85. *An X-Ray and Thermal Examination of the Glycerides. Part X. Symmetrical Mono-oleoyl and Monoelaidoyl Disaturated Triglycerides.*

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2-Oleo-distearin, -dipalmitin, and -dimyristin exist in five solid modifications, namely, vitreous, α, β″, β′, and β, in order of ascending m. p. Thus, they differ from triglycerides previously studied, which exist in four forms; cf. Part IX, *J.*, 1948, 985. The suggestion of Lutton (*J. Amer. Chem. Soc.*, 1946, **68**, 676) that only three forms exist, cannot, therefore, be sustained. Divergent results of Filer, Sidhu, Daubert, and Longenecker (*ibid.*, p. 167) are shown to be probably due to the presence of diglycerides in their specimens. As was expected (Part IX, *loc. cit.*), 2-*elaido-distearin* and -*dipalmitin* are similar to their saturated analogues in their structure and polymorphism.

Daubert and Clarke (*J. Amer. Chem. Soc.*, 1944, **66**, 690) showed by means of cooling and heating curves that 2-oleoyl disaturated glycerides (saturated acids C 10, 12, 14, 16, and 18) exist in four solid modifications, and this was supported by the work of Meara (*J.*, 1945, 22), who reported four m. p.s for 2-oleodistearin isolated from six different natural fats. Later, Filer *et al.* (*loc. cit.*) recorded *X*-ray data for certain of the above glycerides, and shortly afterwards, Lutton (*loc. cit.*), who examined 2-oleodistearin thermally and with *X*-rays, concluded that only three forms exist.* Apart from this difference concerning the number of polymorphs, there are discrepancies in the *X*-ray results of Lutton and Filer *et al.* Thus, the long spacings given by the latter are twice as great as those of Lutton, and the side spacings given for the form of oleodistearin of m. p. 37° are entirely different. It was clearly desirable, therefore, to re-examine these compounds.

Although 2-elaido-disaturated glycerides are not known to exist naturally, we thought it of interest to include them in our study, in view of the probable similarity to their saturated analogues.

Thermal Examination.—Cooling and heating curves taken in the manner described in Part I (*J.*, 1934, 668) showed no unusual features, and were rather similar to those given in Fig. 1, Part IV (*J.*, 1939, 103) for 2-myristodipalmitin and 2-laurodimyristin, the main characteristic of which is the rapid transitions of vitreous ⟶ α ⟶ β′-form, shown by an unusually large rise on the cooling curve during solidification. Apart from a few minor differences in temperature, our results are in good agreement with those of Daubert and Clarke (*loc. cit.*) (cf. Table I), whose curves for 2-oleodimyristin, which show clearly the existence of four solid modifications, give an excellent picture of the behaviour of this group.

One important point, however, appears to have escaped these authors, namely, that the highest m. p. obtained from the curves is almost invariably two or three degrees lower than that of specimens crystallised slowly from solvents, and we find that the four forms shown by the curves do not include the highest-melting stable β-form. Thus, five forms exist, which we term, in harmony with previous nomenclature, vitreous, α, β″, β′, and β, in order of increasing m. p.

2-*Oleodimyristin.*—The cooling curve (ice-jacketed) shows separation in the α-form, followed by a rise in temperature to the neighbourhood of the β″-m. p., due to transitions α ⟶ β″, β″ ⟶ β′. The heating curve taken immediately after cooling shows a slight indication of the presence of β″-form, but the main arrest is at the β′ m. p. With a steeper cooling gradient (ice and salt) an arrest occurs at the vitreous m. p., and the heating curve then shows arrests at the α, β″, and β m. p.s.

* *Added, October 26th*, 1948.—From a recent paper (*J. Amer. Chem. Soc.*, 1948, **70**, 2441), it seems probable that Dr. Lutton's failure to observe forms reported by other workers is due to the rapidity with which his heating curves are taken, since this tends to smooth out details. Thus, his curves 2 and 3, Fig. 2 (*loc. cit.*) give some evidence of arrests at 59° (α-form) and 65° (β′-form) respectively, and in our experience these arrests would be much more marked if the curves were taken about three times more slowly (the normal rate in this laboratory).

2-*Oleodipalmitin*.—Cooling to room temperature (15°), the curve shows separation of α-form, changing rapidly to β″-form with sharp rise in temperature. The heating curve shows the presence of β″- and β′-forms.

2-*Oleodistearin*.—On cooling to room temperature (18°) there is an arrest at the α-m. p., followed at first by a slight fall in temperature, and then by a sharp rise to 37—38°, due to α ⟶ β″ transition. The heating curve shows only one arrest, at the β″-m. p. Thus, the transition β″ ⟶ β′ is very slow, but, if the β″-form is kept for a few hours just below its m. p., the curve then shows an arrest at the β′-m. p.

2-*Elaido-dipalmitin and -distearin*.—As anticipated in Part VIII (*loc. cit.*), these are similar to the related 2-stearodipalmitin and tristearin, and exist in four forms, *viz.*, vitreous, α, β′, and β. Their m. p.s are lower than those of the saturated compounds, and, in harmony with this, the various transitions, particularly vitreous ⟶ α-form, are more rapid.

Curves for both compounds are much alike. Cooling to room temperature, the vitreous form separates first, and changes rapidly to the α-form, since a heating curve taken immediately after cooling shows only α, β′, and β arrests. With a smaller cooling gradient, the α-form is the first to separate.

M. p.s of the various forms, checked by the usual capillary method, are given in Table I, the values in parentheses being those of Daubert and Clarke (*loc. cit.*).

TABLE I.

	Vitreous.	α.	β″.	β′.	β.
2-Oleodimyristin	2·0 (2·1)	11·0 (12·3)	19·0 (21·5)	26·5 (26·3)	28·5
2-Oleodipalmitin.....	12·0 (12·0)	21·5 (20·8)	29·0 (30·4)	35·0 (35·2)	37·5
2-Oleodistearin	23·0 (22·3)	29·5 (29·8)	37·0 (37·0) (37·6)	41·5 (41·6)	43·5
2-*Elaidodipalmitin* *	33·0	42·0	—	52·5	55·0
2-*Elaidodistearin* †	40·0	46·0	—	58·0	61·0

* (Found: C, 76·5; H, 11·8. $C_{53}H_{100}O_6$ requires C, 76·5; H, 12·1%.)
† (Found: C, 77·07; H, 12·01. $C_{57}H_{108}O_6$ requires C, 77·01; H, 12·3%.)

X-*Ray Investigation*.—This was carried out as described in earlier papers, Parts I (*loc. cit.*) and II (*J.*, 1936, 1628), using pressed and melted layers and rods. In addition to the method described in Part II, rods are conveniently made by melting and cooling the specimen in a m. p. capillary tube, and ejecting it, after conversion into any particular form, by means of a thin steel rod. Our data are given in Table II.

TABLE II.

	Form.	Long spacing, A.	Side spacings, A.
2-Oleodimyristin [1]	β′	39·1	3·92s, 4·23s.
,, ...	β	56·7	3·68m, 3·84m, 4·04m, 4·58vs, 5·17w, 5·43m.
,, impure	Fig. 7		3·57m, 3·74m, 4·01m, 4·26s, 4·40m.
2-Oleodipalmitin [2]	β″	68·5	3·58m, 3·87vs, 4·42m, 4·74s, 5·21w.
,, ...	β′	42·1	3·88m, 4·14m, 4·35s.
,, ...	β	60·7	3·7m, 3·8w, 4·0m, 4·56vs, 5·45m.
2-Oleodistearin [3]	α	50·3	4·17s.
	β″	72·5	3·58m, 3·88vs, 4·47m, 4·74s, 5·22w.
	β′	45·2	3·85m, 4·11m, 4·32s.
	β	64·8	3·66m, 3·84m, 4·02m, 4·58vs, 5·44m.
2-Elaidodipalmitin [2]	β′	44·7	3·8m, 4·18s.
	β	42·7	3·77s, 4·04w, 4·17s, 4·34m.
2-Elaidodistearin	α	51·2	4·14s.
	β′	47·2	3·8m, 4·17s.
	β	44·9	3·66m, 3·85m, 4·00w, 4·57s, 5·31m.

s = strong, vs = very strong, m = moderate, w = weak.

[1] α- and β″-Forms unstable at room temperature.
[2] α-Form unstable at room temperature.
[3] A beautifully crystalline specimen from *Garcinia indica*, sent to us in 1939 by Professor Hilditch, gave the same spacings.

Discussion.—The plate, which shows various side spacings, illustrates some of the more important points. Thus, contrary to Lutton's suggestion of the existence of only three crystalline forms, Figs. 1, 2, 3, and 4 show the definite existence of four (to which must be added the vitreous form). Side spacings of oleodipalmitin are indistinguishable from Figs. 2, 3, and 4,

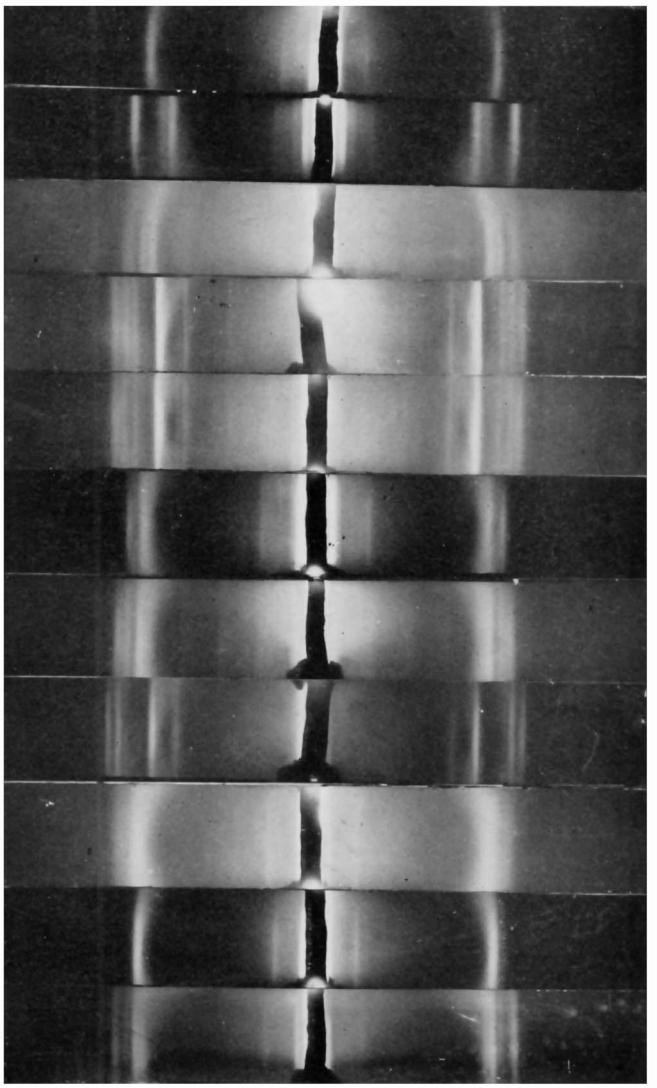


FIG.

1 2-*Oleodistearin*, α

2 ,, , β″

3 ,, , β′

4 ,, , β

5 2-*Oleodimyristin*, β

6 ,, , β′

7 { ,, 1·3-*Dimyristin*

8 2-*Elaidodistearin*, β

9 ,, , β′

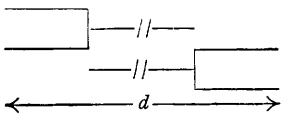
10 ,, , α

11 2-*Elaidodipalmitin*, β

[*To face p.* 370

and all three oleo-compounds are alike in their stable β-form (cf. Figs. 4 and 5). Fig. 7 (impure 2-oleodimyristin, melted rod) is of interest since, within experimental error, the spacings are those given by Filer *et al.*, *loc. cit.* In search of an explanation of the failure of these workers to obtain the spacings shown in Figs. 5 and 6, for 2-oleodimyristin, we added to our specimen some 3—4% of 1 : 3-dimyristin, the most likely impurity, with the result shown. Their failure to obtain the side spacings shown in Fig. 2 (β″-form) for oleodipalmitin and oleodistearin would also appear to be due to contamination with diglyceride, as the spacings they give are of the same spurious type as Fig. 7. Molten specimens of the above two glycerides, allowed to cool to room temperature, always give the spacings shown in Fig. 2.

Our long spacings support Lutton's view of a triple chain length structure for the β″ and β-forms, *viz.* :



cf. Part VIII (—//— = oleoyl).

Filer *et al.* proposed sextuple chain length is based on the presence of a single weak order, not observed by Lutton, lying midway between Lutton's first and second orders, which consequently doubles *d*, the distance between the reflecting planes. This weak order could be the first order of the diglyceride, which appears to be present as an impurity, but we are more inclined to the view that it is the first order of the β′-form. Frequently we find orders of both β and β′-forms present on photographs of oleodimyristin, particularly from melted layers, and even from pressed layers of rapidly crystallised material. Normally, the β-form separates from solvents, but rapid cooling often gives β′- and β-forms, and not infrequently the β′-form only. In fact, one of our methods of obtaining β′-forms for glycerides generally, when other methods fail, is to crystallise rapidly from alcohol. It will be seen from Table II that the long spacings of the β′-forms are roughly two-thirds the magnitude of those of the β-forms, and therefore the first order of the former lies almost midway between the first and second order of the latter.

Our only disagreement with the *X*-ray data of Lutton concerns the long spacing of 80 A. for the α-form of oleodistearin, for which we find no evidence. Our own value of 50·3 A. agrees well with the length of a single molecule, lying vertically across the reflecting planes.

The data for β′-forms, not observed by Lutton, or by Filer *et al.*, are of interest in that they, too, correspond with the single molecular structure proposed by Clarkson and Malkin, as distinct from the triple chain length structure above, and, in view of the observations on this point in Part VIII, it is noteworthy that in spite of the presence of a non-linear *cis*-unsaturated chain, this simple structure is not excluded, albeit only in a metastable form.

The *X*-ray data for 2-elaidodistearin and 2-elaidodipalmitin emphasise again (cf. Part VIII) the great similarity of structures containing elaidoyl and stearoyl radicals. Figs. 8, 9, 10, and 11 are indistinguishable from the corresponding photographs of tristearin and 2-stearodipalmitin (Part IV, *J.*, 1939, 103) respectively. Indeed, it would be extremely difficult to distinguish elaidodistearin from tristearin or elaidodipalmitin from stearodipalmitin by *X*-rays alone, although, of course, m. p.s do so readily.

Experimental.

Preparation of Glycerides.—These were made by the acylation of 1 : 3-diglycerides, the latter being prepared as described in Part III (*J.*, 1937, 1409). The acid chlorides were made by the action of oxalyl chloride on the acids (Adams and Uhlich, *J. Amer. Chem. Soc.*, 1920, **42**, 599). Owing to the sluggish reactivity of the 2-hydroxyl group of the diglyceride, and the impossibility of separating tri- and di-glycerides by crystallisation, these apparently simple preparations are not without their difficulties. Thus, Amberger and Bromig (*Biochem. Z.*, 1922, **130**, 252) isolated only unchanged diglyceride after treating 1 : 3-distearin with oleoyl chloride in quinoline and pyridine at room temperature for several days, and although Jackson, Daubert, King, and Longenecker (*J. Amer. Chem. Soc.*, 1944, **66**, 289) obtained yields of 75% by heating the reagents at 70—85° for 3—6 hours, their products, which are presumably those used by Filer *et al.* (*loc. cit.*), appear to contain diglycerides. In our experience, the only method of obtaining a pure final product is to use an extravagant excess of acid chloride, since we find that large amounts of oleic or elaidic acid are much more readily removed than traces of diglyceride. Two parts by weight of acid chloride to one of diglyceride yielded satisfactory products. The following preparation is typical.

2-*Oleodistearin.*—Oleoyl chloride (2 g.) in dry benzene (50 c.c.) was added to 1 : 3-distearin (1 g.) in warm dry benzene (50 c.c.). Dry pyridine (3 c.c.) was then added, and the mixture refluxed for 2 hours on the water-bath. After 48 hours, it was again refluxed for an hour. Water and ether were then added to the cold mixture, in which was suspended pyridine hydrochloride, and after treatment with dilute sulphuric acid to remove pyridine, and washing until neutral with water, the ethereal benzene solution was dried

(Na_2SO_4). After removal of solvents, the residue was crystallised twice from 100 c.c. of absolute alcohol and thrice slowly from 25 c.c. of "AnalaR" acetone. Yield, 1·15 g. of colourless, long thin prisms, m. p. 43·5° (81%). Alcohol containing a little benzene is also a good final solvent.

The other glycerides were made similarly, the only variation being in the amounts of solvent used for crystallisation, which is reduced for palmitin and myristin compounds. All crystallise in long thin prisms.

Elaidoyl Chloride.—Elaidic acid (5 g.) and oxalyl chloride (7·5 g.; 5 c.c.) were refluxed on the water-bath for 2 hours, a calcium chloride tube being attached to the condenser. Excess of oxalyl chloride was then removed, using the water-pump, and the residue was transferred to a small Claisen flask and distilled under greatly reduced pressure. Yield 5·1 g.; b. p. 130·5—131·5°/0·01 mm.

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