[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Unsaturated Synthetic Glycerides. VI.[1] Polymorphism of Symmetrical Monoöleyl-disaturated Triglycerides[2]

BY B. F. DAUBERT AND T. H. CLARKE

Since studies on the polymorphic phases of glycerides, both natural and synthetic, have been excellently reviewed recently by Ferguson and Lutton,[3] no detailed reference to past investigations will be made in this report.

While much of the earlier and basic work concerning the abnormal melting behavior of fats was confined to simple triglycerides and complex glyceride mixtures of natural fats, it remained for Malkin and associates[4,5,6] to establish a foundation upon which the polymorphism of glycerides could be studied and understood. The latter investigators, on the basis of their experimental work mainly with synthetic compounds, indicate that mixed triglycerides can exist in at least four different modifications (which they designate by Greek letters as β, β', α and γ, each with a characteristic melting point.

Transition point data for the polymorphic forms of synthetic glycerides containing unsaturated acids, only recently synthesized, have not been published. The purpose of the present paper, therefore, is to report the experimental data for a series of symmetrical monoöleyl-disaturated triglycerides.[7]

In this and future publications dealing with polymorphism in glycerides we shall refer to the different polymorphic forms for the unsaturated synthetic glycerides by the use of Roman numerals, *e. g.*, Form I, Form II, etc. Form I will always refer to the highest melting or most stable form.

Experimental

Methods and Apparatus.—The measuring system consisted of an eight-junction copper-constantan thermel, a Leeds and Northrup type Kl potentiometer and a type R galvanometer with a glass scale reading device. The thermel was about 1.5 mm. in diameter and the active section about 7 mm. in length. The ends of the thermel were enclosed in thin-wall glass tubes. The thermel was calibrated against a platinum resistance thermometer from 100 to −79° using the Callender equation above 0° and the van Deusen equation below 0°, in order to determine the temperature of the thermometer at a given point. The Na_2SO_4–$Na_2SO_4 \cdot 10H_2O$ point and the freezing point of mercury (−38.89°) were checked to within ±0.02°. The maximum sensitivity of the system was 0.02° per cm. of scale deflection when the scale was placed at a distance of one meter from the galvanometer mirror. The change in microvolts was 300, on the average, over the temperature range involved.

A sample of the synthetic glyceride (0.7 to 1.0 g.) was weighed into a small glass vial and then the end of the thermel was inserted to a depth of about 25 mm. The vial was then inserted into a small vacuum flask so that a 1-cm. clearance around the vial was available. The small vacuum flask could be lowered into any one of a series of liter vacuum flasks serving as warming or cooling baths. Within reasonable limits any desired rate of warming or cooling could be obtained.

During the determination of a cooling or warming curve, the setting of the potentiometer was changed by even increments and the time recorded when the galvanometer image crossed the zero point on the scale. The magnitude of the increments on the potentiometer dial depended upon the rate of cooling or warming. On a time basis the most rapid practical rate was a reading every six seconds. During a very slow rate of change of temperature, the time interval between readings was as long as two minutes.

For the purpose of checking technique and determining the accuracy of the apparatus, transition points were redetermined for 1-monostearin and 1-monomyristin. Comparison of the results with those previously reported by Malkin and Shurbagy[5] are tabulated in Table I.

TABLE I

TRANSITION POINTS FOR POLYMORPHIC FORMS OF 1-MONOSTEARIN AND 1-MONOMYRISTIN

Form	1-Monostearin, °C.	1-Monomyristin, °C.
I	81.8	71.0
Malkin's β	81.5	70.5
II	78.0	67.5
Malkin's β'	79.0	67.5
III	75.4	55.3
Malkin's α	74.0	56.0
IV	48.5	21.3
Malkin's γ	47.5	24.0

Discussion of Cooling and Warming Curves.—The type of warming curve obtained on heating a sample of a synthetic glyceride depends entirely on its previous history, *i. e.*, the manner by which it was cooled and subsequently stored. This observation, pointed out by other investigators, has been verified in the present study.

Since it was not possible under our experimental conditions to observe the transformations of the different forms of the synthetic glycerides, transition point is used in preference to melting point to indicate the temperature at which the change occurred.

Types of cooling and warming curves for 2-oleyl-1,3-dimyristin, resulting from many thermometric measurements and typical for the series of symmetrical monooleyl-disaturated triglycerides, are shown in Figs. 1 and 2. In these figures the temperature scale is entirely accurate, but certain liberties have been taken with the time axis so that a complete set of curves could be drawn on a single chart. Approximate time intervals are indicated (see below) for certain sections of the curves.

The cooling of a melted sample resulted in its solidification in one of three forms depending on the rate of cooling. Very rapid cooling (three to five minutes) brought about solidification in Form IV (curve CC', Fig. 1). Subsequent warming of the cooled glyceride (curve C'C") produced a pronounced change of slope 0.2 to 0.6° below the transition point of Form IV (this behavior was checked many

---

[1] Earlier communications appeared in THIS JOURNAL, 65, 2142, 2144 (1943); 66, 53, 289, 290 (1944).

[2] A grant from the Buhl Foundation in support of this investigation and the suggestions of Dr. H. E. Longenecker in the preparation of this manuscript are gratefully acknowledged.

[3] Ferguson and Lutton, *Chem. Rev.*, 28, 355 (1941).

[4] Clarkson and Malkin, *J. Chem. Soc.*, 666 (1934).

[5] Malkin and Shurbagy, *ibid.*, 1628 (1936).

[6] Malkin and Meara, *ibid.*, 103, 1141 (1939).

[7] Jackson, Daubert, King and Longenecker, THIS JOURNAL, 66, 289 (1944).

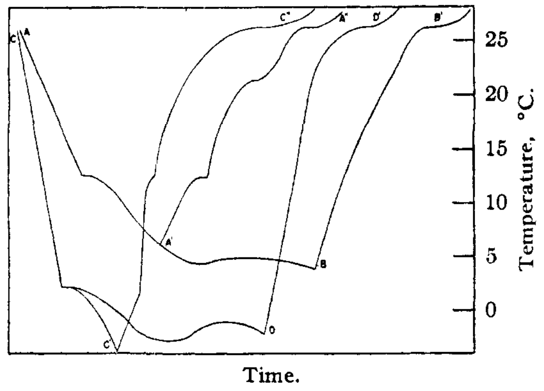

Fig. 1.—Types of cooling and warming curves for 2-oleyl-1,3-dimyristin.

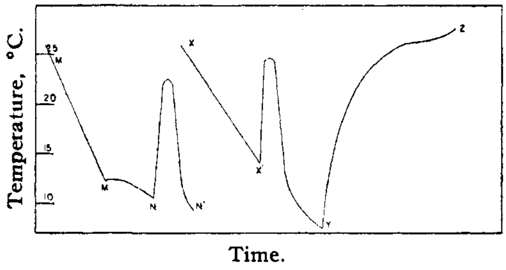

Fig. 2.—Types of cooling and warming curves for 2-oleyl-1,3-dimyristin.

times and seemed very specific) followed by a very sudden rise to the transition point of Form III and a slower rise to the transition point of Form I. The presence of Form II was not indicated on this warming curve. If the rapidly cooled sample (curve CC') was held slightly below the transition point of Form IV for some time (thirty to forty-five minutes) indicated in curve CD, a rise in the curve occurred, indicating a slight heat evolution. This heat evolution was apparently caused by the conversion of Form IV to some higher temperature form or forms, for subsequent warming (curve DD') gave only a slight indication of the presence of Form III, a definite change in slope, and then a good transition point for Form I. Again the presence of Form II was not indicated.

A somewhat slower rate of cooling (eight to twelve minutes) of the original melted sample resulted in solidification of the sample in Form III (curve AA'). Immediate warming gave changes of slope corresponding to the transition points from Form III, Form II and Form I (curve A'A"). As in the case of curve CD, if the sample solidified in Form III was held for some time (thirty to forty-five minutes) as indicated in curve A'B, conversion occurred to the higher temperature forms as shown by curve BB', wherein a small but definite break occurred at the transition point of Form II followed by a marked change of slope at the transition point of Form I. If the cooled samples at points B or D were held at those temperatures for a longer period of time (sixty to seventy-five minutes), subsequent warming indicated practically complete conversion to Form I.

Very slow cooling (twenty to twenty-five minutes) of the melted sample of 2-oleyl-1,3-dimyristin resulted in solidification of Form I (curve XX'Y, Fig. 2). The liquid supercooled to point X'; the temperature then rose very rapidly to a point between the transition points of Form I and Form II as the heat of solidification was evolved and then decreased rapidly. Warming of the sample (curve YZ) showed a transition point of Form I only. Curve MM'NN' would seem to indicate the possibility of crystallization of more than one form at a time from a melted sample. Upon cooling, solidification occurred in Form III at M' on the curve. The sample continued to cool for several degrees to point N and then suddenly increased to a temperature between the transition points of Form I and Form II with no indication of the presence of Form III.

Important factors determining the shape of the curves, time of cooling and warming, etc., are the nature and size of the sample, and the temperature gradient between the sample and surroundings. We believe we have studied a sufficient number of rates of cooling and warming to show that the transition point temperatures, in the main, are not rate dependent. The determination of the transition point of Form IV on a warming curve did show slight rate dependence. The transition point approached that found for Form IV on cooling curves (which were not rate dependent) as the warming rate was increased.

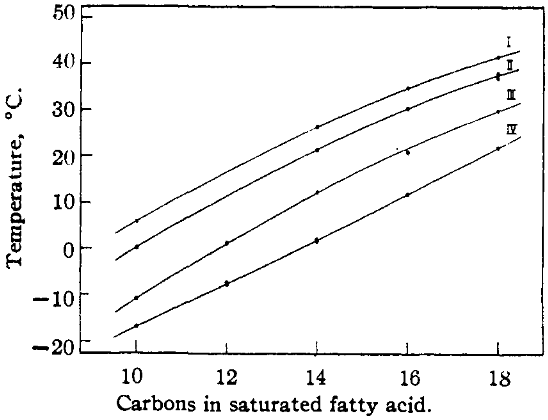

Fig. 3.—Transition point curves for the polymorphic forms of symmetrical 2-oleyl-1,3-diacylglycerols.

The transition points for the polymorphic forms of each member of the series of symmetrical monoöleyl-disaturated triglycerides are given in Table II. A single value is given wherever a transition point could be duplicated to within ±0.1°. The relationships between the various polymorphic forms are shown in Fig. 3. While the consistency of the data is apparent, one anomaly, however, is to be noted. For 2-oleyl-1,3-dilaurin, no transition point clearly defining either Form I or Form II was obtained. Three values, all lying between the curves for Form I and Form II were experimentally obtained, none of which clearly characterizes either form. The capillary melting point for Form I (16.0 to 16.5°) would fall close to the curve for the melting points of other members of the series.

TABLE II

TRANSITION POINTS FOR POLYMORPHIC FORMS OF SYMMETRICAL MONOÖLEYL-DIACYL TRIGLYCERIDES[a]

Acyl radical	Transition points, °C. Form I	Form II	Form III	Form IV
Stearyl	41.6	37.0, 37.6	29.8	22.3
Palmityl	35.2	30.4	20.8	12.0
Myristyl	26.3	21.5	12.3	2.1
Lauryl	16.5[b]	11.0[b]	1.4	− 7.1, −7.5
Capryl	6.2	0.6	−10.2	−16.4

[a] Capillary melting points reported previously.[7] [b] Determined from curve, Fig. 3.

Summary

Transition point data for the polymorphic forms of a series of symmetrical monoöleyl-disaturated triglycerides obtained from cooling and warming curves are reported.

PITTSBURGH, PA. RECEIVED DECEMBER 27, 1943