arrest corresponding to the  $\beta'$ -form. Two arrests are usually observed on the heating curve, but the first always corresponds to that on the cooling curve ( $\alpha$ -form).

FIG. 1.

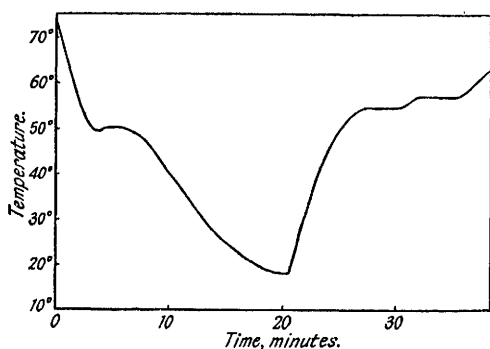
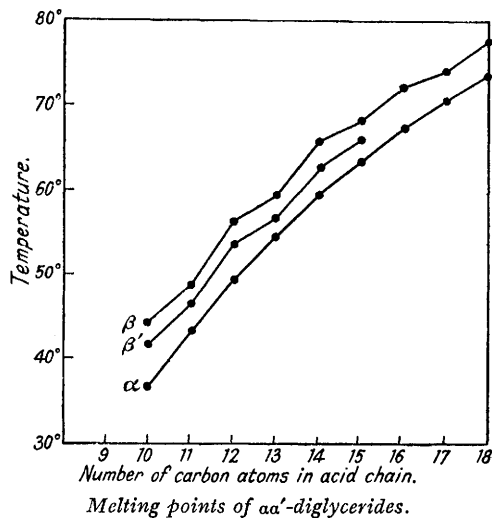


FIG. 2.



Experiments in capillary tubes confirm the above results. When, for example,  $\alpha\alpha'$ -dilaurin is melted in a capillary tube, cooled rapidly (ice), and then heated in the usual manner for a m. p. determination, there is first a change in appearance, accompanied by an increase in volume, slightly below the m. p. of the  $\alpha$ -form, and a slight softening at the  $\alpha$  m. p. On raising the temperature, there is partial melting at the m. p. of the  $\beta'$ -form, and finally complete melting at the  $\beta$  m. p.

With higher members ( $\alpha\alpha'$ -dipalmitin upwards) there is no evidence of a  $\beta'$  m. p. Occasionally complete melting may occur at the  $\alpha$  m. p., but generally the transitions are too rapid for the typical "double melting" of triglycerides to be observed (*i.e.*, complete melting followed by resolidification at a higher temperature).

M. p.'s of  $\beta'$ -forms are accurately determined as follows. After a normal capillary m. p. determination, the specimen is allowed to cool slowly in the apparatus, and the nuclei which form in the neighbourhood of the  $\alpha$  m. p. are allowed to grow until about a third of the liquid has solidified. If now the temperature is slowly raised, the solid melts at the  $\beta'$  m. p. A few trials may be necessary, in order to judge conditions for avoiding transition into the stable  $\beta$ -form. Provided that the initial temperature of the molten diglyceride

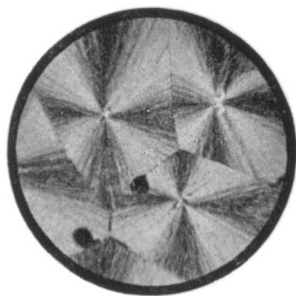


FIG. 4.

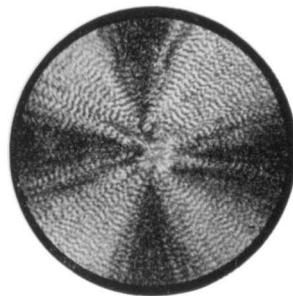


FIG. 5.

*αα'-Dimyristin*

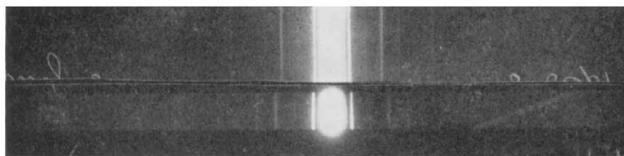


FIG. 6.

*αα'-Dilaurin*



FIG. 7.

*d* spacings.

*a-Type*

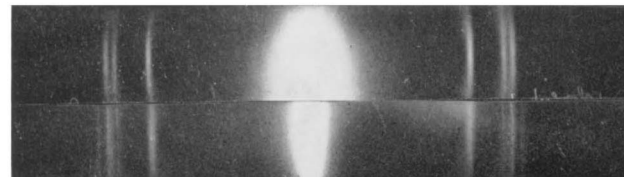


FIG. 8.

*b-Type*



FIG. 9.

*d* spacings.

does not greatly exceed the  $\beta$  m. p., the temperature at which nuclei first appear agrees closely with the  $\alpha$  m. p. Otherwise, supercooling may occur.

The change in appearance below the  $\alpha$  m. p., mentioned above for  $\alpha\alpha'$ -dilaurin, suggests that a vitreous form is produced by rapid cooling. The effect is more noticeable for higher members, but in no case was melting observed below the  $\alpha$  m. p. The m. p.'s for the series investigated are given in Table I and plotted in Fig. 2. The m. p.'s in the last column, denoted by "A. R. & K.," are those of Averill, Roche, and King (*loc. cit.*).

TABLE I.  
*Melting points of  $\alpha\alpha'$ -diglycerides.*

	$\alpha$ .	$\beta'$ .	$\beta$ .	A. R. & K.		$\alpha$ .	$\beta'$ .	$\beta$ .	A. R. & K.
$\alpha\alpha'$ -Didecoin ...	37°	42°	44.5°		$\alpha\alpha'$ -Dipentadecoin	63.5°	66.5°	68.5°	
$\alpha\alpha'$ -Diundecoin	43.5	47	49		$\alpha\alpha'$ -Dipalmitin ...	68	—	72.5	69.5°
$\alpha\alpha'$ -Dilaurin ...	49.5	54	56.5	56.6°	$\alpha\alpha'$ -Diheptadecoin	71.5	—	74.5	
$\alpha\alpha'$ -Ditridecain	54.5	57	59.5		$\alpha\alpha'$ -Distearin .....	74	—	78	79.1
$\alpha\alpha'$ -Dimyristin	60	63	65.5	63.8—64.4					

*X-Ray Examination.*—This was carried out as described in Parts I and II, pressed and melted layers, and rods being examined. Long spacings are given in Table II and plotted

TABLE II.  
*Long spacings (A.) of  $\alpha\alpha'$ -diglycerides.*

No. of C atoms in acid	10	11	12	13	14	15	16	17	18
Pressed layer (stable $\beta$ -form)	32.5a	35.2a	37.4a	40.4a	42.6a	45.0b	44.7a	47.7b	49.5a
Melted layer ( $\beta'$ - or $\beta$ -form)	32.5a	33.2b	35.7b	38.1b	40.5b	42.5b	44.7a	47.7b	49.5a

in Fig. 3. Typical photographs showing the intensity distribution are reproduced in

FIG. 3.

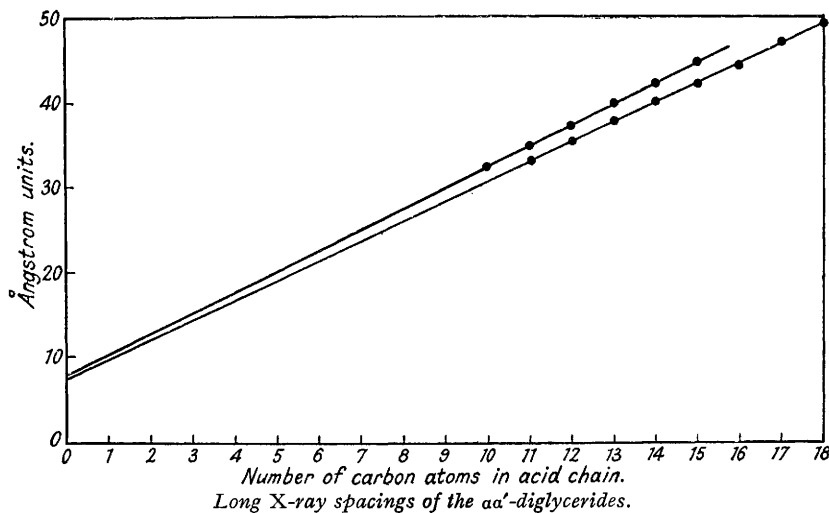


Plate I, Figs. 6 and 7. The suffix letters *a* and *b* denote the associated side spacings, of which two types were found (Plate I, Figs. 8 and 9), *viz.*,

<i>a</i> , A. ....	4.6 strong	3.9 strong	3.73 strong	
<i>b</i> , A. ....	4.6 strong	3.9 weak	3.73 strong	3.6 weak

The long spacings fall on two straight lines and correspond with double molecules tilted at angles of  $72^\circ 12'$  and  $66^\circ 30'$  for the upper and the lower line respectively. The probable arrangement is



but a single linear molecule . . . .  $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2$  . . . . would have approximately the same length and intensity distribution. The intercepts on the curves at *O*-carbon atoms, which are a measure of the length occupied by the glycerol groups and the terminal hydrogen atoms of the hydrocarbon chains, slightly favour the former structure, and although this is not altogether conclusive, further support is given by the close similarity of the side spacings to those of the triglycerides, which have a somewhat similar arrangement of the long chains. These spacings (in Å.) are (Clarkson and Malkin, *loc. cit.*):

5.3 weak                  4.6 strong                  3.9 strong                  3.7 strong

We have been unable to obtain either long or side spacings for the modification that we have provisionally termed the  $\alpha$ -form. Their non-alternation in m. p. indicates that the chains are arranged vertically between the terminal planes (cf. Malkin, J., 1931, 1796), and analogy with long-chain esters and mono- and tri-glycerides makes it probable that they are vertical rotating molecules.

A perplexing feature of our results is the discontinuity at  $\alpha\alpha'$ -dipalmitin shown in the X-ray spacings and also by the absence of a  $\beta'$ -form. From  $\alpha\alpha'$ -didecain to  $\alpha\alpha'$ -dipentadecain, the spacings of the stable  $\beta$ -form and the metastable  $\beta'$ -form lie respectively on the upper and the lower curve, but from  $\alpha\alpha'$ -dipalmitin upwards the spacings of the stable crystalline forms lie on the lower curve. Moreover,  $\alpha\alpha'$ -dipalmitin and  $\alpha\alpha'$ -distearin retain the *a* type of side spacings which for the lower members corresponds with the upper curve. Further,  $\alpha\alpha'$ -dipentadecain gives both long spacings but only the *b* type of side spacings.

We cannot yet offer any convincing explanation of these peculiarities, particularly as this is the first case that we have encountered, but we have recently obtained evidence of similar discontinuities in other series, and the accumulation of further data may provide the explanation.

#### EXPERIMENTAL.

The  $\alpha\alpha'$ -diglycerides were prepared by esterifying  $\alpha$ -monoglycerides either with acids in the presence of 1–2% of *p*-toluenesulphonic acid or *d*-camphor-10-sulphonic acid at 130–140°, or by the action of acid chlorides in the presence of pyridine. Both methods give yields of 65–85%, except in the case of  $\alpha\alpha'$ -didecain, where the yield by the first method is poor. A 5–10% excess of  $\alpha$ -monoglyceride was used in order to avoid the formation of triglyceride, which can only be separated from  $\alpha\alpha'$ -diglyceride with difficulty, excess  $\alpha$ -monoglyceride being easily separated by one or two crystallisations from alcohol. Final crystallisations were from light petroleum (diundecain to ditridecain) and hexane or hexane–benzene (dimyristin to distearin). It was necessary to crystallise didecain throughout from alcohol (ice), owing to the separation of a jelly-like  $\alpha$ -form on cooling the light petroleum solution. The crystallisation is wasteful and brings down the final yield in this case to 50%. Final crystallisations are conveniently controlled by microscopic examination (Figs. 4 and 5), these effects only being given when the  $\alpha\alpha'$ -diglycerides are pure.

In the first method of preparation, it is important, in order to avoid triglyceride formation, not to exceed the temperature limits, but with this precaution there is little to choose between the two methods. A typical preparation by each method is described.

*$\alpha\alpha'$ -Distearin.*—A mixture of 1.9 g. of  $\alpha$ -monostearin, 1.4 g. of stearic acid, and 0.05 g. of *p*-toluenesulphonic acid in a round-bottomed flask, is heated at 120–130° for 5 hours, removal of water being assisted by occasional attachment to the water pump for a few minutes (porous pot). Two crystallisations from alcohol, followed by two from hexane, yield 2.6 g. of crystalline  $\alpha\alpha'$ -distearin, m. p. 79°.

*$\alpha\alpha'$ -Dilaurin.*—To a cold solution of 4.15 g. of  $\alpha$ -monolaurin in 30 c.c. of dry benzene, are added 3 g. of lauryl chloride and then slowly, with shaking, 1.15 c.c. of pyridine. After standing overnight, the benzene is removed on the water-bath, and the residue taken up in ether, washed free from pyridine, and dried (sodium sulphate). After removal of ether, the residue is crystallised from alcohol (ice) and finally from light petroleum or hexane; yield 5.1 g.; m. p. 56.5°.

Analytical data are given for the following  $\alpha\alpha'$ -diglycerides which have not previously been prepared:  *$\alpha\alpha'$ -Didecain* (Found: C, 68.7; H, 11.0.  $\text{C}_{23}\text{H}_{44}\text{O}_5$  requires C, 68.9; H, 11.1%);  *$\alpha\alpha'$ -diundecain* (Found: C, 69.8; H, 11.4.  $\text{C}_{25}\text{H}_{48}\text{O}_5$  requires C, 70.1; H, 11.2%);  *$\alpha\alpha'$ -ditri-*

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*decoin* (Found : C, 71.7; H, 11.9.  $C_{29}H_{56}O_5$  requires C, 71.9; H, 11.6%);  $\alpha\alpha'$ -*dipentadecoin* (Found : C, 73.3; H, 12.1.  $C_{33}H_{64}O_5$  requires C, 73.3; H, 11.9%);  $\alpha\alpha'$ -*diheptadecoin* (Found : C, 74.2; H, 11.9.  $C_{37}H_{72}O_5$  requires C, 74.4; H, 12.1%).

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