

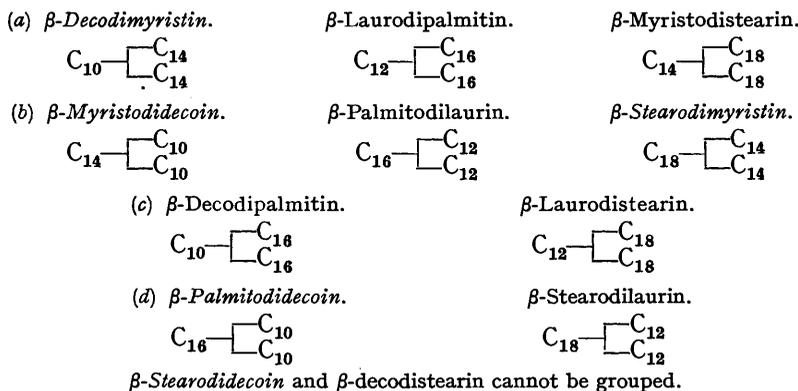
250. *An X-Ray and Thermal Examination of the Glycerides. Part VI. Symmetrical Mixed Triglycerides, CH(O·COR')(CH₂·O·COR)₂ (continued).*

By THOMAS MALKIN and MELVILLE L. MEARA.

The following glycerides have been examined, and their m. p. and X-ray data determined: β -decodimyristin, β -laurodipalmitin, β -myristodistearin; β -myristodidecoin, β -palmitodilaurin, β -stearodimyristin; β -decodipalmitin, β -laurodistearin; β -palmitodidecoin, β -stearodilaurin; β -stearodidecoin; β -decodistearin. All are found to exist in four solid modifications, *viz.*, vitreous, α , β' , and β , the last being the stable modification.

In contrast to glycerides previously examined, long spacings of the β -forms of all except β -palmitodilaurin and β -stearodimyristin correspond to twice the length of a single molecule, but the side spacings do not suggest any fundamental difference in structure.

THE present investigation completes our study of the symmetrical mixed triglycerides derived from the even-membered acids decolic to stearic. For the reasons given in Part IV (this vol., p. 103), the glycerides have been arranged in the following groups, the difference in length between the acyl chains being the same for members of each group, *viz.* :



All the above exist in four solid modifications, *viz.*, vitreous, α , β' , and β (in order of increasing m. p.), and where comparisons are possible, they exhibit normal m. p. relationships (Fig. 2).

For members of the same group, the velocities of the transitions vitreous \rightarrow α , $\alpha \rightarrow$ β' , $\beta' \rightarrow$ β , increase with diminishing chain length, but this does not necessarily hold for members of different groups owing to the factor introduced by the unequal differences in chain length; *e.g.*, the transitions of β -decodistearin are more rapid than those of β -laurodipalmitin which has the shorter total chain length.

In contrast to the glycerides previously studied, long spacings of the stable β -forms of all except β -palmitodilaurin and β -stearodimyristin correspond to twice the length of a single molecule, but side spacings are of the normal type, and do not indicate any fundamental change in crystalline structure.

Spherulite formation was observed with all the above glycerides.

EXPERIMENTAL.

The glycerides were prepared as described in Part IV (*loc. cit.*). All crystallise well from alcohol, or, in the case of those containing higher acids, alcohol-benzene (slow cooling in Dewar vessel). With the exception of the three members of group (a) (above), all possess the characteristic felted appearance mentioned in Part IV.

Analytical data are given for the following, which have not been previously prepared :

β -Decodimyristin (Found : C, 74.0; H, 12.1. $C_{41}H_{78}O_6$ requires C, 73.8; H, 11.8%); β -stearodimyristin (Found : C, 75.9; H, 12.1. $C_{40}H_{74}O_6$ requires C, 75.5; H, 12.2%); β -myristodidecain (Found : C, 72.9; H, 11.5. $C_{37}H_{70}O_6$ requires C, 72.7; H, 11.6%); β -palmitodidecain (Found : C, 73.4; H, 11.9. $C_{39}H_{74}O_6$ requires C, 73.3; H, 11.7%); β -stearodidecain (Found : C, 74.0; H, 11.5. $C_{41}H_{78}O_6$ requires C, 73.8; H, 11.8%).

Thermal Examination.—This was carried out as described in Parts I (J., 1934, 666) and II (J., 1936, 1628) by means of cooling and heating curves and capillary m. p. determinations. Representative curves shown in Fig. 1 (cooling to room temperature) illustrate the increase in

FIG. 1.

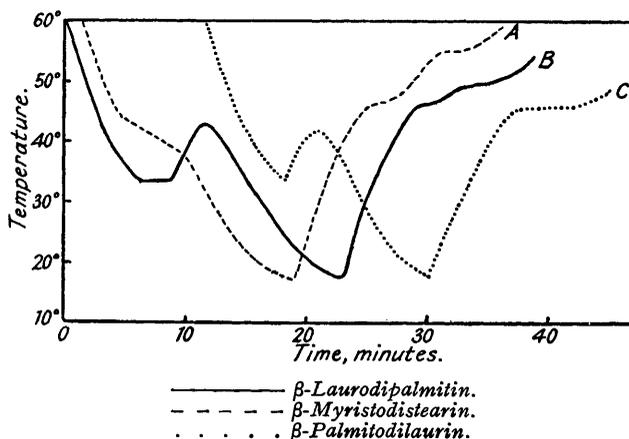
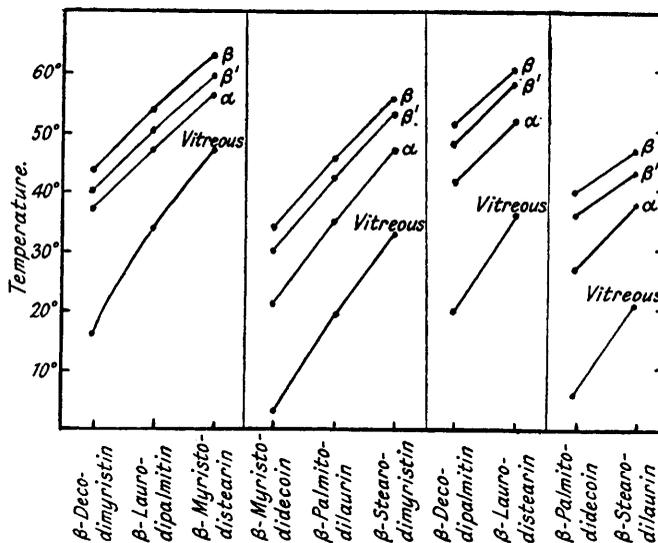


FIG. 2.



speed of the various transitions with diminishing chain length. Curve A, β -myristodistearin, shows separation of the vitreous form, followed on the heating curve by arrests at the m. p.'s of the vitreous and the α -form. Curve B, β -laurodipalmitin, shows a short period of vitreous separation, followed by a sharp rise in temperature as crystallisation of the α -form sets in. On the heating curve arrests occur at the m. p.'s of the α - and the β' -form. Finally, the curve C, β -palmitodilaurin, on reaching the m. p. of the α -form, rises rapidly as crystallisation in the β' - and the β -form occurs. The single arrest at the m. p. of the stable β -form on the heating curve shows that transition into this form is practically complete.

M. p.'s are given in Table I, and plotted in Fig. 2. Those marked with an asterisk were

difficult to determine owing to the rapidity of the transition, but are probably accurate to within 1°.

TABLE I.

	Vitreous.	α .	β' .	β .	Other workers' data.
β -Decodimyristin	16°	37°	40°	43·5°	—
β -Laurodipalmitin	34	47	50	53·5	63·5—64° ¹ †; 54·6° ²
β -Myristodistearin	47	56	59	62·5	63·5 ³
β -Myristodidecain	3	21	30	34	—
β -Palmitodilaurin	19*	35*	42·5*	45·5	47·8 ⁴
β -Stearodimyristin	33	47	53	55·5	—
β -Decodipalmitin	20	42	48*	51·5	66 ¹ †
β -Laurodistearin	36	52	58	60·5	59·8 ³ ; 53·5, 56·5, 68·5 ⁵
β -Palmitodidecain	6	27	36	40	—
β -Stearodilaurin	21	38	43	47	50·9 ¹ ; 37·5 ⁵
β -Stearodidecain	5*	34	40	44·5	—
β -Decodistearin	30*	47*	53*	57	56·2 ³

† These values are obviously far too high; cf. tripalmitin, m. p. 65·5°.

¹ Averill, Roche, and King, *J. Amer. Chem. Soc.*, 1929, **51**, 866.

² Schuster, *J. pr. Chem.*, 1928, **120**, 145.

³ Robinson, Roche, and King, *J. Amer. Chem. Soc.*, 1932, **54**, 705.

⁴ McElroy and King, *ibid.*, 1934, **56**, 1191.

⁵ Grün and Schacht, *Ber.*, 1907, **40**, 1778.

X-Ray Investigation.—This was carried out as described in Parts I, II, and IV (*loc. cit.*), pressed and melted layers and rods being examined. Pressed layers of β -forms, except those of β -palmitodilaurin and β -stearodimyristin, appear to be poor diffractors of X-rays, and required unusually long exposures of some 4 hours each side. Long and side spacings are given in Table II.

TABLE II.

Substance and group.	Long spacings.			Side spacings.						
	α .	β' .	β .	β' .			β .			
β -Decodimyristin	} a	33·7	52·5	3·92	4·15	4·39w	3·84	4·2w	4·6	5·25w
β -Laurodipalmitin		77·0	59·0	3·81	4·08	4·36	"	"	"	"
β -Myristodistearin		44·7	65·8	3·77	4·12	4·26	"	"	"	"
β -Myristodidecain	} b	30·3	46·5	3·9	4·3w	4·6w	3·86	"	4·6	4·96w
β -Palmitodilaurin		36·6	35·5	3·9w	4·09w	4·29	4·44	3·85	4·09w	4·29
β -Stearodimyristin		41·0	40·0	3·88w	4·17	4·34	"	"	4·6	4·96w
β -Decodipalmitin	} c	39·0	74·0	56·5	3·82	4·08	4·31	3·84	4·61	5·32w
β -Laurodistearin		42·4	63·7	"	"	"	"	"	"	"
β -Palmitodidecain		—	49·5	"	"	"	"	"	"	"
β -Stearodilaurin	} d	40·8	37·5	56·8	3·83	4·02w	4·2	4·41w	3·87	4·27w
β -Stearodidecain		—	51·6	"	"	"	"	"	4·58	4·9w
β -Decodistearin		76·3	61·2	3·83	4·11	4·34	3·86	4·24w	4·61	4·9w

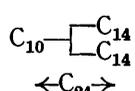
All α -forms give a single side spacing of $\approx 4·19$ A.

w = Weak lines.

vw = Very weak lines.

DISCUSSION.

Long spacings of β -forms, with the two exceptions mentioned above, are too large to correspond with the length of a single molecule; e.g., in β -decodimyristin, with a spacing of 52·5 A., the maximum length of the acyl chains is 30·24 A., i.e., 24 carbon atoms at 1·26 A. per atom (see inset). Even after allowance of a further 5 A. for the length contributed by the glycerol molecule, there is still a wide discrepancy. It would appear, therefore, that the long spacing represents a double molecule, although the spacing is somewhat small, and to account for this it must be assumed that the molecules are tilted at an acute angle across the reflecting planes. This tilt can be calculated for members of group (a), the β -spacings of which are in good linear relationship, and is found to be 41° 18' (increase in length per carbon atom = 0·83 A.). In view of the observed linear relationship, and the small increase in length per carbon atom, on passing from a lower to a higher glyceride of the same group, other possible explanations



of the smallness of the long spacings are not so acceptable as the suggested tilting of the double molecule, but a final solution must await a more detailed *X*-ray analysis.

With two exceptions, side spacings are of the broad and the narrow band type for β - and β' -forms respectively (cf. this vol., p. 107). Photographs of β -forms are closely similar to that reproduced in Part IV, Fig. 9 (*ibid.*).

The results for group (*b*) show a transition from the single to the double molecular structure, which was unexpected in view of the equal chain length difference for each member of the group (4CH_2), and it is clear that the absolute value of chain length difference is not the sole factor determining this structural change.

Side spacings of β -forms of the two anomalous compounds (β -palmitodilaurin and β -stearodimyristin) are of the narrow band type and are almost identical with the spacings of the respective β' -forms. In this respect these two glycerides closely resemble β -myristodilaurin and β -palmitodimyristin respectively (Part IV, *loc. cit.*), with which there is a certain structural relationship.

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THE UNIVERSITY, BRISTOL.

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