THE SOLUBILITY OF TRISTEARIN IN ORGANIC SOLVENTS[1]

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The solubility of tristearin has been determined quantitatively in hexane, benzene, carbon tetrachloride, chloroform, ethyl acetate, acetone and ordinary unhydrogenated cottonseed oil. The solubility of this triglyceride is decreased markedly by increased polarity of the solvents. In the presence of solvents, tristearin exhibits three distinct solubility curves corresponding to the three crystalline forms established previously by melting point determinations and X-ray measurements. The occurrence of a fourth crystalline form reportedly melting at 70° is not confirmed by the solubility studies.

The polymorphic behavior of the triglycerides has received more attention than all other aliphatic compounds. Probably because of differences in reported results, particular emphasis has been placed on investigation of the saturated, single-acid triglycerides. Malkin,[2-3] Lutton[4-6] and others[7,8] have reported numerous attempts to characterize the several crystalline modifications of these triglycerides by correlating their observed melting points with the X-ray diffraction measurements of the respective crystal lattices. Until recently, there has been some question as to whether three or four basic configurations of triglycerides occur, and the various investigators have differed further over correlation of observed melting points with the respective crystal forms revealed by the X-ray diffraction studies. It now appears that three distinct crystal forms of the saturated, single-acid triglycerides have been established quite definitely.[9,10]

With the exception of a report on solubilities in aceto- and butyroglycerides,[11] no solubility studies comparable to those on other aliphatic compounds have been reported for the triglycerides. This paper reports the solubility of tristearin in hexane, benzene, carbon tetrachloride, chloroform, ethyl acetate, acetone and ordinary unhydrogenated cottonseed oil. The observed polymorphic behavior is correlated with the known thermal characteristics and crystalline structure of tristearin.

Experimental

The tristearin used in this investigation was prepared by Dr. R. R. Allen by the interesterification of triacetin with highly purified methyl stearate using sodium methoxide as the catalyst. The product was recrystallized repeatedly from acetone.

Cooling and heating curves were obtained by the usual procedure used in this Laboratory.[12] Fifteen-gram samples of tristearin were placed in a jacketed Pyrex test-tube equipped with a mercury thermometer and Nichrome wire stirrer. The thermometer which was graduated in 0.1° intervals had been calibrated by the National Bureau of Standards. The stirrer was actuated uniformly by means of an oscillating device operated by an electric motor controlled by a Variac transformer. Samples were stirred during cooling only until crystals appeared; the samples were not stirred

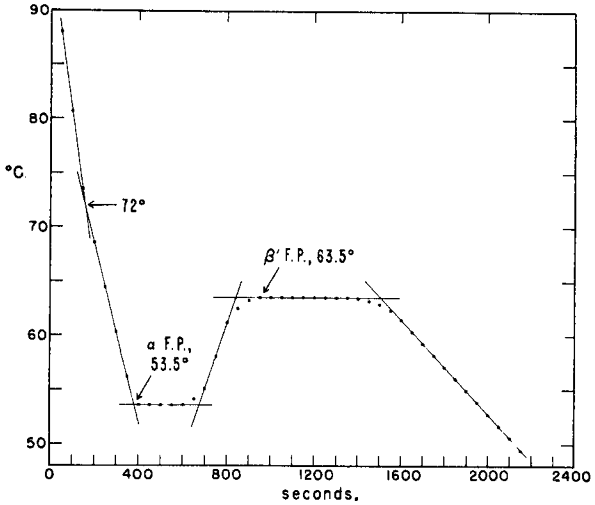

Fig. 1.—Cooling curve of tristearin showing plateaus at the α and β' freezing points.

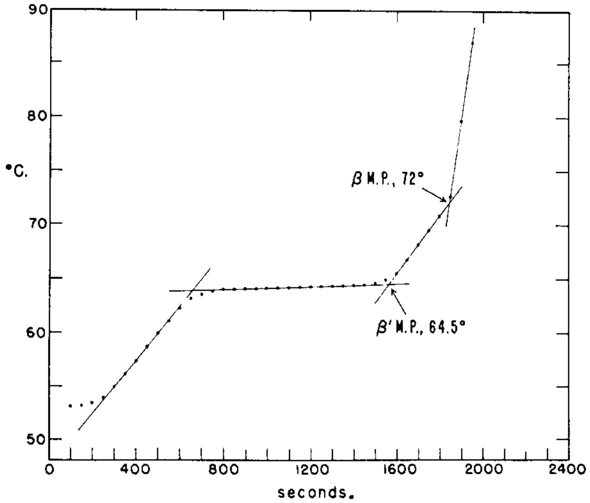

Fig. 2.—Heating curve of tristearin after minimum holding time showing a plateau at the β' melting point and a change of slope at the β melting point.

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[1] Presented before the Division of Paint, Plastics and Printing Ink Chemistry at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September, 1955.

[2] (a) T. Malkin, *J. Chem. Soc.*, 2796 (1931). (b) C. E. Clarkson and T. Malkin, *ibid.*, 985 (1948).

[3] T. Malkin, "Glyceride Polymorphism," "Progress in the Chemistry of Fats and Other Lipids," Vol. II, Academic Press, Inc., New York, N. Y., 1954.

[4] E. S. Lutton, *J. Am. Chem. Soc.*, **67**, 524 (1945).

[5] E. S. Lutton, *ibid.*, **70**, 248 (1948).

[6] E. S. Lutton, F. L. Jackson and O. T. Quimby, *ibid.*, **70**, 2441 (1948).

[7] A. E. Bailey, M. E. Jefferson, F. B. Krieger and S. T. Bauer, *Oil and Soap*, **22**, 10 (1945).

[8] L. J. Filer, Jr., S. S. Sidhu, B. F. Daubert and H. E. Longenecker, *J. Am. Chem. Soc.*, **68**, 167 (1946).

[9] O. T. Quimby, *ibid.*, **72**, 5064 (1950).

[10] E. S. Lutton, *ibid.*, **77**, 2646 (1955).

[11] T. L. Ward, A. T. Gros and R. O. Feuge, *J. Am. Oil Chemists' Soc.*, **32**, 316 (1955).

[12] C. W. Hoerr, R. A. Reck, G. B. Corcoran and H. J. Harwood, THIS JOURNAL, **59**, 457 (1955).

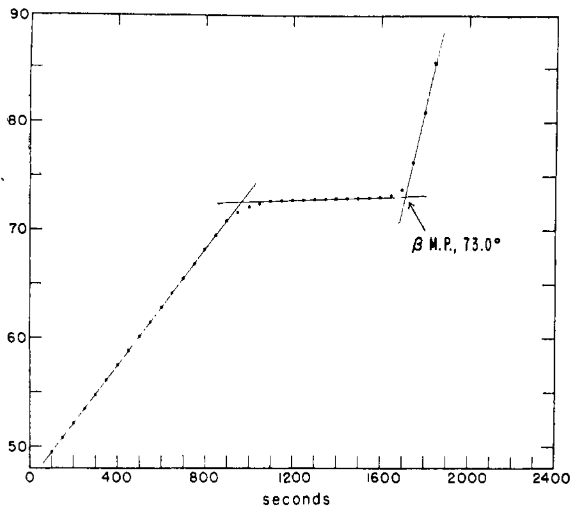

Fig. 3.—Heating curve of tristearin after extended holding time showing only a plateau at the β melting point.

during heating to avoid channeling. For cooling curve determinations the jacketed tubes were placed in a water-bath maintained at about 40° after initially heating the samples to 100° to destroy all crystal nuclei.[9] For heating curves the bath was held at about 90°. Time was measured by means of an electrical timer, and temperatures were recorded at 100 sec. intervals throughout the cooling and heating experiments. The time-temperature curves obtained by this procedure are shown in Figs. 1–3.

The solubility of tristearin was determined by the usual methods employed in this Laboratory.[12,13] For solubilities in the higher temperature ranges, particularly near the boiling points of the solvents, weighed amounts of solute and solvent were sealed in small glass tubes which were rotated slowly in a 4-l. water-bath. Temperatures of the bath were increased gradually or held constant at desired levels by means of a special Glas-Col heating mantle.

For solubility measurements in the lower temperature ranges, weighed amounts of the components were put into jacketed test-tubes similar to those used for the cooling and heating curve determinations. The temperature of the samples was raised or lowered by the use of water-baths of appropriate temperatures.

In both solubility procedures, temperatures at which visible changes occurred in the samples were recorded. The solubility curves shown in Figs. 4–7 were obtained by plotting solution temperatures against weight per cent. of solute.

The solvents were similar to those used in the previous solubility studies. They were of the best grade commercially available and were freshly distilled through a Stedman-packed column before use. The cottonseed oil used was a

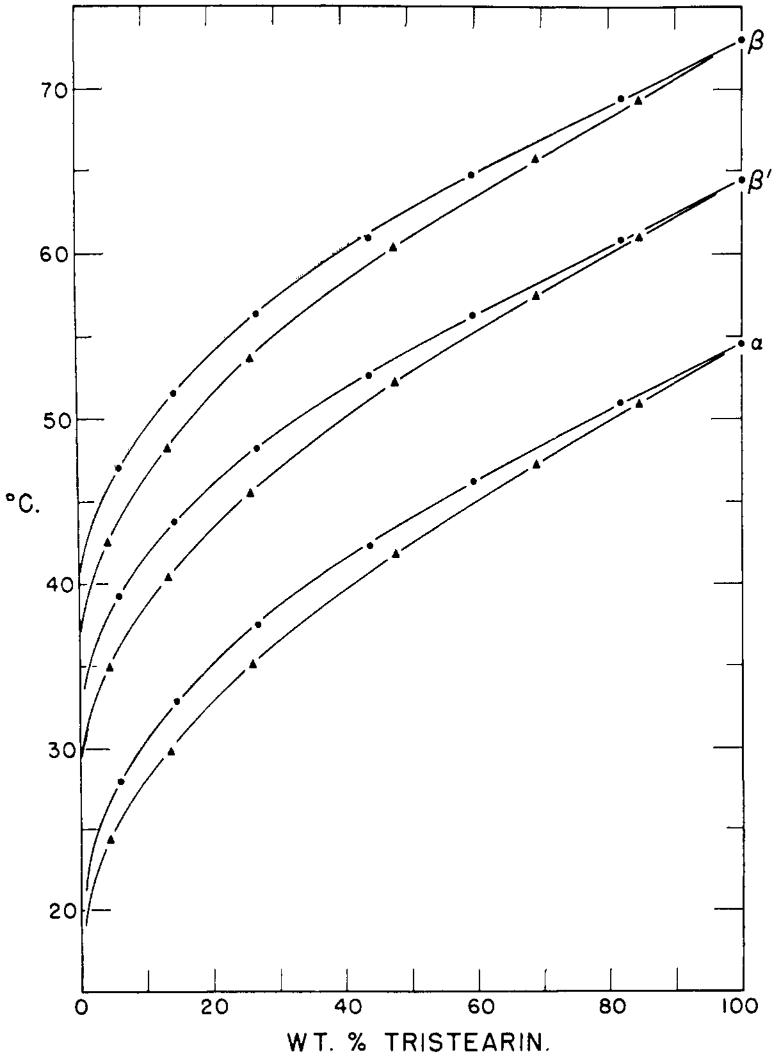

Fig. 4.—Solubility of tristearin in hexane ● and in benzene ▲.

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[13] P. L. DuBrow, C. W. Hoerr and H. J. Harwood, *J. Am. Chem. Soc.*, **74**, 6241 (1952).

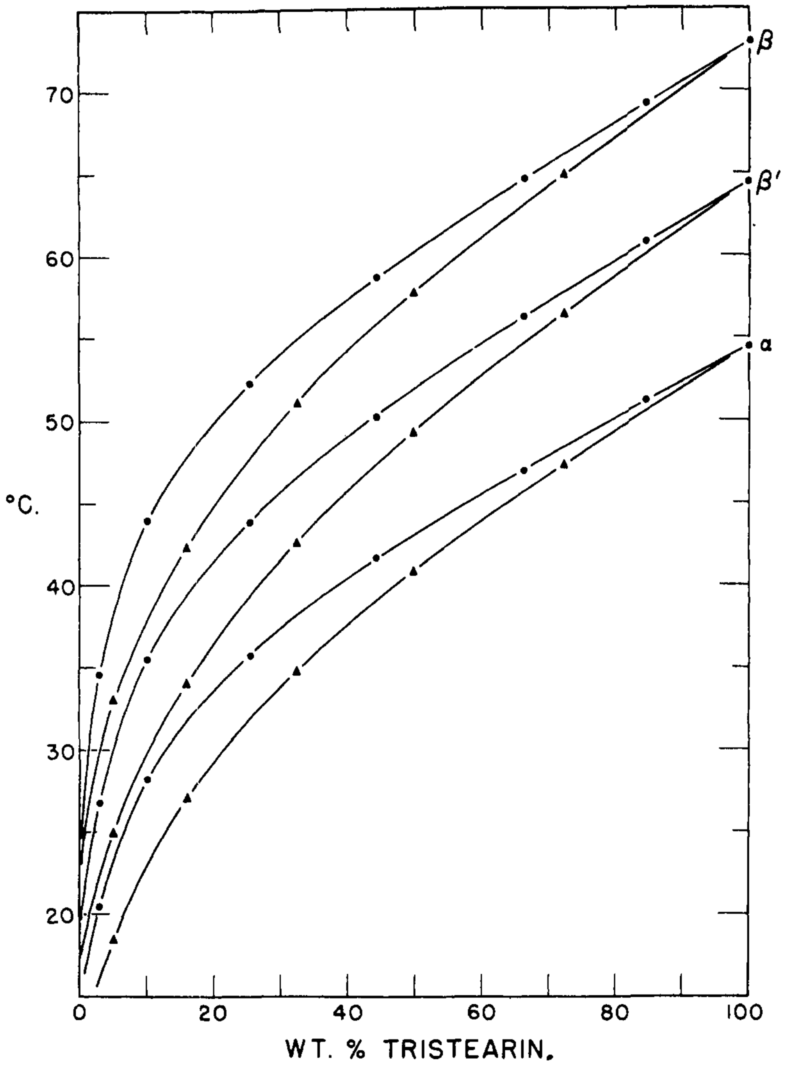

Fig. 5.—Solubility of tristearin in carbon tetrachloride ● and in chloroform ▲.

high-grade, refined, winterized, unhydrogenated oil obtained from regular plant production.

Results and Discussion

The behavior of tristearin during cooling and heating shown in Figs. 1–3 is generally typical of long-chain compounds which exhibit more than one crystalline form.[14] The curves for tristearin are quite similar to those obtained for other triglycerides.[6]

The cooling curve in Fig. 1 shows that tristearin begins to crystallize from the liquid in the α-form. In a matter of minutes, transformation causes the temperature of the sample to rise to the β' freezing point and crystallization in this latter form continues until the sample has solidified.

If the sample is heated as soon as crystallization is essentially complete, behavior shown by the curve in Fig. 2 is observed. The initial portion of the curve below 64.5° represents melting of mixtures of the α- and β'-form; between 64.5 and 72° mixtures of β' and β are melting. Insufficient quantities of the β-form were present in this sample to produce a 72° plateau.

If, however, a sample is held for an hour or two at temperatures a few degrees below the β' freezing point (or overnight at room temperature), a curve like that in Fig. 3 is obtained upon heating. Under these conditions, transformation from the β'- to the β-form is complete, and only the melting of this latter form is observed.

It will be noted in Fig. 1 that there is an inflection in the cooling curve in the neighborhood of 72°. This inflection, which is reproducible, suggests that the energy of the system has been reduced to such an extent that there occurs some sort of preliminary orientation which restricts the free rotation of the molecules in the liquid state. No visible crystallization occurs during cooling until the α freezing point is reached.

The following freezing and melting points of the crystalline forms of tristearin were estimated from the cooling and heating curves:

Form	F.p., °C.	M.p., °C.	Lit. m.p., °C.[9,10]
α	53.5	. .	54.0
β'	63.5	64.5	64.5
β	. .	73.0	73.0

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(14) E. J. Hoffman, C. W. Hoerr and A. W. Ralston, *J. Am. Chem. Soc.*, **67**, 1542 (1945).

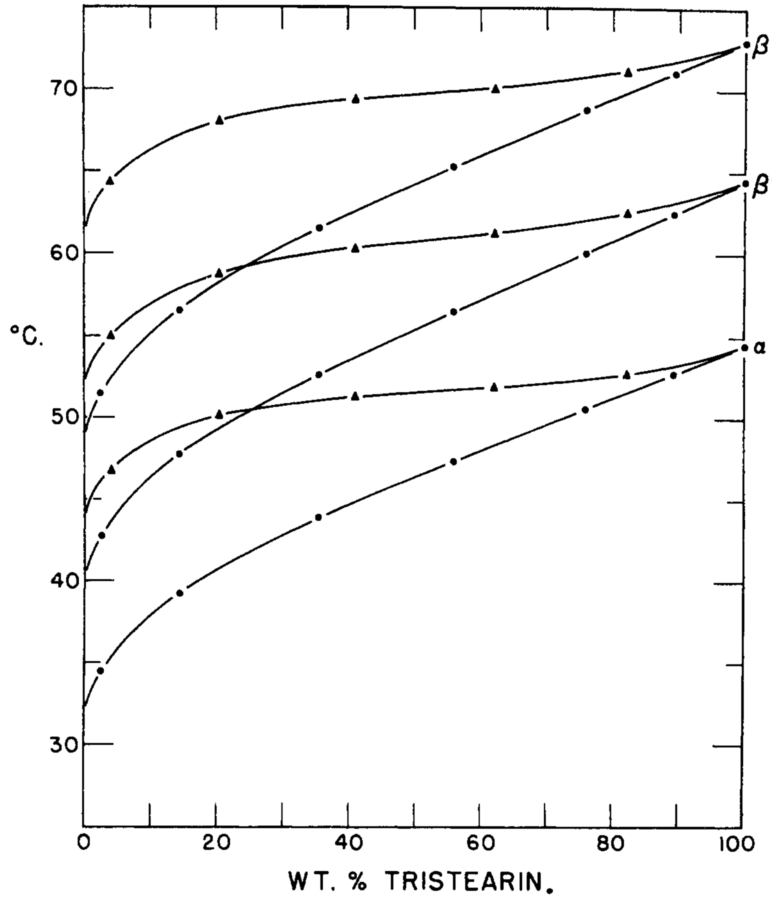

Fig. 6.—Solubility of tristearin in ethyl acetate ● and in acetone ▲.

The α freezing point determined by this method is about 0.5° lower than the reported α "cloud point."[9,10] The other values indicate that the purity of the tristearin used in these experiments was equal to that reported elsewhere.[9,10]

The solubility curves in Figs. 4–7 show that tristearin is more soluble in the non-polar solvents than in those of higher polarity. It is somewhat more soluble in the chlorinated hydrocarbons than in hexane or benzene. Its solubility in cottonseed oil corresponds quite closely to that in the simple ester, ethyl acetate. In the highly polar solvents, such as methanol and acetonitrile, the solubility of tristearin is so limited (determined approximately as 1–2% in boiling solvent) that its systems with these solvents exhibit immiscible liquid regions over most of the concentration range at temperatures above the β melting point.

The noteworthy feature of these solvent systems is the fact that tristearin exhibits a distinct solubility curve for each of its three crystalline forms in each of the solvents investigated. In every case, the triglyceride precipitated from isotropic solution at temperatures on the curve for the α-form. If the mixtures are heated slowly, the solute gradually dissolves until almost clear solution is obtained in the neighborhood of the β' curve. As temperatures on this curve are approximated, however, the material abruptly reprecipitates in its intermediate-melting form. As heating is continued this material gradually redissolves until final solution is obtained at temperatures on the β curve.

The α or β' crystals which are precipitated upon cooling can be caused to dissolve to isotropic solution at temperatures on their respective solubility curves by placing the mixtures immediately in baths of appropriate temperatures. If the precipitated crystals are maintained for some time (a half-hour or more) at temperatures below the β' curve, no apparent solution occurs upon heating until temperatures of the β curve are attained.

Visible observation of the crystals during precipitation from solution seems to confirm reports that the α form is definitely crystalline[9,10] rather than "vitreous".[3] This lowest-melting form precipitates as transparent platelets which transform within a short time to a visibly more opaque form.

It was found that by seeding isotropic solutions which were maintained at appropriate predetermined temperatures, tristearin could be induced to precipitate in either the β'- or β-forms. As in the case of experiments in the absence of solvent,[9] this proved to be a difficult and tedious procedure. In all cases, the higher-melting forms were obtained far more readily by transformation of the lower-melting forms.

As was observed in the cooling curve experiments, the crystalline transformations of tristearin in the presence of solvents always proceed irreversibly from α- to β'- to β-forms. The rate of transformation appears to be much the same in all

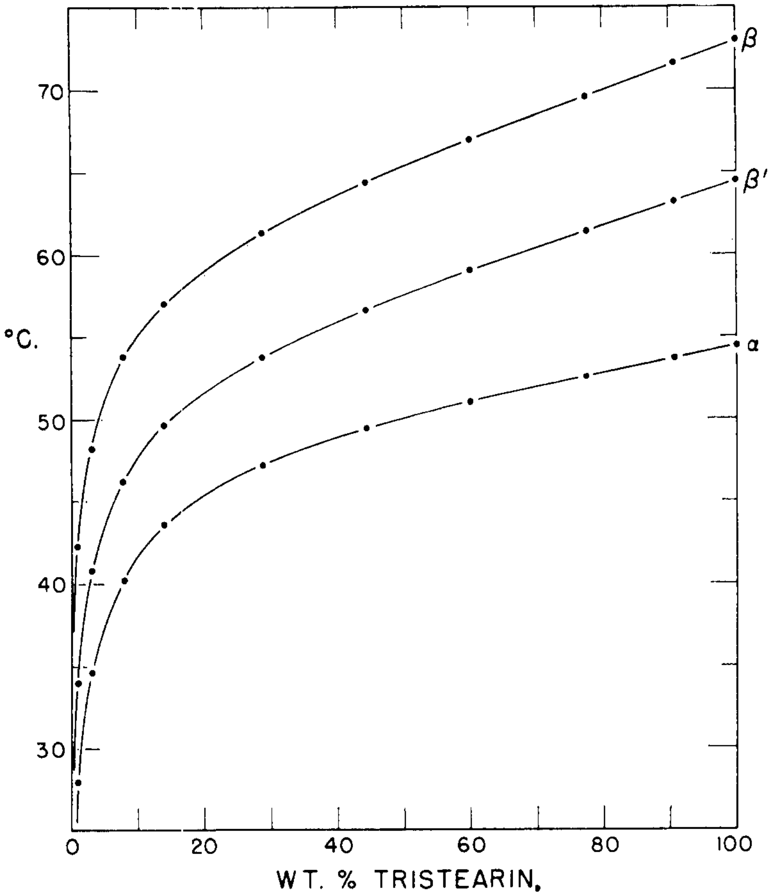

Fig. 7.—Solubility of tristearin in cottonseed oil.

the solvents, and does not seem to be altered appreciably by change of concentration of the solute.

The solubility studies confirm clearly that tristearin exhibits three distinct crystalline forms which have already been characterized by unique lattice spacings. The three forms evidenced by the solubility determinations possess melting points which coincide with those which have been established by other methods.[9,10] The occurrence of a form melting at 70°, designated β' by Malkin,[3] is not confirmed. If this form exists, it is highly probable that the solubility studies would have evinced some indication of the fact.