360. *An X-Ray and Thermal Examination of the Glycerides. Part II. The α-Monoglycerides.*

By THOMAS MALKIN and MOSTAFA RIAD EL SHURBAGY.

ALTHOUGH numerous workers have studied the peculiar melting phenomena of the triglycerides, little attention has been paid to the similar behaviour of the monoglycerides. Fischer, Bergmann, and Bärwind (*Ber.*, 1920, **53**, 1591) observed two solid modifications of α-monostearin and α-monopalmitin, but the only systematic study of the melting phenomena of monoglycerides appears to be that by Rewadikar and Watson (*J. Indian Inst. Sci.*, 1930, **13**, *A*, 128), who showed that α-mono-laurin, -myristin, -palmitin, and -stearin exist in two solid forms and exhibit the property of " double melting."

The present investigation, which followed the lines of that on the triglycerides (Clarkson and Malkin, J., 1934, 666 *), confirms the above results and establishes also the existence of a third form. All the monoglycerides that we have examined (monodecoin to monostearin) exist in three solid modifications, *viz.*, a low-melting α-form (vertical rotating chains, m. p.'s non-alternating) and two higher-melting forms, β' and β (inclined chains, m. p.'s alternating). When the molten glyceride is cooled, the α-form is the first to separate; this changes into a more stable β'-form, which finally changes much more slowly into the stable β-form. The last is the form normally obtained by crystallisation from solvents.

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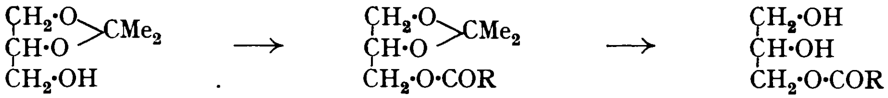
* Since an extended study of the glycerides is in progress, this paper is regarded as Part I of the series.

In the preparation of the monoglycerides, a considerable saving of time has been effected by a slight modification of Fischer, Bergmann, and Bärwind's method (*loc. cit.*), outlined below :



$$\begin{array}{l} CH_2\cdot O\!\!>\!CMe_2 \\ CH\cdot O \\ CH_2\cdot OH \end{array} \longrightarrow \begin{array}{l} CH_2\cdot O\!\!>\!CMe_2 \\ CH\cdot O \\ CH_2\cdot O\cdot COR \end{array} \longrightarrow \begin{array}{l} CH_2\cdot OH \\ CH\cdot OH \\ CH_2\cdot O\cdot COR \end{array}$$

Instead of using acid chlorides for the first stage, we carried out the esterification rapidly, and in good yield, by means of dry hydrogen chloride. It was found, too, in the final stage, that, although concentrated hydrochloric acid is satisfactory for the higher members (tridecoin upwards), yet with the lower members it tends to bring about complete hydrolysis to glycerol. In these cases, the *iso*propylidene group is best removed by treatment at 0° with concentrated hydrochloric acid saturated with calcium chloride.

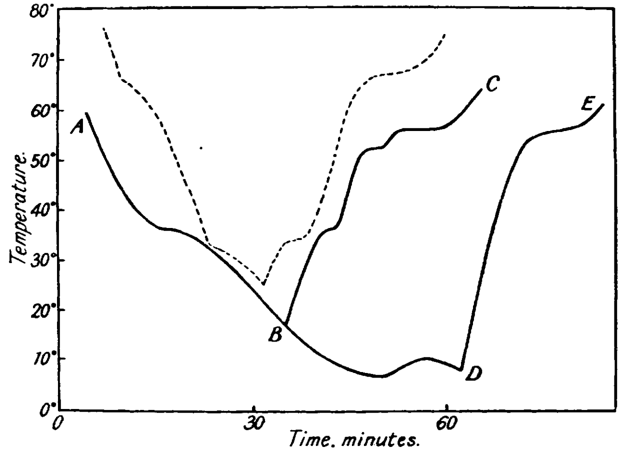
Attempts to prepare monoglycerides by the direct esterification of fatty acid and glycerol yielded mainly αα'-diglycerides, even when a large excess of glycerol was employed. Our experience with this method is entirely in agreement with that of Hilditch and Rigg (J., 1935, 1774), who carried out a quantitative study of the reaction.

In the synthesis of the odd-membered acids used in the work, we have also effected some economy in time by converting the nitriles directly into ethyl esters, thus avoiding a long and tedious hydrolysis with alkali. The conversion is brought about quantitatively by refluxing the nitrile with alcohol and slightly diluted sulphuric acid. Concentrated acid under the same conditions yields the imino-ester, which, like the nitrile, is comparatively resistant to hydrolysis.

Thermal Examination.—For the cooling and the heating curves, 0·7—1 g. of monoglyceride, in a small glass-jacketed tube, was placed in a Dewar flask filled with ice, or with water at a suitable temperature to give the required cooling and heating gradients. For many of the cooling curves the Dewar flask could be dispensed with, since room temperature provided a suitable gradient. Temperatures were recorded every half minute by means of a thermocouple and a sensitive recording millivoltmeter.

The curves for monoundecoin are given in Fig. 1 : *AB* (cooling to room temperature) shows the separation of the α-form, and *BC* the melting of the α, β', and β-forms. If ice is used for the cooling curve, a second arrest is observed, *BD*, and the heating curve *DE* now rises to the m. p. of the β-form, with, however, some indication of the presence of a trace of the β'-form. The arrest on *BD* therefore corresponds to the transitions into the β'- and the β-form.

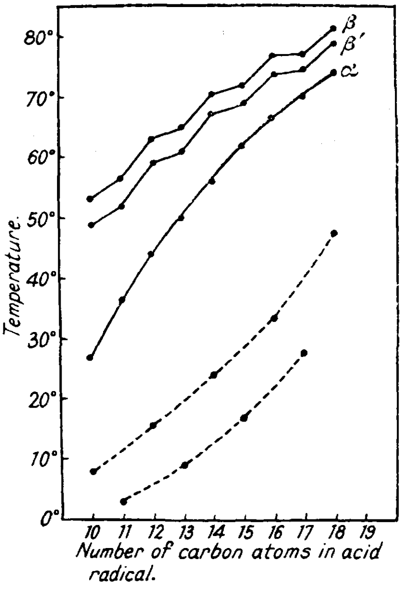
Fig. 1.



The above curves, and also those for monolaurin, which are closely similar, may be regarded as the ideal curves for the series. Curves for other members differ in a gradated manner according to the length of the acid chain, since, as would be expected, changes of form are more rapid with shorter than with long chains. Thus, the α and the β′ arrest on the heating curve of monodecoin are less pronounced, owing to the rapidity of the changes α ⟶ β′ and β′ ⟶ β. On the other hand, the corresponding arrests are more marked in the case of monotridecoin, and the final β arrest is slight. On ascending the series to myristin and monopentadecoin, the β arrest disappears, owing to the slowness of the change β′ ⟶ β. If, however, the specimen is first cooled very slowly (*e.g.*, in a Dewar flask, initially filled with warm water), the latter change takes place to a greater or less extent, and the β arrest can then be observed. Alternatively, the change may be brought about by keeping the β′-form at a temperature near its m. p. for several hours. With still higher members, both the β′ and the β arrest are normally absent; after very slow cooling, the β′ arrest is usually observed, but the transition β′ ⟶ β can only be brought about by maintaining the temperature of the specimen in the region of the m. p. of the β′-form for several days.

The cooling curves for the series are alike in showing two arrests. In all cases, the first represents the change liquid ⟶ α-form, but the changes at the lower arrest are more complex and, as indicated above, in the discussion of Fig. 1, are interpreted by a consideration of the subsequent heating curve. The transitions become less complex with increasing length of chain; for instance, from monodecoin to monolaurin, the heat evolution is considerable and corresponds to transitions into the β′- and the β-form; from monotridecoin to monopentadecoin, the arrest is less marked, and corresponds almost entirely to a transition into the β′-form, whilst for monopalmitin upwards, there is no appreciable formation of either of the β-forms, and the arrest appears to be due to a reversible transition into an intermediate modification, since a corresponding arrest now appears on the heating curve (Fig. 1, broken curve).

Fig. 2.



Melting points and transition temperatures of α-monoglycerides.

Table I.

α-Monoglyceride.	α-Form.	β′-Form.	β-Form.
Decoin	27°	49°	53° (54°)
Undecoin	36·5	52	56·5
Laurin	44 (45)	59·5	63 (63)
Tridecoin	50	61	65
Myristin	56 (57)	67·5	70·5 (70)
Pentadecoin	62	69	72
Palmitin	66·5 (65)	74	77 (76)
Heptadecoin	70	74·5	77
Stearin	74 (74)	79	81·5 (82)

Values in parentheses are due to Rewadikar and Watson (*loc. cit.*). The m. p.'s of the various forms can be determined by capillary methods, in the manner described for triglycerides (*loc. cit.*).

This intermediate form seems somewhat akin to a glass, in that, owing to a rapid increase in the viscosity of the solid, the molecules are prevented by too rapid cooling from orienting to form a regular crystal lattice. The same modification is produced to some extent when the lower members are subjected to a steeper cooling gradient (*e.g.*, monopentadecoin and monomyristin, ice and salt being used), and conversely, for the higher members, a small gradient diminishes the amount formed and permits the transition into the β′-form.

Increasing length of chain naturally increases the viscosity of the solid, and favours the formation of this metastable semi-vitreous form.

An interesting feature, observed only in the curves of monostearin, is the separation of the lower arrest into two distinct reversible arrests, differing by a few degrees, the first being considerably larger than the second. Any explanation now would be somewhat speculative, and this point is receiving further attention.

The m. p.'s of the three forms of the monoglycerides and the temperatures of the lower arrests on the cooling curves are given in Tables I and II and plotted in Fig. 2.

It is seen from the table that, for the α- and the β-forms,* our values and those of Rewadikar and Watson are in close agreement. According to those authors, the molten glyceride changes on cooling into the α-form, which, when heated, melts and then changes into the β-form. They emphasise, however, that once the glyceride has been melted, it does not revert completely into the high-melting form, but always melts a few degrees lower, and for this reason they consider the transition $\alpha \longrightarrow \beta$ incomplete. It is clear from our results that these low-melting forms were β′-forms. Thus, they found for monolaurin and monomyristin m. p.'s of 60° and 67° respectively, which compare well with those of our corresponding β′-forms, *viz.*, 59·5° and 67·5°.

The failure of Rewadikar and Watson to observe the monodecoin transitions is not surprising, since, in the high temperatures of India, where their experiments were carried out, the changes would be almost instantaneous.

TABLE II.

α-Monoglyceride.	Temp. of lower arrest.	α-Monoglyceride.	Temp. of lower arrest..	α-Monoglyceride.	Temp. of lower arrest.
Decoin	8°	Tridecoin	9°	Palmitin	34°
Undecoin	3	Myristin	24	Heptadecoin	28
Laurin	15	Pentadecoin	17	Stearin	47·5 42

The values for the lower members vary over a degree or two, and those for the higher members to a less extent, depending on the rate of cooling. The temperatures given are mean values.

When plotted, the above temperatures fall on two similar curves (Fig. 2, broken curves), the curvatures of which are in the opposite sense to those of the m. p. curves. This would appear to reflect the rapid rise in viscosity of the solid with increasing carbon content of the chain. If produced, the two series of curves would intersect in the neighbourhood of C_{22}, which suggests that, for higher members of the series, transitions from one form into the other would be so excessively slow as to be scarcely realisable. The alternation exhibited implies a greater mobility of the chains in the glycerides containing odd-membered acids, and affords an interesting link with the simple ethyl esters of these acids. These esters have been shown to assume the rotating α-form more readily than esters of even acids (Malkin, *Trans. Faraday Soc.*, 1933, **29**, 977).

X-*Ray Investigation.*—This was carried out as previously described (Clarkson and Malkin, *loc. cit.*), " pressed " and " melted " layers being used. Both types of layer readily give long spacings, but appear to be particularly unfavourably oriented for the production of side spacings, which appeared rarely from pressed and less frequently than usual from melted layers. We were, however, able to obtain good photographs of side spacings by a simple and ingenious method due to Dr. Piper. The specimen was packed tightly into a stout-walled metal cylinder of 0·5 mm. diameter, closed at one end by a screw cap, and was ejected, after removal of the cap, in the form of a rod 1 cm. long. This was then mounted vertically in the path of the *X*-ray beam.

The long spacings of the stable β-form (pressed layers) are given in the following table and plotted in Fig. 3. They exhibit the normal linear relationship, the spacings of the glycerides of odd-membered acids being slightly longer in proportion than those of the even.

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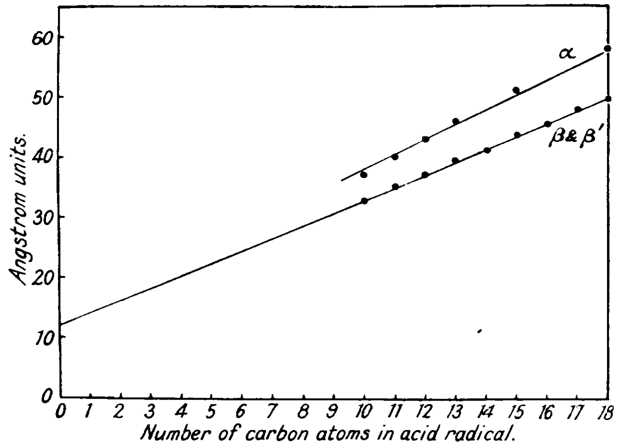
* In this and previous papers the term α is used to denote the first form which separates from the melt, and β to denote the stable crystalline form. Rewadikar and Watson reverse the signification of the two letters, but in order to avoid confusion, we have used our terminology in the discussion of their results.

The spacings are too long to correspond with the length of a single molecule, but, upon the usual assumption of a tetrahedral zig-zag carbon chain, they agree with a double molecule tilted at an angle of ≃ 59°.

Long spacings (A.) of the α-monoglycerides.

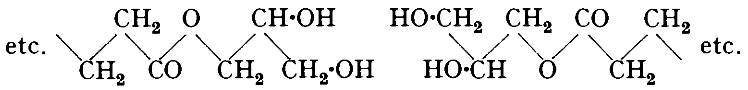
No. of C atoms in acid	10.	11.	12.	13.	14.	15.	16.	17.	18.
β′- and β-Forms	32·9	35·2	37·3	39·6	41·5	43·8	45·8	48·2	50·0
α-Form	37·2	40·2	43·2	46·2	—	51·3	—	—	58·3

FIG. 3.



Long X-ray spacings of α-monoglycerides.

The intercept of the curve on the axis at C = 0 gives a distance of 12 A. for the length occupied by the glycerol radicals and the two terminal hydrogen atoms at the opposite ends of the double molecule. This agrees well with the view that the two glycerol radicals are arranged in alinement with the acid chain, thus :



The spacings obtained from melted layers depend upon the rate of cooling of the specimen and its temperature during the *X*-ray exposure. If, by means of a small heating element on the spectrograph mount, the molten glyceride is allowed to cool to a temperature just below the m. p. of the α-form and is then maintained at this temperature, the longer spacing of the vertical α-form is obtained (table, and Fig. 3), together with the long spacing of the β-form, transition into which is favoured by the high temperature. We experienced considerable difficulty in obtaining these spacings, owing to the small time and temperature range of stability, and were unable to maintain layers of palmitin and higher members sufficiently long in the α-form to obtain reliable photographs. Only the first order usually appears, and consequently the measurements are not of the same accuracy as those of the β-form, but probably the error is not greater than ± 0·3 A.

The long spacings of the β′-forms were found to be identical with those of the β-forms, and were obtained from melted layers cooled at a suitable rate (*i.e.*, quickly for lower members, slowly for higher). Owing to the rapid transitions $\beta' \longrightarrow \beta$ of monodecoin and monoundecoin, it is possible that the spacings observed were actually those of the β-forms, but there is no question of this with the higher members, since the two forms are easily distinguished by their side spacings. These are reproduced on the plate, Fig. 7 showing the β′-form (3·86 and 4·24 A.) and Fig. 8 the β-form (3·94 and 4·65 A.).

The increasing rate of the transition $\beta' \longrightarrow \beta$ with decreasing length of chain is well shown by the side spacings. From monopentadecoin upwards, the β′-form appears to be

Long spacings of α-monoglycerides.

FIG. 4.

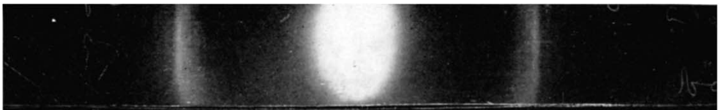
α-Monolaurin, β-form.

FIG. 5.

α-Monomyristin, β-form.

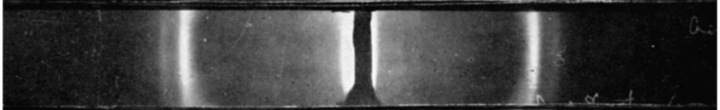
Side spacings of α-monoglycerides.

FIG. 6.



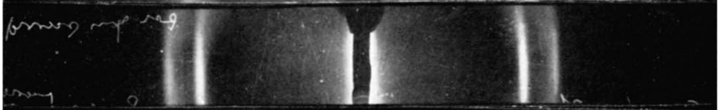
α-Form changing to β′-form.

FIG. 7.



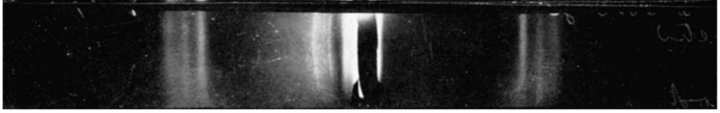
β′-Form.

FIG. 8.



β-Form.

FIG. 9.



β′- and β-Forms.

[*To face p.* 1632.

indefinitely stable at room temperature, with monomyristin the transition takes place overnight, and with monotridecoin it proceeds during the *X*-ray exposure and both sets of side spacings appear (Fig. 9).

Fig. 6 shows the side spacings of the α-form, consisting of a strong line (4·2 A.) associated with weak lines on either side. α-Forms of greater stability (*e.g.*, ethyl esters of fatty acids) give the single strong line of 4·2 A., and occasionally this alone was obtained with the monoglycerides. The weak accompanying lines suggest that transitions into other forms are taking place during the exposure.

The explanation of Fischer, Bergmann, and Bärwind's low-melting forms is clear from an examination of the side spacings. They obtained these by crystallising pure β-forms of monopalmitin and monostearin rapidly from ether (ice), and we found that specimens treated in this manner gave side spacings of the α- and β-forms. In one experiment, using stearin, we were also able to detect the long spacing of the α-form. The latter would not be expected to consist of rotating molecules at room temperature, and is probably in the same " frozen " state as the stable α-forms of the triglycerides. A perfectly pure monoglyceride may therefore melt over a considerable range of temperature, unless it has been allowed to crystallise slowly.

An interesting question arising out of the investigation is the nature of the solid between the two arrests on the cooling curves. The *X*-ray evidence shows that it is not the α-form, since this is stable only very near its m. p.; it cannot be the β′-form, since the lower arrest on the cooling curve is reversible for the higher members, whereas the change α ⟶ β′ is irreversible. Presumably, therefore, the solid consists of aggregates of molecules in all intermediate stages from vertical rotating to tilted rigid (*i.e.*, vertical oscillating, tilted oscillating) and possesses the mobility of the liquid crystalline rather than the crystalline state. It has been suggested (Malkin, *Trans. Faraday Soc.*, **1933**, **29**, 977) that the vertical rotating form is typical of liquid crystals, and it seems not improbable that this form and the less mobile vibrating form correspond with the nematic and the smectic state respectively. The two states are not very precisely defined, but it is accepted that the smectic is intermediate between the nematic and the crystalline state, and that substances in the nematic state behave as uniaxial crystals.

The liquid-crystalline properties of the monoglycerides may be observed under a polarising microscope, fitted with a heating stage. The glyceride is melted on a slide, covered with a slip, and placed on the heated stage at a temperature just below the m. p. of the α-form. With crossed nicols, there appear dark greyish pools which give a strong uniaxial interference figure. These usually disappear within a few minutes, and the specimen assumes a variety of irregular shapes, typical of the smectic state. Finally, with the lower members, particularly if the specimen is allowed to cool slightly, a further change is observed as crystallisation in the β′- and the β-form sets in. Considerable patience and repetition is often required in order to observe the uniaxial form, which we found for all glycerides from monodecoin to monopentadecoin, but the smectic form is readily observed for the whole series.

The smectic form of monopalmitin and higher members changes on cooling into a vitreous form, the molecules of which are at a much lower potential than is the case with a typical glass, since the heat evolution during transition is considerable. This would be expected owing to the fact that typical glasses are formed by a transition from a much more disordered state (*i.e.*, liquid). The reversibility of the change smectic ⟶ vitreous, which is not typical of a glass, is probably due merely to the excessively slow rate of crystallisation of the β-forms of the higher members.

X-Ray photographs of the vitreous form, obtained by rapid cooling, show a single diffuse side spacing of 4·2 A. With slower cooling, this is accompanied by weak long spacings of the β′-form.

EXPERIMENTAL.

The even-membered acids used were Kahlbaum's purest, submitted to a further purification by fractionation of the ethyl esters. Odd-membered acids were synthesised from pure alcohols (Fraenkel and Landau) *via* the iodide, nitrile, and ethyl ester.

Conversion of Nitriles into Ethyl Esters.—A mixture in the proportion of 1 g. of nitrile, 1 c.c. of water, 3 c.c. of concentrated sulphuric acid, and 9 c.c. of alcohol is refluxed for several hours, the progress of the reaction being followed by observing the ester layer which separates to the surface. When this no longer appears to increase, refluxing for a further hour usually completes the reaction, a good indication of the success of which is a deposit of ammonium sulphate on cooling. The ester layer is separated, taken up in ether, washed free from acid, dried (sodium sulphate), and purified by distillation. The yield is almost quantitative. With a higher proportion of acid, the imino-ester is also produced, and with a higher proportion of water, the conversion into ester is slow and incomplete.

αβ-iso*Propylidene Glycerol* (*Acetone Glycerol*).—Dry hydrogen chloride is passed into a mixture of 100 g. of glycerol and 200 c.c. of acetone for a few minutes, until the two layers of liquid become homogeneous. The slightly warm liquid is shaken with a good excess of lead carbonate to remove hydrogen chloride, filtered, and dried over anhydrous sodium sulphate. After removal of excess acetone on the water-bath, the product is distilled in a vacuum over a small amount of silver oxide. It is important to remove as much hydrogen chloride as possible before the final distillation; b. p. 75°/4 mm.; yield 110—120 g.

The above method is a modification of that of Fischer and Pfähler (*Ber.*, 1920, **53**, 1607), who shook together for 12 hours a mixture of 100 g. of glycerol, 600 c.c. of acetone containing 1% of hydrogen chloride, and 40 g. of anhydrous sodium sulphate. We found that the amount of acid required was not sufficiently critical to necessitate making up a 1% solution; moreover, the large excess of acetone and the use of sodium sulphate did not appear to be advantageous.

α-Monopalmitin.—Dry hydrogen chloride is passed into a mixture of 5 g. of palmitic acid and 5 g. of *iso*propylidene glycerol, warmed just sufficiently to melt the acid. After a minute or two, the mixture becomes cloudy, slowly separating into two layers, and the reaction is completed by passing the gas for a further ¼ hour. After cooling, the product is treated with 20 c.c. of ether, and poured into a 250 c.c. bottle, standing in ice; the sluggish residue, which appears to be glycerol, is washed by decantation with a further 20 c.c. of ether. 40 C.c. of ice-cold concentrated hydrochloric acid are now added slowly with shaking, and the solid monoglyceride begins to separate. The separation is usually complete after ½ hour's shaking, and after addition of 150 c.c. of ice-cold water with vigorous shaking, the palmitin is filtered off at the pump, and crystallised from ether; yield 5 g., m. p. 77°.

The above method can be used for the glycerides of tridecoic acid upwards, but for the lower members, the yields become progressively smaller, owing to the further hydrolysis of the monoglycerides, due probably to their increasing solubility. For the lower members, we used concentrated hydrochloric acid saturated with fused calcium chloride for hydrolysis, and obtained yields of 60—80%.

α-Monodecoin.—Dry hydrogen chloride is passed into a mixture of 3 g. of decoic acid and 5 g. of *iso*propylidene glycerol for 15 minutes. After cooling, the product is washed into a stoppered bottle with 35 c.c. of ether, and is shaken vigorously for 2 minutes (ice-cooling) with an ice-cold solution of 8 g. of fused calcium chloride in 20 c.c. of concentrated hydrochloric acid. The product, which is now solid owing to the separation of monoglyceride and calcium chloride, is treated with a good excess of ice-cold water, and the monoglyceride extracted with ether. After being washed free from acid, and dried (sodium sulphate), the ether is removed, and the residue crystallised from light petroleum (b. p. 40—60°; ice); yield 2·5 g.

All the monoglycerides crystallise well in glistening, thin, flat prisms. For the lower members, light petroleum is a good solvent, and for the higher, ether or hexane.

Analytical data are given for the *monoglycerides* of odd-membered acids, which do not appear to have been previously prepared: monoundecoin (Found: C, 64·8; H, 10·9. $C_{14}H_{28}O_4$ requires C, 64·6; H, 10·8%); monotridecoin (Found: C, 66·6; H, 11·3. $C_{16}H_{32}O_4$ requires C, 66·6; H, 11·2%); monopentadecoin (Found: C, 68·1; H, 11·5. $C_{18}H_{36}O_4$ requires C, 68·3; H, 11·4%); monoheptadecoin (Found: C, 69·85; H, 11·8. $C_{20}H_{40}O_4$ requires C, 69·8; H, 11·7%).

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