Polymorphism of Synthetic Glycerides*[1]

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ALTHOUGH considerable information has been accumulated in recent years concerning the abnormal melting behavior of fats, much of the reported data has been obtained on mixtures of glycerides or on natural fats (1). Malkin and coworkers (2) have made many major contributions to our present knowledge of the polymorphism of glycerides, principally through the correlation of thermometric curve and x-ray diffraction data on synthetic glycerides. These investigators, while primarily interested in glycerides containing saturated fatty acids, reported thermometric data for a few simple triglycerides containing unsaturated acids. The polymorphism of other unsaturated mono- and triglycerides (3, 4, 5) has been studied recently by thermometric methods.

Among the several methods by which phase transformations in glycerides may be followed, in addition to thermometric measurements and dilatometry, the x-ray diffraction method provides, perhaps, the most conclusive evidence of phase transformations. While the transition point data reported in this paper are the result exclusively of thermometric measurement it is our intention, nevertheless, later to correlate these data with x-ray diffraction studies.

Since relatively little information is available on the polymorphism of unsaturated mixed triglycerides, the present investigation is concerned mainly with the results of a thermometric study on symmetrical and unsymmetrical synthetic mixed triglycerides containing oleic acid. In addition, the saturated 2-monoglycerides were studied to determine whether these monoglycerides exhibited the same type of transition phenomena as the isomeric 1-monoglycerides.

The system of nomenclature for the various transition forms used in this investigation is the same as that suggested in a previous study (5), i.e., Form I, Form II, etc. Form I always refers to the highest melting form.

Experimental

Preparation of Glycerides. All of the unsaturated mixed triglycerides and the saturated 2-monoglycerides were prepared by methods previously described (6, 7, 8).

Methods and Apparatus. Since it was of interest to observe visually the phase transformations of the glycerides during cooling and warming of the samples, certain alterations were made in the apparatus as used for the thermometric measurements as previously described (5).

An unsilvered vacuum flask of 2.5 cm. internal diameter and approximately 9 cm. deep was employed as the jacket for the system. A layer of acetone 5 cm. deep was placed in the flask and there was inserted, through a fitted three-hole stopper, (a) a glass tube extending to the bottom of the flask and connected to the air line for stirring, (b) a glass-enclosed electrical heater and (c) the thermel, over the end of which a small vial containing the glyceride (0.8 to 1.0 g.) was placed. The depth of the thermel was adjusted so that the glyceride sample was above the heater. The heater was about 1 cm. in length and approximately 1.5 mm. in diameter and had a resistance of 10 ohms. The heating coil was connected to a voltage supply of 18 volts with a variable resistance and an ammeter in the circuit. Heating rates from 0.02° per minute to 1.5° per minute were easily attainable and were found to be entirely satisfactory for the compounds under investigation. An eight-junction copper-constantan thermel was again used but the remainder of the system consisted of a White potentiometer (100,000 microvolt range) and an H. S. galvanometer. The apparatus, drawn to scale, is shown in Figure 1.

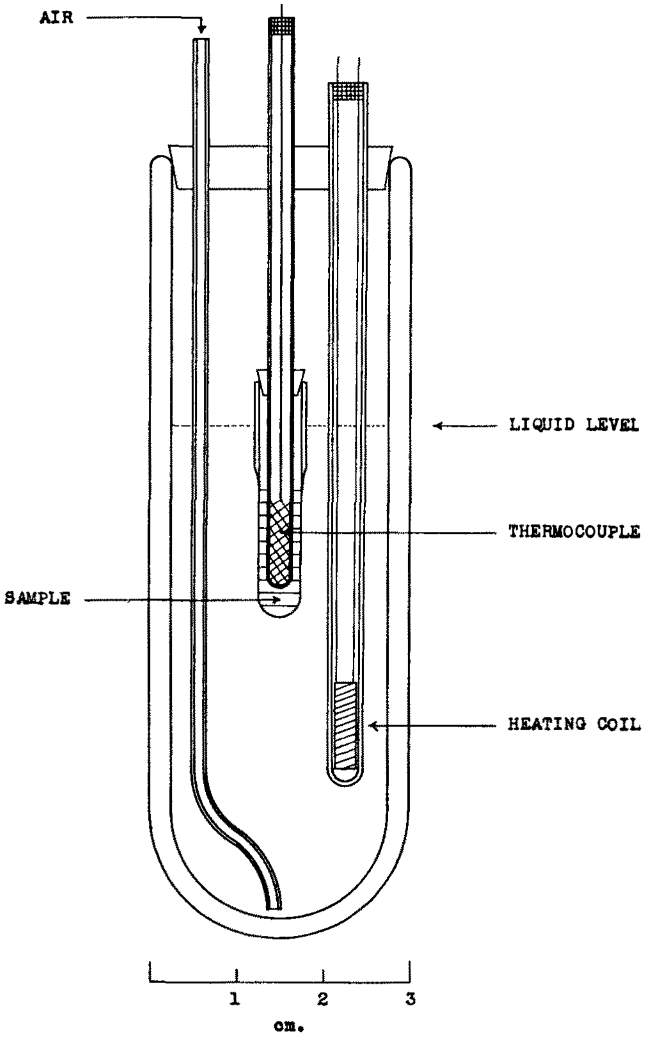

FIG. 1. Jacket system of the apparatus used for Thermal Studies of Synthetic Glycerides.

Discussion

IT HAD been anticipated on the basis of previous thermometric measurements on bulk samples of symmetrical 2-oleyl-1,3-disaturated triglycerides, that no great difficulty would be experienced in obtaining

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thermometric data to indicate that the unsymmetrical isomers of the above mentioned triglycerides were capable of exhibiting at least four different crystalline forms. It may be observed, however, in Table I and Figure 2 that in only two compounds, namely, 1-oleyl-2,3-dicaprin and 1-oleyl-2,3-dilaurin, were there so many as four forms indicated on warming curves. The solid black dots in Figure 2 represent capillary tube melting points while the open circles indicate transition points obtained from warming curves. These data support our prior experience with thermometric measurements on bulk samples of triglycerides, i.e., that triglycerides of lower molecular weight undergo relatively rapid and complete phase transformation. This fact no doubt accounts for the sharpness of the transition points for 1-oleyl-2,3-dicaprin and 1-oleyl-2,3-dilaurin. The capillary melting point of the highest melting form (Form I) for 1-oleyl-2,3-dilaurin previously reported (6) as 20.0° was found to be in error. The compound melted at 16.0° when determined by the capillary tube method and from warming curves the melting point was 15.5°

TABLE I

Transition Point Data for the Polymorphic Forms of Unsaturated Triglycerides

Acyl Radical	Form I	Form II	Form III	Form IV	Capillary m.p.[1]
1-Oleyl-2,3-diacyl Glycerides					
capryl	5.3°	— 2.5°	—15.0°	—27.0°	3-4°
lauryl	15.5°	4.8°	—10.0°	—15.5°	16.0°
myristyl		22.7°	18.6°	3.8°	25.0°
palmityl			29.8°	18.5°	34.5°
stearyl				26.7°	38.5°
1-Acyl-2,3-dioleins					
caproyl	—14.5°		—34.2°	—56.5°	—11 to —10°
caprylyl	—18.5°[2]			—50.0°	— 6.6 to — 5.6°
capryl	— 0.6°		—16.5°	—40.5°	— 0.5 to 0.5°
lauryl	4.3°		—10.9°	—32.0°	5.5 to 6.5°
myristyl	13.3°		— 4.2°	—21.8°	12.5 to 13.5°
palmityl	15.8°		2.5°	—13.2°	18.0 to 19.0°
stearyl	22.9°		8.6°	— 1.5°	22.5 to 23.5°

[1] The sample contained in thin-walled capillary tubes was cooled to —20° and held at —20° for twenty-four hours before determination of the melting point.

[2] The transition point probably of a mixture of phases.

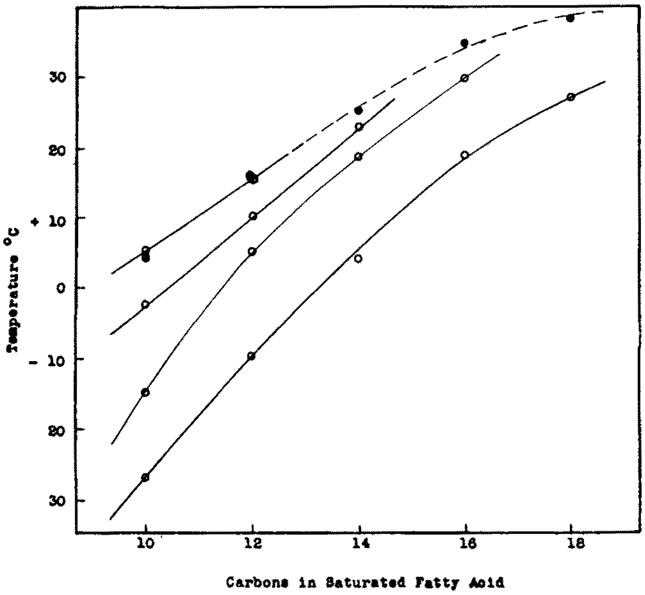

FIG. 2. Melting Points for the Polymorphic Forms of the 1-Oleyl-2,3-disaturated Triglycerides.
● Capillary melting points
○ Transition points obtained from warming curves

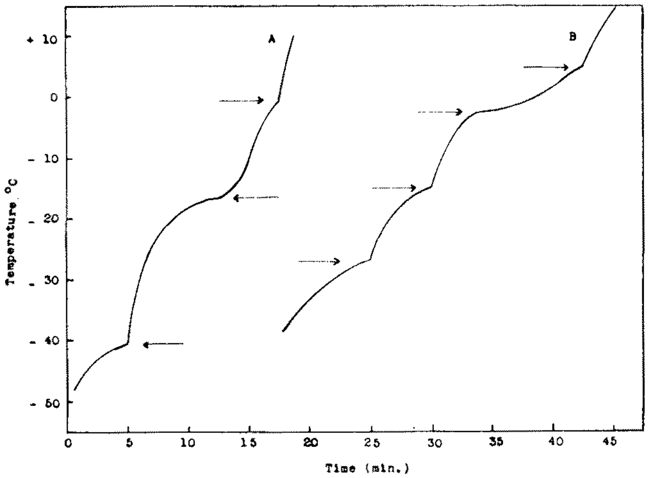

FIG. 3. Warming Curves for (A) 1-Capryl-2,3-diolein and (B) 1-Oleyl-2,3-dicaprin.

In our experience with both 1-oleyl-2,3-dicaprin and 1-oleyl-2,3-dilaurin, as well as the symmetrical monooleyl-disaturated triglycerides, Form IV, the lowest melting form, was always obtained by rapid cooling of a well-melted sample. It, therefore, seems reasonable that the lowest transition point as indicated in Figure 2, for the unsymmetrical monoöleyl-disaturated triglycerides containing myristic, palmitic and stearic acids respectively, is correctly identified as Form IV for each compound. The curve drawn through these points extends smoothly through the points for Form IV of the other two members of the series.

In spite of repeated attempts involving long periods of time and different rates of warming under varying conditions of time and rate of temperature change with time, bulk samples of 1-oleyl-2,3-dimyristin, 1-oleyl-2,3-dipalmitin, and 1-oleyl-2,3-distearin did not transform completely to Form I. For this reason we cannot be positive, in the absence of supporting x-ray diffraction data, that the transition points indicated in Figure 2 as Form II and Form III for 1-oleyl-2,3-dimyristin and 1-oleyl-2,3-dipalmitin are the transition points for the pure phases.

A type of warming curve from which transition point data were obtained for the series of unsymmetrical monoöleyl-disaturated triglycerides is illustrated in Figure 3 for 1-oleyl-2,3-dicaprin.

A COMPOSITE of the transition point data for the series of 1-monosaturated-2,3-dioleins is given in Figure 4 and also in Table I. It may be seen in Figure 4 that each of the triglycerides of this series, with one exception, exhibited three different forms, each with a characteristic transition point. For 1-caprylyl-2,3-diolein, no transition point clearly defining either Form I or Form III was obtained. The transition point at —18.5° does not fall on the smooth curves drawn through the transition points for Form I or Form III of other members of the series. Repeated efforts to set up a pure phase in Form I or Form III, in the bulk sample, were not successful. In contrast, however, it was relatively easy to cause the 1-caprylyl-2,3-diolein to crystallize in Form I when placed in a thin-walled capillary tube, chilled to —20° and held at —20° for twenty-four hours. The melting point of Form I as determined by the capillary tube method was 5.6 to 6.6°.

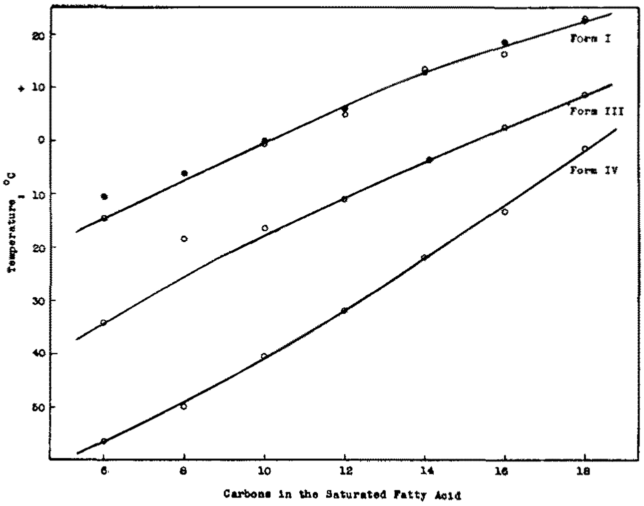

FIG. 4. Melting Points for the Polymorphic Forms of the 1-Acyl-2,3-dioleins.

● Capillary melting points
○ Transition points obtained from warming curves

It is assumed that the transition points intermediate between the highest and lowest melting forms, i.e. Form I and Form IV, correspond to the transition points of Form III. It is not likely this form corresponds to the Form II typical of the symmetrical 2-oleyl-1,3-disaturated triglycerides. While complete knowledge is lacking in the absence of x-ray diffraction data, the magnitude of the difference in temperature between the transition points of Form I and the transition points of the intermediate form (Form III) does not support an assumption that the intermediate form is Form II.

A warming curve for 1-capryl-2,3-diolein and typical for the series of the unsymmetrical monosaturated-dioleins is shown in Figure 3.

Since several highly purified saturated 2-monoglycerides were available in our laboratory, it was thought it would be highly desirable to determine whether these 2-monoglycerides exhibited the same kind of abnormal melting behavior as the isomeric 1-monoglycerides. The polymorphic nature of the 1-monoglycerides had been established by Malkin and associates (2) and later verified by others (5). An homologous series of 2-monoglycerides, containing capric, lauric, myristic, palmitic and stearic acids respectively, was subjected to thermometric measurement under the same variations of cooling and warming conditions as the previously mentioned unsaturated triglycerides. No evidence for polymorphism was found either by thermometric measurements or by capillary tube methods. Regardless of the rapidity with which a 2-monoglyceride was cooled and subsequently warmed either in bulk sample or in thin-walled capillary tubes the melting point was consistently identical with the melting point of the solvent crystallized (Form I) compound. X-Ray diffraction studies of the 2-monoglycerides cooled under varying conditions invariably gave a diffraction pattern identical with the solvent crystallized compound. While the x-ray diffraction data in themselves because of the long exposure time does not preclude the possibility of transition of other forms to Form I, the supporting evidence of thermometric measurement seems to indicate that 2-monoglycerides of saturated fatty acids do not exhibit polymorphism.

Summary

Transition point data are reported for a series of unsymmetrical monoöleyl-disaturated triglycerides and a series of unsymmetrical monosaturated-dioleins. The results of thermometric measurements on a series of saturated 2-monoglycerides are also reported.

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Determination of Monoglyceride in Fats and Oils by Oxidation With Periodic Acid[1]

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SINCE Malaprade's (14) original work on the oxidation of polyalcohols with periodic acid and periodates, numerous studies and applications have been made of this reaction. Fleury *et al.* studied the action of periodic acid on hydroxy acids and sugars (3,4,5), glycerol phosphoric acid (6), glycerol in the presence of sugar (7), lactic acid and pyruvic acid (8) and tartaric acid (9). Hudson and co-workers (10, 12, 13) have used the reaction in their studies of sugars, and Nicolet and Shinn (15) showed that periodic acid reacted rapidly and quantitatively with alpha-amino alcohols. The kinetics of the periodic acid oxidation of 1, 2 glycols have been investigated by Price and associates (16,17). Oxidation with periodic acid has been applied by Bradford, Pohle, Gunther and Mehlenbacher (2) to the determination of glycerol, by Allen, Charbonnier and Coleman (1) to the determination of glycerol, ethylene glycol and diethylene glycol in the presence of each other and by Hoepe and Treadwell (11) to the determination of glycerol, ethylene glycol and 1, 2 propylene glycol in the presence of one another.

Fleury and Paris (6) showed that periodic acid oxidized alpha-glycerol phosphoric acid in a few minutes at ordinary temperatures. These results indicated that the fatty acid monoglycerides, which exist almost exclusively in the alpha form, might be determined directly by an oxidation with periodic acid. Di- and tri-glycerides are not oxidized by periodic acid at room temperature because it oxidizes poly-

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