106. *An X-Ray and Thermal Examination of the Glycerides. Part VIII. Glycerides of Erucic, Brassidic, Oleic, and Elaidic Acids.*

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

The α-monoglycerides and αα′-diglycerides of erucic, brassidic, oleic, and elaidic acids, and the triglycerides of erucic, brassidic, and elaidic acids are found to exhibit the same type of polymorphism as the corresponding saturated compounds. The *X*-ray examination reveals an interesting difference in structure between the *cis*- and the *trans*-compounds, which appears to be general for long-chain compounds.

Some observations are made on the misleading *X*-ray data for α-monoglycerides reported by Filer, junr., Sidhu, Daubert, and Longenecker.

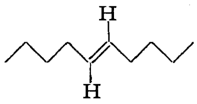
Resuming our study of the glycerides, interrupted in 1939, we have now completed our examination of the α-monoglycerides, αα′-diglycerides, and the simple triglycerides of oleic and erucic acids and their geometric isomers, elaidic and brassidic acids.

Although in their melting phenomena and polymorphism these compounds show no marked differences from the corresponding glycerides of saturated acids, yet a most interesting difference between the derivatives of *cis*- and *trans*-acids is revealed by the *X*-ray results.

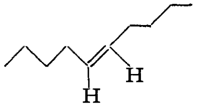
It has been shown in Parts I, II, and III (*J.*, 1934, 666; 1936, 1628; 1937, 1409) that mono-, di-, and tri-glycerides each give rise to a distinctive diffraction pattern, referred to in this field as " side spacings ", and it is now found that, whilst glycerides of *trans*-unsaturated acids give rise to the same type of side spacings as their saturated analogues, derivatives of *cis*-acids give quite different spacings. The same distinction holds for simpler *cis-trans*-isomers, *e.g.*, erucic and brassidic acids, and it would seem, in general, that saturated and *trans*-olefinic chains pack together in a similar manner, which differs from the arrangement of *cis*-chains.

This is not altogether surprising, as it is seen at once from a model that, whilst a *trans*-bond causes no appreciable change in the alinement of the hydrocarbon chain, a *cis*-bond brings about a decided change, thus :

trans-.



cis-.



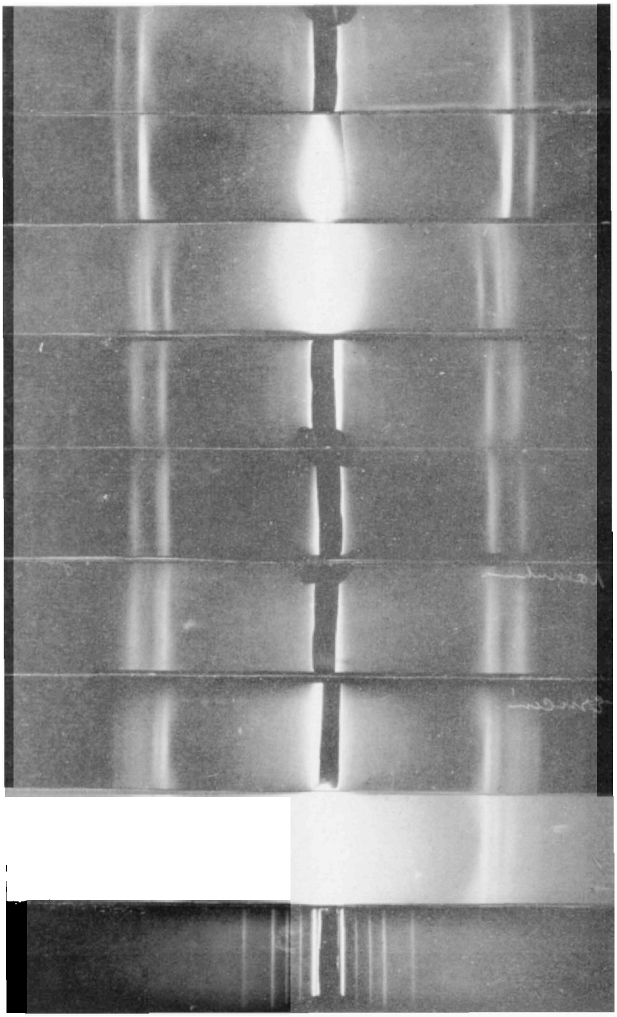
The above differences in side spacings will be clear from the *X*-ray photographs in Plates I and II.

It is hoped to pursue the more general implications of the above observations, but of immediate interest is their bearing on the structure of β-oleodistearin recently proposed by Filer, jun., Sidhu, Daubert, and Longenecker (*J. Amer. Chem. Soc.*, 1946, **68**, 169) and Lutton (*ibid.*, p. 676). These authors find a long spacing greater than the maximum length of a single molecule, and propose respectively structures (I) and (II) which differ from the more compact structure (III) proposed by Clarkson and Malkin (Part I, *loc. cit.*) for simple triglycerides.

Our own unpublished long spacing for β-oleodistearin agrees with that of Lutton, whose proposed structure (II) finds additional support in our present results. Thus, structure (III), surrounded by similar units, would require, in the case of β-oleodistearin, a non-linear chain to be packed between four straight chains, which appears less likely than structures (II), where the oleic chains are adjacent. Arising out of this is the interesting case of β-elaidydistearin, where the unsaturated chain is linear, and which might therefore be expected to have the same structure as tristearin, (III).

Numerous long spacings which could not be satisfactorily explained on the basis of structure (III) have been reported in Parts VI and VII of this series (*J.*, 1939, 1143, 1521) which deal with mixed glycerides of acids differing by at least four carbon atoms, and it is probable that

PLATE I.



Behenic acid (*saturated*).

Brassidic acid (trans).

Erucic acid (cis).

a-*Monoelaidin* (trans).

a-*Monostearin*.

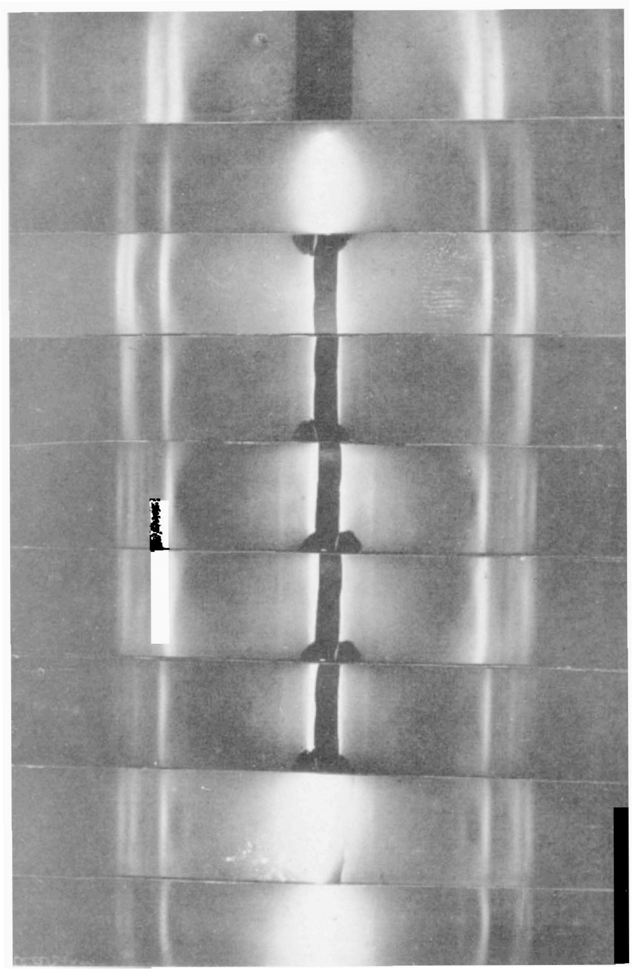
a-*Monopalmitin*.

a-*Monoerucin* (cis).

a-*Mono-olein* (cis).

a-*Monoelaidin* (*long spacing*).

PLATE II.



α-Monoelaidin (circular camera).

αα′-Dipalmitin (β).

αα′-Dibrassidin (β).

αα′-Dibrassidin (β′)

αα′-Dierucin (β′)

αα′-Dierucin (β).

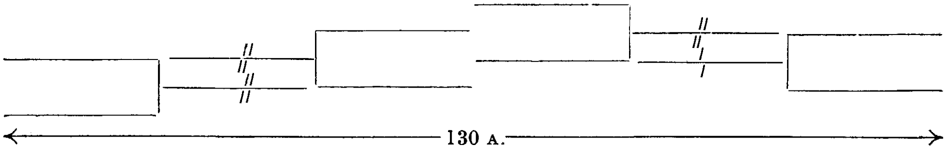
Trierucin.

Trielaidin.

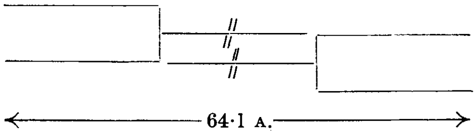
Tristearin.

certain of these are arranged as in structure (II), although in these cases the problem is complicated by the possibility of interpenetration of the chains of unequal length.

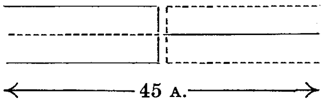
(I.)

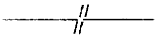


(II.)



(III.)



 = oleoyl radical.

EXPERIMENTAL.

Thermal Investigation.—This was carried out by means of cooling and heating curves, and capillary m. p. experiments (as described in Parts I, II, and III, *locc. cit.*) for saturated glycerides. M. p.'s of the various polymorphic forms are given in Table I.

TABLE I.

	Vitreous.	*α*.	*β'*.	*β*.	Lit. m. p.'s.
α-Monoerucin	15°	36°	47°	50°	
α-Monobrassidin	37	62	68·5	71	
α-Mono-olein	12·5	25	32	35	35 [1]; 26—27, 35 [2]; 35·5 [3]
α-Monoelaidin	29·5	42	56	58·5	58·5 [4]
αα'-Dierucin	—	41	44·5	46·5	47 [5]
αα'-Dibrassidin	—	63·5	66·5	68·5	65 [5]
αα'-Diolein	—	18	—	25	
αα'-Dielaidin	—	49	53	55	
Trierucin	6	17	25	30	31 [6]
Tribrassidin	43	50	—	59	36, 47 [4]; 57 [7]
Trielaidin	15·5	37	—	42	38 [8]; 16·6, 42·0 [9]

[1] Krafft, *Ber.*, 1903, **36**, 4343.

[2] Täufel and Künkel, *Fettchem. Umschau*, 1935, **42**, 27.

[3] Daubert, Fricke, and Longenecker, *J. Amer. Chem. Soc.*, 1943, **65**, 2142.

[4] Filer, junr., Sidhu, Daubert, and Longenecker, *ibid.*, 1944, **66**, 1333.

[5] Reimer and Will, *Ber.*, 1886, **19**, 3322.

[6] *Idem, Ber.*, 1887, **20**, 2386.

[7] Stohmann and Langbein, *J. pr. Chem.*, 1890, **42**, 372.

[8] Duffy, *Jahresber.*, 1852, 511.

[9] Filer, Sidhu, Daubert, and Longenecker, *loc. cit.*

Comparison of the above data with those given for the saturated mono-, di-, and tri-glycerides in Parts I, II, and III shows the closest parallel in the polymorphism. The heating and cooling curves now obtained are very similar to those obtained for the saturated compounds, and the general discussions of results in the thermal sections of the above papers hold, so that only a brief summary of the present results is necessary.

α-Monoglycerides. The upper and the lower curve in Fig. 1, Part II, are practically identical in form with those of α-monobrassidin and α-monoerucin, respectively. In the case of the latter, the transitions, vitreous → *α*, *α* → *β'*, *β'* → *β*, take place at room temperature, and according to the duration of the cooling curve, arrests for *α*- and *β'*-forms may or may not appear on the heating curves (cf. curves, *A. B, C, D, E*, Fig. 1, Part II). The slowest change in this series is the transition *β'* → *β*, and unless the curves are taken very slowly the highest m. p. observed is that of the *β'*-form.

αα'-Diglycerides. Here again the curves are similar to that given in Fig. 1, Part III. The cooling curve shows one arrest (melt → *α*-form), and the heating curve shows usually one (m. p. of *β'*-form), with occasionally a smaller higher arrest (m. p. of *β*-form). The transition *α* → *β'* takes place rapidly in the solid state, and therefore the *α* m. p. is not observed on the heating curves, except in the case of dibrassidin, after very rapid cooling. The transition *β'* → *β* is again very slow, and it is usually necessary to hold the *β'*-form near its m. p. for some time, to bring about conversion into the stable *β*-form.

Triglycerides. Cooling curves for all three are similar. They fall to the region of the vitreous m. p., whereat crystallisation sets in with marked rise in temperature to the m. p. of the *α*-form, if the cooling gradient is not too steep. With very steep cooling gradients, this conversion into *α*-forms is prevented, and solidification in the vitreous form sets in. Heating curves differ slightly from those of saturated triglycerides, owing to the greater speed of the transition α → β (in the case of trierucin α → β′), and no arrest corresponding to the α m. p. was observed. These curves show one arrest for tribrassidin and trielaidin (β m. p.) and two for trierucin (β′ and β m. p.'s). There is some slight suggestion in the heating curve of tribrassidin of a β′-form, m. p. 56—57°, but so far we have not found confirmation in the *X*-ray results, and the question is being further investigated.

X-*Ray Examination*.—This was carried out as described in Parts I and II, pressed and " melted " layers and rods of the specimens being used. Since our last paper, notable improvement in the quality of *X*-ray films and plates has reduced times of exposure to about one-quarter of those given earlier, and has improved definition of side spacings in particular. The *X*-ray data are given in Table II.

α-*Monoglycerides*. Although, as in the case of saturated α-monoglycerides, only one long spacing was found for each member, side spacings show the existence of β′- and β-forms (obtained from rods of solidified melt and solvent-crystallised material, respectively). The existence of the α-forms is deduced from the general similarity of the m. p. data with that of the saturated α-monoglycerides, and from the fact that α-mono-olein occasionally solidifies in a form which gives a uniaxial interference figure, a characteristic of vertical rotating chains (cf. Part II, p. 1633, also Malkin, *J.*, 1935, 726).

It is seen from the photographs (Plate I) that the side spacings of α-monoelaidin and α-monobrassidin are of the same type as those of α-monostearin, but differ quite markedly from those of α-monoerucin and α-mono-olein, which are themselves very similar.

αα′-*Diglycerides*. The examination closely parallels that of the saturated diglycerides (Part III), and confirms the existence of β′- and β-forms. The transition α → β′ is so rapid that *X*-ray data for α-forms could not be obtained. In order to obtain the stable β-form, specimens should be crystallised very slowly from hexane–benzene. Melted layers and rods give β′-forms. The side spacings of dibrassidin and dielaidin are identical with those of saturated diglycerides, within experimental error, whilst those of dierucin and diolein are more complex. Only one form was obtained for diolein, and although the data probably represent the β-form, an absolute decision between β and β′ is difficult.

TABLE II.

	Long spacings, A.			Sidè spacings, A.*	
	α.	β′.	β.	β′.	β.
α-Monoerucin	—	—	58·3	4·65 (s), 4·3, 4·05, 3·87, 3·68	4·57 (s), 4·33 (m), 4·08, 3·9, 3·75, 3·61
α-Monobrassidin	—	—	58·8	4·14 (s), 3·9, 3·75, 3·59	4·56 (s), 4·4, 4·15, 3·93 (s)
α-Mono-olein	—	—	49·5	—	4·58 (s), 4·32 (ms), 4·05, 3·77, 3·58
α-Monoelaidin	—	—	50·3	4·13 (s), 3·88, 3·73, 3·59	4·55 (s), 4·38, 4·14, 3·93 (s)
α-Monostearin for comparison	—	58·3	50·0	—	4·58 (s), 4·37, 4·12, 3·88 (s) †
αα′-Dierucin	—	47·8	46·4	4·68 (s), 4·24, 4·04, 3·85 (m), 3·66 (m), 3·49, 3·32	4·7 (s), 4·38, 4·28, 4·05 (m), 3·95 (ms), 3·64 (m), 3·49
αα′-Dibrassidin	—	58·8	63·1	4·59 (s), 4·0, 3·75 (s), 3·57	4·6 (s), 3·91 (s), 3·72 (s)
αα′-Diolein	—	—	39·7	—	4·7 (s), 4·44 (m), 4·23, 4·06 (m), 3·85 (ms), 3·64
αα′-Dielaidin	—	49 8	52·6	4·61 (s), 3·95, 3·75 (s), 3·6	4·6 (s), 3·9 (s), 3·7 (s)
αα′-Distearin, for comparison	—	—	49·5	—	4·6 (s), 3·9 (s), 3·73 (s)
Trierucin	—	54·7	51·1	4·53 (m), 4·28 (m), 4·07, 3·88 (m)	5·24, 4·6 (s), 4·03, 3·84, 3·7
Tribrassidin	59·3	—	53·6	—	5·3, 4·6 (s), 3·9 (m), 3·7 (m)
Trielaidin	—	—	44·1	—	5·3, 4·6 (s), 3·9 (m), 3·7 (m)
Tristearin, for comparison	50·6	—	45·0	—	5·3, 4·6 (s), 3·9 (m), 3·7 (m)

* s = strong; m = moderate. Other side spacings weak. Long spacings are accurate to ≏ 0·2A., and side spacings, because of the diffuse lines, cannot be regarded as more accurate than to 0·03—0·04 A.

† With the better definition we are now getting, we consider these values more accurate than our earlier ones, which were slightly high.

Triglycerides. The data for the stable β-forms were obtained from pressed layers and rods. Melted layers gave the α-form for tribrassidin and the β′-form for trierucin. In the case of trielaidin, the transition α → β was so rapid at room temperature that melted layers gave only the β-form. The long spacing of the α-form has, however, been reported recently by Filer, Sidhu, Daubert, and Longenecker (*loc. cit.*, 1946), working at low temperatures. They found 44·8 A. for the β-form and 48·0 A. for the α-form. Here again the side spacings of tribrassidin and trielaidin are identical with those of saturated simple triglycerides (Part I), whilst those of trierucin are different.

In their reported *X*-ray examination of α-monoglycerides, Filer, Sidhu, Daubert, and Longenecker (*J. Amer. Chem. Soc.*, 1944, **66**, 1333) stated that " powder diffraction data suitable for the identification of synthetic glycerides are not available in the literature " : in view of this astonishing statement, it is pertinent to point out that in the present series of papers, *X*-ray data, which readily establish identity, have been reported for some *eighty* synthetic glycerides. The authors then continued with an account of their investigation of α-monoglycerides, which is mainly a repetition of the results and deductions of

Malkin and Shurbagy (*loc. cit.*), the only new feature of which is an extensive table of diffraction data, termed " Interplanar Spacings ", which they consider superior to the data of Malkin and Shurbagy for identification purposes. Their data differ from the latter in that (*a*) the number of values is unusually large, and (*b*) the side spacings, contrary to all previous experience in the field, are not distinctive for the series.

With regard to (*a*), it is at once obvious that this profusion of data is due mainly to the use of non-homogeneous *X*-rays, and that the authors, not realising this, have calculated all their values with the wave-length Cu-K_α, $\gamma = 1{\cdot}5386$ A., whereas approximately half the values should have been calculated with the wave-length Cu-K_β, $\gamma = 1{\cdot}389$ A. This is well illustrated by their long-spacing data given for α-monoelaidin (upper figures in their table) reproduced in Col. 2, Table III. In the third column we give the order of reflection and the type of radiation, and after correction of the β values, by dividing by the ratio of the α and β wave-lengths, *i.e.*, $1{\cdot}5386/1{\cdot}389 = 1{\cdot}11$, they are found, as expected, to be in good numerical agreement with the corresponding α values (col. 4).

Table III.

Intensity.	*d*/*n*.	Order of reflection (*n*), and type of radiation.	*d*/*n*,* β values (corr.).	*d*, long spacing, in A.
s	25·5	2α	25·5	51·0
w	21·1	—	—	—
w	19·1	3β	17·2	51·6
vw	17·6	—		
s	17·1	3α	17·1	51·3
vw	13·4	4β	12·1	48·4
s	12·6	4α	12·6	50·4
vw	11·3	5β	10·2	51·0
vw	10·4	5α	10·4	52·0
vw	9·19	6β	8·28	49·68
w	8·95	—		
m	8·36	6α	8·36	50·16
vw	6·88	8β	6·2	49·6
m	6·79	—		
m	6·19	8α	6·19	49·52
w+	5·64	10β	5·07	50·7
w	5·24	—		
w+	4·94	10α	4·94	49·4

* It will be appreciated that these values are merely *n*th order reflections of the long spacing (*d*). Without appropriate indices (002, 003, 004, etc.) their description as interplanar spacings is somewhat ambiguous, and tends to obscure the relationship between the length of the molecule and the long spacing.

We know of no satisfactory explanation for the remaining five values in the second column. Our own photographs give no evidence of these, but it is possible that at least two are due to the use of nylon capillary tubes for mounting the specimen. Nylon, a long-chain polymer, is known to give a long spacing of 17·4 A. and side spacings of 3·7 and 4·4 A. (cf. Baker and Fuller, *J. Amer. Chem. Soc.*, 1942, **64**, 2399). The values 17·6 and 8·95 might well be first and second orders of this long spacing.

With regard to the side spacings reported by Filer *et al.* (the lower values in their table), our objection lies in the quantity and the variability of the data. It has been shown in Part II (*loc. cit.*) that all the saturated α-monoglycerides from monodecoin to monostearin give two identical strong side spacings; *e.g.*, the photographs of α-monopalmitin and α-monostearin, reproduced in Plate I, are indistinguishable, whereas Filer *et al.* report seven and four strong side spacings, respectively.

Here again, the use of non-homogeneous *X*-rays, and probably the use of nylon, increases the number of lines; but further, some error enters into their intensity estimation. Thus, in the above two photographs, the two accompanying weaker lines (4·38 and 4·14 A.), between the two strong lines, are denoted as strong, and a still more glaring case is that of α-monoelaidin, Plate II, where the faint line furthest out from the centre (2·46 A.), which is barely visible, is stated to have the same intensity as the second of the strong lines (3·96 A.).

From the above it will be seen that the data of Filer and his co-workers only serve to confuse a sufficiently complicated field. Their mass of data, even when accurately calculated, is unnecessary for purposes of identification, for the long spacing and the characteristic side spacings suffice. It is only when the question of structure arises that additional data and accurate intensity relationships are of value.

Preparation of Glycerides.—The erucic and oleic acids used were Fraenkel and Landau's purest, the former purified by fractionation of the ester and subsequent crystallisation of the acid, and the latter by low-temperature crystallisation from acetone (cf. Brown and Shinowara, *J. Amer. Chem. Soc.*, 1937, **59**, 6; Smith, *J.*, 1939, 974). Brassidic and elaidic acid were made by the standard nitrous acid method as follows (cf. Rankoff, *J. pr. Chem.*, 1931, **131**, 293) : *Brassidic acid.* 10 G. of erucic acid were added to a mixture of 75 c.c. of concentrated nitric acid and 175 c.c. of water, in a beaker, and the mixture heated to 50—55° on a water-bath. 2 G. of finely powdered sodium nitrite were slowly added, with stirring, and after a short time the molten layer gradually solidified as it was converted into brassidic acid. The aqueous acid was decanted from the solid cake, which was clarified two or three times over fresh distilled water. After crystallisation from alcohol, the yield was 7·5 g., m. p. 59·5°. *Elaidic acid.*

This was made in exactly the same manner except that the reaction temperature was 35—40°; yield, from 10 g. of oleic acid, after crystallisation from alcohol, 6·7 g., m. p. 44·5°.

All the monoglycerides were prepared by the methods given in Part II (*loc. cit.*, p. 1634).

a-Monoerucin. A mixture of 7·5 g. of *iso*propylidene glycerol and 5 g. of erucic acid was gently warmed to melt the acid, and dry hydrogen chloride passed through for ¼ hour. After cooling, the cloudy liquid was transferred to a stoppered bottle, standing in ice, and washed in with about 25 c.c. of ether. 70 C.c. of well-cooled concentrated hydrochloric acid were then added gradually, with shaking, during one hour, after which 150 c.c. of ice-cold distilled water were added gradually, with shaking, during a further ½ hour. The monoerucin separated as a fine powder and was filtered off and well washed free from acid with water. In order to remove all traces of mineral acid before crystallisation it was taken up in ether, washed till neutral, dried over sodium sulphate, and after removal of the ether, crystallised from light petroleum (b. p. 40—60°); yield, 4·4 g., m. p. 50°.

a-Mono-olein, a-monoelaidin and a-monobrassidin. These glycerides were made as described for a-monodecoin in Part II, the only difference being that in the case of monobrassidin the hydrolysis of the intermediate compound takes a little longer (2—3 mins.). Yields of crystallised product from 5 g. of acid were: a-mono-olein, 3 g., m. p. 35°; a-monoelaidin and a-monobrassidin, 4 g., m. p.'s 58·5° and 71°, respectively.

All the monoglycerides crystallise well from light petroleum, hexane, and hexane–benzene.

aa'-Diglycerides. These were made by the action of the acid chloride on the a-monoglyceride, as described for aa'-dilaurin in Part III (p. 1412), the acid chlorides having been made by the action of oxalyl chloride on the acid (Adams and Uhlich, *J. Amer. Chem. Soc.*, 1920, **42**, 599). The main point in these preparations is to avoid formation of triglyceride, as this is removed from diglyceride only with great difficulty whereas a-monoglyceride is removed easily by crystallisation from alcohol: the a-monoglyceride should, therefore, be in slight excess. Yields of the order of 70% (on the acid chloride used) of crystallised material were obtained, except in the case of diolein, where crystallisation losses are high (1 g. from 3 g. of a-mono-olein). All crystallise well from hexane and hexane–benzene.

Triglycerides. These are made by the action of the acid chloride on the a-mono-compound as described for diglycerides, except that slight excess of the theoretical amount of acid chloride may be used, but the simplest method is to heat the a-monoglyceride with the theoretical amount of acid on the water-bath for one hour, in the presence of ½% of toluene-*p*-sulphonic acid, applying a vacuum from the water pump. Unchanged a-monoglyceride and acid are readily removed by crystallisation from alcohol, the final crystallisation being from alcohol for trierucin, and alcohol–benzene for trielaidin and tribrassidin; yields, 75—80%.

The following three glycerides are new: *a-monobrassidin* (Found: C, 73·0; H, 11·8. $C_{25}H_{48}O_4$ requires C, 72·8; H, 11·7%); *a-monoerucin* (Found: C, 72·8; H, 11·8. $C_{25}H_{48}O_4$ requires C, 72·8; H, 11·7%); *aa'-dielaidin* (Found: C, 75·3; H, 11·7. $C_{39}H_{72}O_5$ requires C, 75·5; H, 11·6%).

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