II.—THE PREPARATION AND PHYSICAL PROPERTIES OF α-MONOGLYCERIDES.

By R. S. Rewadikar and H. E. Watson.

Simultaneously with the investigation of the triglycerides outlined in the previous paper, experiments of a similar nature were conducted with the α-monoglycerides, the literature of which is even more scanty than that of the triglycerides. The glycerides of acids with an even number of carbon atoms from lauric to stearic have been previously prepared, but in most cases, the melting point is the only physical constant which has been measured and the figures given by different authors vary considerably as shown in Table I.

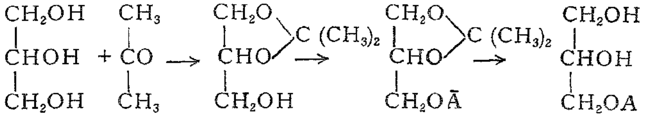
TABLE I.

Melting Points of α-Monoglycerides.

...	Berthelot.	Hundes-hagen.	Smith.	Thieme.	Guth.	Krafft.	Grün.	Fischer.	Brash.	Adam, Berry and Turner.
Laurin ...	...	...	...	58·9	...	59	61	62–63	...	...
Myristin ...	...	...	...	...	...	68	69	...	...	70-71
Palmitin ...	58	...	63	...	65	72	74	78–79	68	76–77
Stearin ...	61	60–62	...	...	73	78	80	81–82	...	...

Berthelot (*Compt. rend.*, 1853, **37**, 398) was the first to attempt the synthesis of the monoglycerides from the acids and glycerin. His work was repeated more systematically by Chittenden and Smith (*Am. Chem. J.*, 1885, **6**, 225) and Belucci (*Gazzetta*, 1912, **42**, 283), but the products obtained were found to be mixtures. Guth (*Z. Biol.*, 1902, **44**, 78), Krafft, (*Ber.*, 1903, **36**, 4342) and Grün (*Ber.*, 1910, **43**, 1288; 1912, **45**, 3421) used the chlorhydrins as starting materials by allowing them to react with the sodium or potassium salts of the acids or by esterifying a di-halogen hydrin and then converting the halogens into hydroxyl groups. Thieme (*Ber.*, 1913, **46**, 1653) pointed out that reactions of this type were not simple, but yielded other products as well as those desired, and Fischer (*Ber.*, 1920, **53**, 1589, 1621) showed that the acid radicle might change its position during the course of the reaction so that the constitution of the glyceride produced in this way could not be definitely established.

Abderhalden (*Ber.*, 1914, **47**, 2888) appears to have been the first to prepare α-monoglycerides of definite constitution. He isolated the optically active epihydrin alcohol and esterified the lower members of the fatty acids, with it. The products were purified by distillation in vacuo. Fischer and his collaborators (*Ber.*, 1920, **53**, 1589) achieved the same result by using as starting material isopropylidene glycerin, the constitution of which had been definitely established by Irvine, Macdonald and Soutar (*J.C.S.*, 1915, **107**, 342). This was condensed with fatty acid chloride and the isopropylidene linking removed, giving the α-glyceride.



The glycerides could be readily condensed with acetone giving the intermediate isopropylidene glyceride thus showing that the acid radicle had not changed place on hydrolysis, since acetone will only condense with two adjacent hydroxyl groups. (*Ber.*, 1920, **53**, 1606.)

Fischer (*Ber.*, 1920, **53**, 1640) also prepared the α-monoglycerides by the alcoholysis of alkyl esters of fatty acids with glycerin and by the degradation of triglycerides using excess of glycerine. Bergmann and Sabety (*Z. physiol. Chem.* 1924, **137**, 47) prepared optically active α-monolaurin from 2-phenyl 5-chlormethyl oxazolidine. While the present experiments were in progress, Brash (*J. Soc. Chem. Ind.*, 1927, **46**, 481 T) prepared α-monopalmitin by a method which he considered superior to that of Fischer, *viz.*, by heating the lead salt of the fatty acid with α-monochlorhydrin. His palmitic acid was admittedly impure and this was no doubt a contributory cause to the low melting point (68°) of his product. Still more recently Adam, Berry and Turner (*Proc. Roy. Soc. A.* 1928, **117**, 540) have prepared monomyristin and palmitin by Fischer's method. The only property recorded was the melting point as given in Table I.

We have now prepared in a pure state the α-monoglycerides of acids with an even number of carbon atoms from C_8 to C_{18} and determined their melting points, refractive indices, densities, viscosities and surface tensions. As far as possible, alternative methods of preparation have been adopted in order to compare the products obtained in different ways.

It has been shown by Fischer (*loc. cit*) that on replacement of the iodine in α-iodo-βγ-acylated glycerin by hydroxyl, the αγ-acylated glycerin results. It appeared of interest to see if a similar change would take place with a di-halogen compound and consequently allyl laurate and stearate, and their dibromides were prepared. Attempts to prepare the monoglycerides by substituting hydroxyl groups for the bromine were not successful as the bromine could not be completely removed.

EXPERIMENTAL.

Isopropylidene glycerin was prepared by Fischer's method (*Ber.* 1920, **53**, 1607) and obtained in 70 per cent. yield; b. p. 79°/9 mm.

α-monostearin.—The stearic acid used for this preparation was crystallized 3 times from 90 per cent. alcohol and melted at 69·3°. Its equivalent weight agreed with theory.

(*a*) Stearyl chloride was condensed with isoproplylidene glycerin dissolved in dry quinoline by standing at room temperature (25°) for 48 hours according to Fischer's method. The yield of acetone compound was 80 per cent. of the theoretical value and the crude product was used as such, since recrystallization seemed liable to produce hydrolysis. α-monostearin was obtained in 80 per cent. yield on hydrolysis with concentrated hydrochloric acid (1·19) at 20–25°. After washing with ether and crystallizing from the same solvent, the melting point was 82°, agreeing with Fischer's value.

(*b*) Methyl stearate m. p. 38·5–39° made from the stearic acid and methyl alcohol was heated with 4 mols. of glycerin containing 4 per cent. hydrochloric acid on the water-bath for various periods, moisture being excluded, but no alcoholysis took place.

(*c*) A mixture of methyl stearate (7g.) and glycerin (9·2g.) was dissolved in 8·7 g. of acetone containing 2 per cent. of hydrochloric acid and refluxed for 5 hours. The product was poured into water, and the solid which formed was recrystallized repeatedly from ether. 1 g. of a substance melting at 82° was obtained and the melting point did not change on mixing with the specimen obtained by method (*a*).

A similar experiment with 15 g. of methyl stearate in which the refluxing was continued for 48 hours, acetone removed by distillation and the residue dissolved in ether, yielded 2 g. of α-monostearin and 8 g. of a neutral product m. p. 40°–50° (probably crude isopropylidene monostearin which gave 3 g. of α-monostearin after hydrolysis and recrystallization from benzene.

(*d*) An attempt to obtain the glyceride by heating methyl stearate with isopropylidene glycerin in benzene solution containing hydrochloric acid was unsuccessful.

(*e*) Methyl stearate (10 g.) and anhydrous glycerin (9 g.) were dissolved in dry pyridine (50 cc.) and 1 cc. of a 7 per cent. solution of sodium methylate added. The mixture was heated for 24 hours on the water-bath, the pyridine distilled and the residue treated with a mixture of N/2 sulphuric acid and ether. 4·5 g. of α-monostearin with the same melting point as before were obtained.

(*f*) An alternative method of producing the glyceride was by oxidation of allyl stearate.

Allyl stearate was obtained in 80 per cent. yield by the action of allyl iodide on silver stearate suspended in benzene. It forms shining plates from methyl alcohol m. p. 35°. (Found: C, 77·6; H, 12·3. $C_{21}H_{40}O_2$ requires C, 77·7; H, 12·3).

Allyl stearate dibromide was prepared by adding a solution of bromine (1 mol.) in dry chloroform to a solution of allyl stearate (1 mol.) in the same solvent cooled to –3° with stirring. The reaction is very slow but the yield is quantitative. The substance forms a white solid from methyl alcohol; m. p. 45°. (Found : Br. 33·3. $C_{21}H_{40}O_2Br_2$ requires Br, 33·1.)

Oxidation of allyl stearate.—An attempt at oxidation with benzoylhydroperoxide was not successful, but a small yield of glyceride was obtained by permanganate oxidation in acetone solution at room temperature (30°). After a number of trials, the best yield (30 per cent.) was obtained as follows :—Allyl stearate (4 g.) was dissolved in acetone (700 cc.) containing 1·2 g. of magnesium sulphate at 2° (this amount of acetone is necessary to keep the ester in solution) and potassium permanganate (1·6 g.) equivalent to 1 atom of oxygen per 1 mol. of ester added slowly with stirring, the temperature being kept at 2°. The manganese dioxide was separated by filtration, suspended in water, dissolved by passing sulphur dioxide and the solution extracted with ether. This solution was washed with 10 per cent potassium bicarbonate solution and the ether distilled. The acetone solution was distilled and the residue taken up in ether. After recrystallization, the product melted at 82° and mixture with α-monostearin produced no change. (Found: C, 70·2 : H, 11·7. $C_{21}H_{42}O_4$ requires C. 70·4; H, 11·7.) Experiments with larger quantities of permanganate did not result in increased yield but caused the formation of stearyl glycollic acid previously obtained by Grün (*loc. cit.*) by the oxidation of α-monostearin.

α-monopalmitin.—The palmitic acid used for this preparation was a specially pure sample recrystallized 3 times from 90 per cent. alcohol. It had the correct equivalent weight and melted at 62·5°.

(*a*) A quantitative yield was obtained by condensing the acid chloride with isopropylidene glycerine. After recrystallizing from ether, the melting point was 76°.

(*b*) 5·4 g. of methyl palmitate gave by glycerolysis in pyridene solution (*cf.* α-monostearin (*e*)) 2·5 g. of glyceride with the same melting point. Glycerolysis in acetone solution gave a small yield.

(*c*) Equimolecular proportions of potassium palmitate and α-monochlorhydrin (b. p. 115°/7 mm.) were heated in a sealed tube at 180° for 6 hours and the product treated according to the method of Krafft. (*Ber.* 1903. **36**, 4342.) A very low yield of an impure product melting at 72–73° was obtained.

α-monomyristin.—Myristic acid was recrystallized from alcohol and melted at 53·6°.

(*a*) Myristyl chloride prepared from the above was redistilled and boiled at 169°/15 mm. A 75 per cent. yield of myristyl isopropylidene glycerin was obtained on condensation and a 90 per cent. yield of the glyceride on hydrolysis with hydrochloric acid (1·19) at –5°. The product was recrystallized from a mixture of ether and petroleum ether in which it is not very soluble and melted at 70°.

(*b*) 1 g. of the monoglyceride with the same melting point as the above was obtained from 7 g. of trimyristin and 2·8 g. of glycerin in a pyridine solution containing sodium methylate after standing for 3 days at room temperature (25°).

α-monolaurin melting at 63° was obtained in 90 per cent. yield by Fischer's method. The lauric acid was made from a pure specimen of methyl laurate prepared in the laboratory and melted at 43°. The acid chloride boiled at 123–124°/7 mm.

Allyl laurate.—Laurylchloride (13·2 g.) and quinoline (8 g.) were dissolved in dry chloroform (30 cc.). Allyl alcohol (3·5 g.) was gradually added at 0° while stirring and the mixture allowed to stand for 24 hours at room temperature. It was then extracted with chloroform and the solution shaken in succession with half-normal sulphuric acid, 10 per cent. potassium bicarbonate solution and distilled water. After drying with anhydrous magnesium sulphate and distilling the solvent, a neutral pale brown liquid (13·1 g.) was obtained which became semi-solid at –6°. The distillate was a colourless, mobile liquid boiling at 162–164°/20 mm.

Allyl laurate dibromide—Allyl laurate (9 g.) was dissolved in dry chloroform (50 cc.) and cooled in ice; bromine (6 g.) dissolved in the same solvent (10 cc.) was added while stirring and the reaction flask allowed to stand for 4 hours in ice. After removing the chloroform, the residue distilled at 220–222°/10 mm. as a pale yellow mobile liquid. (Found: Br. 39·3; $C_{15}H_{28}O_2Br_2$ requires 40·0.)

Attempts to prepare halogen hydrins from the above two compounds were not successful, inseparable mixtures only being obtained.

α-monocaprin.—Kahlbaum's synthetic capric acid boiling at 140–141°/6 mm. was used for this preparation. The acid chloride boiled at 97°/8 mm. The condensation of the acid chloride with isopropyliden glycerine was effected at – 10° giving a 75 per cent. yield. Some difficulty was experienced in hydrolysing the acetone compound, but an 80 per cent. yield was finally obtained by treating an ethereal solution with 30 per cent. hydrochloric acid at – 10° to – 15° for 1 hour. The product after recrystallization from petroleum ether melted at 54°, and had saponification value 227·3 (calc. 228·1).

Diphenylurethane—α-monocaprin (1 mol.) was mixed with phenyl isocyanate (2 mols.) and the mixture allowed to stand during 48 hours at 25°. It was then made into a paste with carbon tetrachloride and filtered. The residue was dissolved in hot benzene and filtered and an 80 per cent. yield of a colourless substance melting at 101° obtained from the filtrate. (Found: C, 67·1; H, 7·4; $C_{27}H_{36}O_6N_2$ requires C, 66·9; H, 7·5.) The substance is therefore the diphenyl urethane of α-monocaprin.

*Di-*p*-nitrobenzoyl derivative.*—*p*-nitrobenzoyl chloride b. p. 156–157°/6 mm. was prepared from the acid and phosphorus pentachloride and a chloroform solution added to a solution of α-monocaprin in dry pyridine cooled to – 10°. After standing for 3 days the pyridine was removed with acid and an almost theoretical yield of the mixed triglyceride obtained. Crystallised from hot alcohol it forms small pale yellow needles m. p. 94°. (Found: C, 59·4; H, 6·1, $C_{27}H_{32}O_{10}N_2$ requires C, 59·6; H, 5·9.)

α-monocaprylin was prepared from a sample of synthetic caprylic acid b. p. 115°/7 mm. the acid chloride of which boiled at 77°/8 mm. in the same way as α-monocaprin. The theoretical yield of an oil was obtained and this solidified on keeping in a vacuum desiccator for three days. On filtering at 0°, white shining plates m. p. 40° were separated and a further yield obtained by stirring the slightly acid filtrate with a little sodium carbonate and extracting with ether. The melting point was not raised on recrystallizing from petroleum ether. The saponification value was 257 agreeing with theory.

The *diphenyl urethane* was obtained in 80 per cent. yield in the same way as the caprin derivative. It forms a fine colourless powder from benzene m. p. 114°. (Found: C, 65·9; H, 7·2; $C_{25}H_{32}O_6N_2$ requires C, 65·8; H, 7·0.)

The *di*-p-*nitrobenzoyl derivative* was prepared in 80 per cent. yield in the same way as the caprin derivative. It forms pale yellow needles from alcohol m. p. 91·5°. (Found: C, 58·9; H, 5·6; $C_{25}H_{28}O_{10}N_2$ requires C, 60·0; H, 5·6.)

PHYSICAL PROPERTIES.

Melting points were determined in a capillary tube with a standard thermometer and corrected for exposed stem.

Refractive indices were measured on an Abbé refractometer at 93·1°, 85·7°, 78·7° and 65·0° except those of palmitin and stearin which could not be determined at the lowest temperature.

Densities were determined at the boiling point of water (97·3°) in a pyknometer consisting of a glass bulb of approximate volume 4 cc. with two capillary tubes of measured bore attached to it. This was calibrated by filling it with mercury at the temperature employed. After cleaning it was placed in a steam oven with one limb dipping into a vessel containing the molten glyceride and filled by suction. Caps were then placed over the ends of the side tubes and the instrument immersed almost completely in boiling water. When equilibrium was attained the distances of the liquid in the limbs from two marks was measured thus giving the volume.

Viscosities were measured in an Ostwald's viscometer with a second bulb containing an overflow device so that a constant volume of the hot liquid could be run through. The constant was determined at 30° with a 61·44 per cent. solution of glycerin as described in the previous paper.

Surface tensions were determined by Sugden's maximum bubble pressure method (*J.C.S.*, 1924, **125**, 28), the radii of the tubes used being approximately 0·018 and 0·335 c.m. The apparatus was calibrated at 30° with benzene and the value obtained used for the measurements at the higher temperature.

Table I summarises the values obtained for the physical properties.

TABLE I.

Physical properties of α-monoglycerides.

Glyceride	M. P.	$n_D^{85·7}$	$d^{97·3}$	$\eta^{97·3}$	$\gamma^{97·3}$	P.	P. calc.	Diff.
Caprylin	40°	1·4309	0·9646	0·0603	26·69	514	529	—15
Caprin	54°	1·4331	0·9399	0·0772	25·43	588	607	—19
Laurin	63°	1·4350	0·9248	0·0985	25·28	664	685	—21
Myristin	70°	1·4366	0·9121	0·1210	24·88	740	763	—23
Palmitin	76°	1·4484	0·9014	0·1472	25·54	823	841	—18
Stearin	82°	1·4400	0·8959	0·1691	25·07	894	919	—25

Temperature coefficient of refractive index 0·00038.

The variation with the number of carbon atoms is regular as may be seen from Fig. I except in the case of the surface tension which appears to fall to a minimum for myristin. The parachor P ($M\gamma^{\frac{1}{4}}/d$) has been calculated and the value compared with those computed from Sugden's data as in the case of the triglycerides, the value 20·0 being assumed for both the non-ester oxygen atoms. The differences show a regular increase except for palmitin, and it is possible that the specimen was not sufficiently pure in spite of the special attention bestowed upon it in view of the variation of the melting point from Fischer's value.

It is noteworthy that the values found for the parachor are all lower than those calculated, whereas with the triglycerides the reverse is the case. The difference for C_2H_4 is 76, compared with 81·0 for the triglycerides and Sugden's value of 78. If the values for the monoglycerides are all raised by 2·8 per cent., the agreement between the theoretical and measured values is almost exact, but such a change would require a constant error of 11·2 per cent. in the surface tension determinations which can hardly be regarded as probable. It is possible that when dealing with these large molecules certain factors enter which are not apparent with substances of smaller molecular weight.

DOUBLE MELTING POINTS AND SOLIDIFYING POINTS.

It is well known that triglycerides exhibit double melting points, but little attention has been drawn to the corresponding phenomenon in the case of monoglycerides. Fischer (*Ber.* 1920, **53**, 1591) remarked that α-monostearin which melted at 81–82°, melted after solidification at 75–76° and similarly α-monopalmitin exhibited two melting points 78–79° and 72–73°. Brash, however (*loc. cit.*), stated that he was unable to obtain double melting points with his preparation of monopalmitin, the reason probably being that it was impure.

We have succeeded in obtaining two well-defined melting points for each of the four higher monoglycerides examined and they thus resemble the triglycerides. Measurements were made by means of the capillary tube method, a small quantity of the substance being melted in each of several thin-walled, narrow capillaries, retained above the melting point for five minutes and chilled in a freezing mixture. The tubes were then plunged into baths differing slightly in temperature in the neighbourhood of the expected melting point and the temperature of the bath which caused melting to take place within three seconds taken as the melting point of the β-form. The results appeared to be correct to within a degree.

The stability of the β-form varied greatly for different glycerides and showed a regular gradation. Thus, in the case of monostearin, the melting point was 74° and on warming to 75°, no solid appeared in 45 minutes. With monopalmitin the lower melting point was 65° and at 68° a trace of solid formed which increased very slowly. After half-an-hour at the same temperature, the contents of the tube were mainly solid. Monomyristin melts at 57° and resolidifies at a temperature just above this in about 2 minutes. On keeping the chilled melt at room temperature, a slow transformation takes place, as the melting point is found to rise with time, and on rubbing or grinding the change into the α-form is rapid. In the case of monolaurin β, melting and re-solidification are almost simultaneous while with monocaprin no double melting point could be detected, doubtless owing to the extreme rapidity of the change from one form to the other.

Table II gives the melting points of the glycerides, their solidifying points (see next section) and the melting points of the fatty acids with 4 more carbon atoms than the acids from which the glycerides are derived. The corresponding values are nearly the same, a fact which is worthy of note although possibly due merely to coincidence.

TABLE II.

Melting points of α-monoglycerides and fatty acids.

Glyceride	M. P. α	M. P. β.	S. P.	Acid	M.P.
Caprylin	40	...	...	Lauric	43·5
Caprin	54	...	...	Myristic	53·6
Laurin	63	45	60·0	Palmitic	62·5
Myristin	70	57	67·0	Stearic	69·5
Palmitin	76	65	70·2	Arachidic (*n*)	75·5
Stearin	82	74	...	Behenic (*n*)	82·0

The value found for palmitin β is 8° lower than Fischer's figure while with stearin the difference is only 2°. The discrepancy in the former case may be due to the different methods employed, but considering the comparative stability of palmitin β, it appears unduly large. It has already been pointed out that the parachor for our sample is high, but at the same time the melting point agrees with that of the material used by Adam Berry and Turner and in spite of several attempts, we have been unable to obtain a specimen with a higher melting point. It seems unlikely that the true melting point could be two degrees higher as given by Fischer. To settle the question, it is intended to make another preparation using an entirely different sample of palmitic acid as the starting material.

SOLIDIFYING POINTS.

Attention has been drawn to the fact that in the case of triglycerides (*cf.* preceding paper), preparations of one substance with the same melting point may vary several degrees in their solidifying points and only after repeated recrystallization is it possible to produce a specimen with a solidifying point approximating to the melting point. Even then the two do not coincide. The same phenomenon is met with in a more marked degree with the α-monoglycerides and the present experiments point to the conclusion that the solidifying points observed are those of an equilibrium mixture of the two forms, the exact proportion depending upon very small traces of unidentifiable impurity.

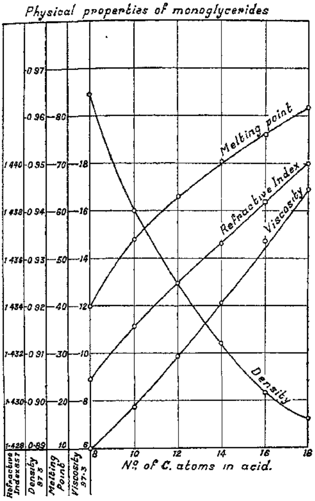
The determination of the solidifying point offers considerable difficulty owing to the presence of two forms of the substance and the small amount of heat evolved on solidification. In order to obtain consistent values, it was necessary to follow the procedure adopted in the case of the triglycerides, of conducting the determination in a water-bath the temperature of which could be closely controlled so as to be always cooler than the melt but never more than 1° less. This was effected by using a comparatively small beaker of water (500 cc.) mechanically stirred and electrically heated, with hand regulation. A supplementary gas burner was used for increasing the temperature rapidly during solidification. Not less than 3 g. of the substance was filtered hot into a 3 × ½ inch hard glass test-tube fitted with a very small thermometer and placed in an air jacket in the bath. Scarcity of material precluded the use of larger quantities which would have been desirable, but the results, as well as unpublished results with triglycerides, indicate that the amount taken was sufficient to yield accurate values.

A sample of carefully purified α-monomyristin melting at 70° was first examined because the transition from one form to the other takes place fairly rapidly. A definite maximum at 62·4° was obtained in a number of experiments even when the bath was at room temperature (30°). On raising the bath temperature as previously described, the maximum rose to 63·4°, as shown in Fig. II, curve VIII. The cross on the curve marks the point at which the liquid was seeded with a crystal of the α-form. If this was not done, excessive supercooling was apt to result or a delay to occur in the transition.

On recrystallizing the specimen from ether, the melting point remained unaltered, but the maximum temperature reached rose to 65·2°. After allowing the substance to stand during 24 hours and repeating the experiment, an identical value was obtained as shown in curve X. After another recrystallization the value rose to 67·0° (curves XI & XII, the slight difference in position being due to different seeding temperatures). Further crystallization produced no appreciable change (curve XIV).

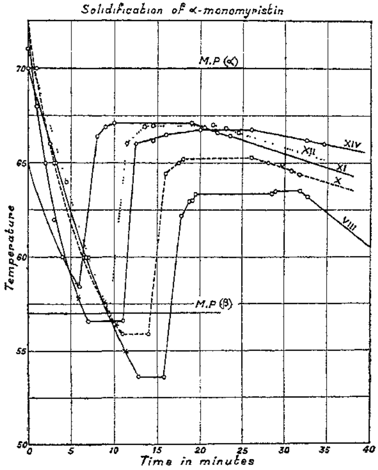
An inspection of the curves in Fig. II suggests that the maximum temperature depends to some extent upon the temperature at which a seeding crystal was added. This was shown not to be the case both in preliminary experiments and in a test made by adding some of the original material to the specimen used for experiment XII. Seeding was performed at 58°, but no temperature rise occurred until the melt had cooled at 52·4°, and the maximum attained was only 65·2°. It appears fairly certain therefore that the maximum depends upon traces of impurity too small to affect the melting point. The same impurity also seems to retard the transition to the α-form because, in general, the less pure samples had to be cooled to a lower temperature before

Fig. I



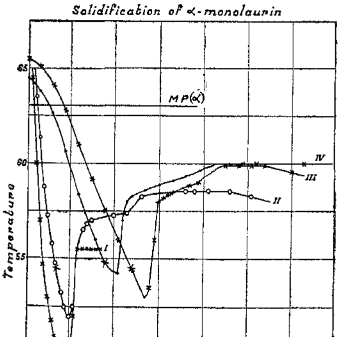
Physical properties of monoglycerides

Fig. II



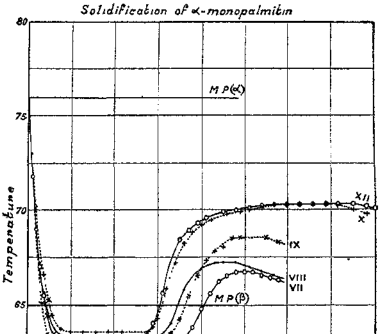
Solidification of α-monomyristin

Fig. III



Solidification of α-monolaurin

Fig. IV



Solidification of α-monopalmitin

liberation of heat occurred. A specimen of the solid after the conclusion of experiment XIV was heated in a capillary tube and found to melt at 67·0°, the maximum temperature reached during solidification. It is thus evident that it must be an equilibrium mixture of the two forms, since the α-form melts at 70°.

Similar phenomena were observed with α-monopalmitin but owing to the slow rate of transition very careful regulation of the jacket temperature was required. For example, the first sample tested, melting at 76°, rose in temperature from 60·9 to 64·8° when the temperature of the bath was kept within 1° of that of the melt, but with the bath maintained at 55° no rise at all could be recorded. Crystallization from benzene raised the maximum temperature to 66·7 (Fig. IV curve VII) but it is doubtful if this is a true solidifying point as the maximum temperature was not maintained for any length of time. The same applies in a less degree to curve VIII obtained after a crystallization from ether. In experiment IX with the same substance the bath was maintained still nearer to the temperature of the melt and a higher maximum was reached. Three more recrystallizations from ether resulted in a steady maximum 70·3° (X), this value then remained unchanged on further crystallization (XII). The solid from this experiment melted at 70·2°.

With α-monolaurin the rise in temperature was much more sudden as might be expected from the rapidity with which the β-form changes to the α-form. After the initial rise, however, a period of slow increase in temperature was observed as may be seen in Fig. III. This suggests that there may be a third form of α-monolaurin just as there appears from the work of Loskit (*Z. physical Chem.*, 1928, **134**, 135), to be a third form of some of the triglycerides. No definite opinion can be expressed, however, without further experimental data.

The first sample rose to a maximum temperature of 55·5°; successive crystallizations from ether raised this to 58·6°, 59.9°, 60·0° and 60·0° as shown by curves I, II, III and IV in Fig. III. The curve for the last experiment was practically identical with IV and has not been drawn.

On comparing the solidifying points and melting points shown in Table II, it will be noted that the depression from the melting point of the α-form is 3° for laurin and myristin and 6° for palmitin. It has been found that the initial depression in the melting point of laurin mixed with a small quantity of palmitin or *vice versa* is 0·9° for 1 per cent. impurity in both cases, so that if the assumptions are made that the solidifying point is that of an equilibrium mixture of the α and β-forms and that the depression produced by the presence of β-form is of the same order as by the addition of a second monoglyceride (an admitted approximation), the quantity of β-form in the mixture would be about 3 per cent for laurin and myristin and 6 per cent. for palmitin.

This involves the assumption that what have been termed the α and β-forms are single bodies. According to Smidts (*Allotropy*) it is more probable that both are equilibrium mixtures. The formation of a definite equilibrium mixture with a melting point lower than that of the α-form makes it appear unlikely that the α-form itself is another equilibrium mixture, but the composition of the β-form cannot be decided without further investigation.

Another noteworthy feature is the very considerable super-cooling which appears to be necessary before the change $\beta \rightarrow \alpha$ takes place even in presence of the α-form. This is probably a spurious effect due to the slow rate of transformation and the tendency of the β-form to remain in the metastable state and has been already discussed in the case of tristearin (p. 121).

In conclusion we wish to express our best thanks to Dr. J. J. Sudborough and Dr. J. L. Simonsen for valuable assistance during the course of this work.

SUMMARY.

The α-monoglycerides of the fatty acids with an even number of carbon atoms from caprylic to stearic have been made in a state of high purity and their densities, refractive indices, viscosities and surface tensions measured.

The glycerides of the four higher acids exhibit two definite melting points corresponding with those of two forms α and β. The rate of the change $\beta \rightarrow \alpha$ increases with decrease in molecular weight and is almost instantaneous in the case of α-monolaurin.

The solidification point of the fused glyceride always lies below the melting point of the α-form indicating that the transformation $\beta \rightarrow \alpha$ is not complete.

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Department of General Chemistry,
Indian Institute of Science,
Bangalore.