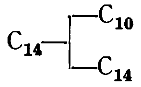
320. *An X-Ray and Thermal Examination of the Glycerides. Part VII. Unsymmetrical Mixed Triglycerides,* $CH_2(O{\cdot}COR){\cdot}CH(O{\cdot}COR){\cdot}CH_2(O{\cdot}COR')$.

By M. G. R. Carter and T. Malkin.

The following glycerides have been examined and their m. p. and X-ray data determined: *α-decodimyristin,* α-laurodipalmitin, α-myristodistearin; *α-myristodidecoin,* α-palmitodilaurin, *α-stearodimyristin*; α-decodipalmitin, α-laurodistearin, *α-palmitodidecoin,* α-stearodilaurin; *α-stearodidecoin*; α-decodistearin. All are found to exist in four solid modifications, *viz.*, vitreous, α, β′, and β, the last being the stable modification. Long spacings of the above, with the exception of the first three, correspond to twice the length of a single molecule. Side spacings are, however, of the normal type. The importance of the X-ray method in the identification of naturally occurring glycerides is indicated.

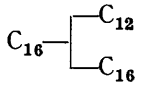
The present account completes our study of the unsymmetrical mixed triglycerides derived from the even-membered acids decoic to stearic, all of which have now been investigated. As in Part VI (this vol., p. 1141), which deals with the corresponding symmetrical compounds, the glycerides are arranged in the following groups, the difference in length between the acyl chains being the same for members of each group, *viz.*:

(a) α-Decodimyristin.



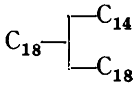
$\mathrm{C_{14}}-\begin{cases}\mathrm{C_{10}}\\ \mathrm{C_{14}}\end{cases}$

α-Laurodipalmitin.



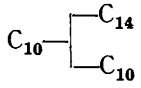
$\mathrm{C_{16}}-\begin{cases}\mathrm{C_{12}}\\ \mathrm{C_{16}}\end{cases}$

α-Myristodistearin.



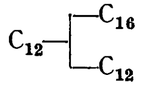
$\mathrm{C_{18}}-\begin{cases}\mathrm{C_{14}}\\ \mathrm{C_{18}}\end{cases}$

(b) α-Myristodidecoin.



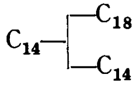
$\mathrm{C_{10}}-\begin{cases}\mathrm{C_{14}}\\ \mathrm{C_{10}}\end{cases}$

α-Palmitodilaurin.



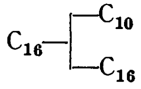
$\mathrm{C_{12}}-\begin{cases}\mathrm{C_{16}}\\ \mathrm{C_{12}}\end{cases}$

α-Stearodimyristin.



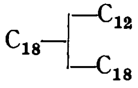
$\mathrm{C_{14}}-\begin{cases}\mathrm{C_{18}}\\ \mathrm{C_{14}}\end{cases}$

(c) α-Decodipalmitin.



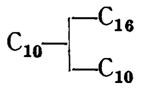
$\mathrm{C_{16}}-\begin{cases}\mathrm{C_{10}}\\ \mathrm{C_{16}}\end{cases}$

α-Laurodistearin.



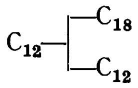
$\mathrm{C_{18}}-\begin{cases}\mathrm{C_{12}}\\ \mathrm{C_{18}}\end{cases}$

(d) α-Palmitodidecoin.



$\mathrm{C_{10}}-\begin{cases}\mathrm{C_{16}}\\ \mathrm{C_{10}}\end{cases}$

α-Stearodilaurin.



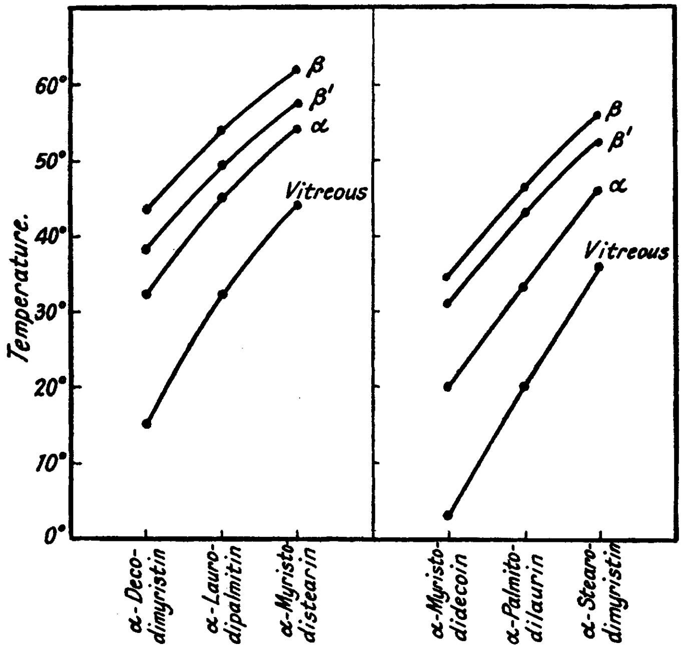
$\mathrm{C_{12}}-\begin{cases}\mathrm{C_{18}}\\ \mathrm{C_{12}}\end{cases}$

Also α-Stearodidecoin. α-Decodistearin.

All the above exist in four solid modifications, *viz.*, vitreous, α, β′, β (in order of increasing m. p.) and their m. p. and *X*-ray data exhibit normal relationships (Figs. 1 and 2). The polymorphism is similar to that found for other unsymmetrical mixed glycerides (Part V, this vol., p. 577), the characteristic feature of which is the exceedingly slow transition, $\beta' \longrightarrow \beta$.

FIG. 1.

Group (a). *Group (b).*



M. p.'s of unsymmetrical mixed triglycerides.

It was found for glycerides discussed in Part IV (this vol., p. 103) and Part V (*loc. cit.*) that the m. p.'s of unsymmetrical compounds are lower than those of the symmetrical, but the present results show that this cannot be taken as a general rule. M. p.'s of members of groups (a) and (b) are in fact so close to those of their symmetrical isomers (Part VI, *loc. cit.*) that differentiation between pairs of isomers by m. p.'s alone would be almost impossible. The two types are, however, readily distinguished by their *X*-ray data.

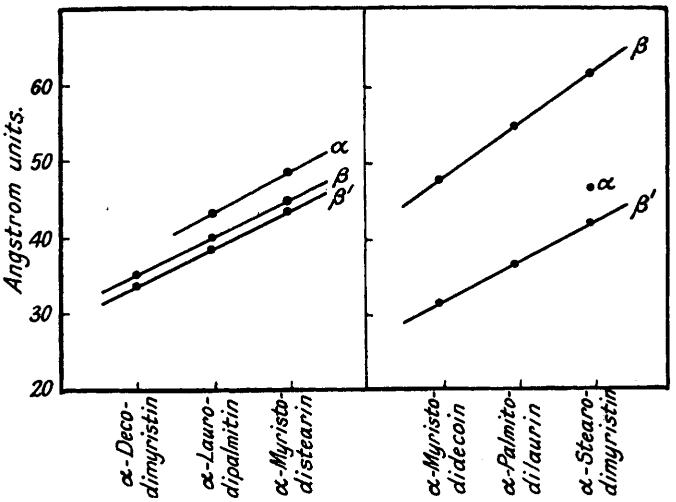
The above affords a particularly good illustration of the value of the *X*-ray method in the identification of natural products, hitherto based on m. p. comparisons. Neither the *X*-ray nor the capillary m. p. method alone is wholly conclusive, but used in conjunction, a correct identification is highly probable.

As is the case with the corresponding symmetrical compounds (Part VI), a transition occurs in this series from a single to a double molecular structure, long spacings, with the exception of those found for group (a), being much too long to represent a single molecule. This change in structure does not appreciably affect the side spacings, which are of the normal type.

All the glycerides examined exhibit typical spherulite formation.

FIG. 2.

Group (*a*). *Group* (*b*).



Long X-*ray spacings.*

EXPERIMENTAL.

The glycerides were prepared as described in Part V (*loc. cit.*). We again experienced difficulty in obtaining the stable β-form, very slow cooling of benzene or benzene–alcohol solutions being necessary. Throughout our investigations, the poor crystalline appearance of unsymmetrical compounds, compared with symmetrical, has been most marked, and this characteristic should afford a valuable clue of identity to workers on natural products.

The following compounds have not been previously prepared : *α-decodimyristin* (Found : C, 74·0; H, 11·5. $C_{41}H_{78}O_6$ requires C, 73·8; H, 11·8%), *α-myristodidecoin* (Found : C, 72·6; H, 11·5. $C_{37}H_{70}O_6$ requires C, 72·7; H, 11·6%), *α-palmitodidecoin* (Found : C, 73·2; H, 11·7. $C_{39}H_{74}O_6$ requires C, 73·3; H, 11·7%), *α-stearodidecoin* (Found : C, 73·7; H, 11·8. $C_{41}H_{78}O_6$ requires C, 73·8; H, 11·8%), and *α-stearodimyristin* (Found : C, 75·2; H, 12·5. $C_{49}H_{94}O_6$ requires C, 75·5; H, 12·2%).

Thermal Investigation.—This was carried out as described in Part I (J., 1934, 666) and Part II (J., 1936, 1628) by means of cooling and heating curves, and capillary m. p. determinations.

Both cooling and heating curves are of the same type as those shown in Part V, Fig. 1 (this vol., p. 578). Cooling to room temperature, glycerides with vitreous forms melting higher than 30° (see Table I) yield curves similar to that given for α-stearodipalmitin (separation of vitreous form) and the remainder give the type of curve shown for α-decodilaurin (separation of α-form). Heating curves of the former group show arrests at the m. p.'s of the vitreous and α-forms, and those of the latter group show arrests at the m. p.'s of the α- and β'-forms. Arrests on the heating curves, at the m. p.'s of the stable β-forms, were observed only after the specimen had been maintained in the neighbourhood of the m. p. of the β′-form for considerable periods. Capillary m. p.'s were determined as described in Part V (*loc. cit.*) and did not offer special difficulty, with the exception of those of the vitreous forms of the didecoin compounds, where the transition, vitreous ⟶ α-form, is rapid.

M. p.'s of the various forms are given in Table I, and those of groups (a) and (b) are plotted in Fig. 1.

TABLE I.

	Vitreous.	α.	β′.	β.	Other workers' data.
α-Decodimyristin	15°	32°	38°	43·5°	—
α-Laurodipalmitin	32	45	49·5	54	54·5°,[1] 53·5°[2]
α-Myristodistearin	44	54	57·5	62	58·5,[3] 52, 59, 62[4]
α-Myristodidecoin.........	3	20	31	34·5	—
α-Palmitodilaurin	20	33	43	46·5	44·8,[5] 47—48[6]
α-Stearodimyristin	36	46	52	56	—
α-Decodipalmitin	23	37	41	45·5	60[1]
α-Laurodistearin	36	47	52	—	49—50,[6] 49, 47,[4] 50·9,[1] 50·6[3]
α-Palmitodidecoin	2	24	32	35	—
α-Stearodilaurin	20	31	41·5	45	44, 46,[4] 45·4[1]
α-Stearodidecoin	13	32	38	41	—
α-Decodistearin............	33	42·5	46	49	48·2[3]

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

[2] Heiduschka and Schuster, *J. pr. Chem.*, 1928, **120**, 145.

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

[4] Grun and Theimer, *Ber.*, 1907, **40**, 1792.

[5] McElroy and King, *J. Amer. Chem. Soc.*, 1934, **56**, 1191.

[6] Fischer, Bergmann, and Bärwind, *Ber.*, 1920, **53**, 1589.

TABLE II.

Substance, and group.		α.	β′.	β.	β′.				β.				
α-Decodimyristin	a	—	33·8	35·2	3·8	4·12	4·33		3·72	3·9	4·53	4·67	5·4
α-Laurodipalmitin		43·4	38·5	39·8	3·78	4·09w	4·26	4·5w	,,	,,	,,	,,	,,
α-Myristodistearin		48·5	43·4	45·0	3·78	4·09w	4·26	4·5w	,,	,,	,,	,,	,,
α-Myristodidecoin	b	—	31·3	47·5	3·8	4·1w	4·26		3·84	—	4·6	4·84w	5·21w
α-Palmitodilaurin		—	36·2	54·6	3·78	4·09w	4·26		,,	—	,,	,,	,,
α-Stearodimyristin		46·4	41·7	61·4	3·8	4·15	4·27		,,	—	,,	,,	,,
α-Decodipalmitin	c	—	74·1	56·2	3·82	4·1	4·35		3·84	4·27w	4·6	4·85w	5·26w
α-Laurodistearin		47·4	42·8	—	3·82	4·18	4·35		—	—	—	—	—
α-Palmitodidecoin	d	—	—	49·7	3·94	—	4·35		3·84	4·27w	4·6	4·85w	5·26w
α-Stearodilaurin		—	38·7	57·0	3·86	4·11	4·35		,,	,,	,,	,,	,,
α-Stearodidecoin		—	51·0	52·6	3·8	4·1	4·35		3·84	—	4·6	—	5·3
α-Decodistearin		73·7	—	60·0	—	—	—		3·74	4·02	4·33	4·6w	—

All α-forms give a single side spacing of ≏ 4·19 A. w = weak lines.

X-*Ray Investigation.*—This was carried out as described in Parts I and II (*locc. cit.*) and Part IV (this vol., p. 103). Exposures of at least 4 hours each side were required for layers, and ¾—1 hour for rods. Long and side spacings are given in Table II, and long spacings of groups (a) and (b) are plotted in Fig. 2.

As was found for the corresponding symmetrical compounds, the majority of the long spacings of β-forms are too large to correspond with layers of single molecules, but smaller than would be expected from layers of double molecules. Various factors, such as interweaving layers, interpenetration of the unequal hydrocarbon chains, or tilt of the chains, could explain the smallness of the diffracting period, but the regularities in m. p. and *X*-ray data, and the small increase in length per carbon atom on passing up any particular group, favour the view that tilt of the molecule is mainly responsible.

Subject to the usual assumptions, the angles of tilt for β′- and β-forms of groups (a) and (b) may be calculated to be : Group (a), β′- and β-forms, 75¼° (increase in length per carbon atom 1·22 A). Group (b), β′-form, vertical; β-form, 43¼° (increase in length per carbon atom 1·275 and 0·865 A resp.). These values are approximate, as there are only three members in each of the above groups, but the error is not great. Side spacings are of the normal type, β′- and β-forms giving rise to a narrow and a broad band of lines respectively.

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