

# THE POLYMORPHISM OF GLYCERIDES

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## I. INTRODUCTION

Although the multiple melting of glycerides has been known for more than a century and been studied by numerous workers, it has long been a field for confusion and controversy. As long ago as 1849, tristearin was observed (52) after melting and quick solidification to melt at 51–52° while on further heating it resolidified and melted at 62–62.5°. In 1853, tristearin was shown to have (38) three melting points 52, 64.2, and 69.7°. The highest melting point was identical with that of the solvent crystallized glyceride and the lowest practically coincided with the setting point. It was assumed at this time that this melting behavior was due to the occurrence of some form of isomerism. Other workers (10, 50, 65), however, reported only two melting points for tristearin, tripalmitin, and trimyristin. Later the three melting points of tristearin were rediscovered (92) and this was supported by the observation of three melting points for tripalmitin (67). The subject

was again confounded in 1930, when only two melting points were reported (61) for a number of triglycerides thought to be of high purity. Later in 1932, the existence of as many as seven different forms was claimed for the saturated mono-acid triglycerides (118).

As a result of X-ray investigations Malkin and colleagues (30, 78) demonstrated conclusively that the basis of the multiple melting behavior was actually polymorphism, *i.e.*, the occurrence for a given compound of different crystalline forms distinguishable by X-ray diffraction pattern (40). Later workers (7, 46, 68) came to conclusion that there was an error in this association of melting points with X-ray diffraction patterns. Lutton (72), in particular, was particularly prominent in this assertion. Malkin (83) vigorously denied this, suggesting rather that the work of Lutton was incorrect. This unfortunate controversy spread to a wide area of the field and led to considerable confusion in the literature, which was further accentuated by the

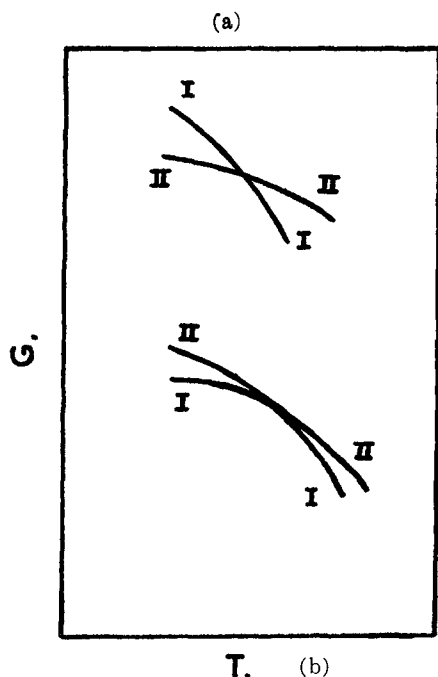


FIG. 1.—The relationship between free energy ( $G$ ) and temperature for transitions of (a) the first and (b) the second kind.

use of these workers of the same symbols with differing association with polymorphic forms. The latest reviews of the field, in 1950 by Lutton (72), and in 1954 by Malkin (83) emphasize the confusion and dichotomy of opinion since both workers stand rigidly on the correctness of their differing views. Although some attempts have been made to arrive at a compromise (95, 109) of the two viewpoints they have not been accepted. Disagreement also occurs concerning the polymorphism of the di- and monoglycerides.

In recent years new techniques have been applied to this field—notably dielectric measurements, the use of differential heating apparatus, X-ray single crystal studies, infrared spectroscopy and nuclear magnetic resonance spectroscopy. The purpose of the present article is to review this controversial field, particularly in the light of this new evidence, and to assess critically the main areas of controversy. The additional information required for further understanding of the polymorphic behavior of glycerides is pointed out.

## II. PHASE EQUILIBRIUM

The phenomenon of polymorphism, *i.e.*, the existence of two or more crystalline modifications for the same substance, was discovered by Mitscherlich (86) in 1821. The polymorphic modifications of a substance differ from one another in all physical properties but yield identical liquids and vapors since they are merely crystal structures.

### A. FIRST-ORDER TRANSITIONS

The thermodynamic description of the transition

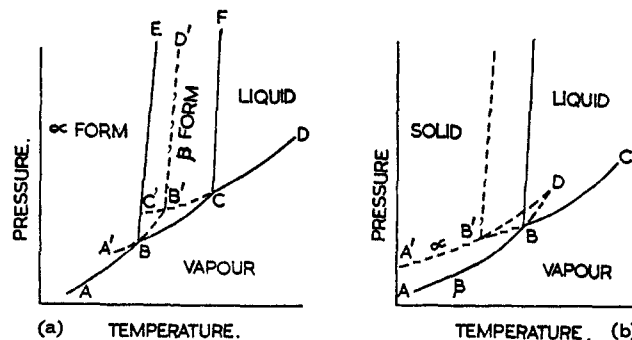


FIG. 2.—(a) The enantiotropic and (b) the monotropic conditions.

from one solid form to another is straightforward. At the transition point the Gibbs free energies of equal masses of the two solid forms are equal and the free energy curves at constant pressure intersect as shown in Fig. 1a. Following Ehrenfast (39)

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

The change from the low temperature to the high temperature form takes place with the absorption of latent heat, and is accompanied by a sudden entropy increase and abrupt volume change. The effect of pressure on the transition temperature is determined by the Clapeyron–Clausius equation

$$\frac{dp}{dT} = \frac{\Delta s}{V_{II} - V_I}$$

Two types of transition of this type can occur, enantiotropic and monotropic.

If a substance has two forms, and each form is stable within some region of temperature and pressure—one being stable under the conditions when the other is unstable, the transformation being reversible—then the polymorphism is termed enantiotropic. If one form is unstable under all conditions, the polymorphism is monotropic and the transformation here is irreversible.

The enantiotropic condition is illustrated in Fig. 2a. The area ABE gives the conditions under which the  $\alpha$ -modification is stable, EBCF is the area for the  $\beta$ -form, FCD that for the liquid state, and below ABCD the substance exists as a vapor. The curves AB, BC, and CD are the vapor pressure curves for the  $\alpha$ -form,  $\beta$ -form, and liquid, respectively; B is the transition point between the  $\alpha$ - and  $\beta$ -forms. At higher pressures the transition temperature is given by points on the line BE. Point C is the melting point of the substance under its own vapor pressure.

A reluctance to change is observed to some extent in the transformation of enantiotropic forms if all traces of the form toward which the change is directed are excluded so that AB and CD may extend to B' and A', respectively.

The monotropic condition is illustrated in Fig. 2b.

AB is the vapor pressure curve for the stable  $\beta$ -form

and A'B' that for the unstable  $\alpha$ -form; B and B' are the respective melting points when the substance is under the pressure of its own vapor; D is a transition point which lies at a higher temperature than either of the melting points and is not realized in practice. Below the melting points the  $\alpha$ -form is always unstable in relation to the  $\beta$ -form.

When a substance possesses more than two polymorphic forms they may all be enantiotropic, all monotropic, or may be combinations of the two. If a substance has three enantiotropic modifications there will be two transition points.

Most transformations which occur with glycerides are of the monotropic type.

#### B. SECOND-ORDER TRANSITIONS

Some transitions in solids do not occur sharply at a definite temperature but over a temperature range, though most of the change may occur within a very narrow part of this range. These are known as second-order transitions. They include transitions where the setting in of free rotation of molecules or polyatomic ions occurs.

Second-order transitions differ from first-order transitions in that there is no evolution of absorption of latent heat and no abrupt change in volume—though there is a marked change in the rate of change of volume with temperature. The specific heat-temperature curve shows an anomaly—it rises to a sharp and often very high peak. The temperature at which the peak occurs is termed the transition point.

In a first-order transition there is a discontinuous increase in the entropy at the transition point as the temperature is raised, while in a second-order transition there is an increase in the rate of increase of entropy with temperature in passing through the transition point.

Thus there is equal free energy of the two forms and of their first differential coefficients, but a discontinuity occurs in their second differential coefficients. At constant pressure and at a certain temperature the curves will touch with the same slope but different curvature (Fig. 1b), then

$$\frac{\partial^2 G}{\partial T^2} = -\frac{C_p}{T} \quad \text{and} \quad \frac{\partial^2 G}{\partial T \partial p} = \frac{\partial V}{\partial T}$$

and the effect of pressure on the transition point is determined by

$$\frac{dp}{dT} = \frac{C_{pII} - C_{pI}}{T \left( \frac{\partial V_{II}}{\partial T} - \frac{\partial V_I}{\partial T} \right)}$$

Second-order transitions may or may not involve a change of crystal structure, but where this does occur it is never very large. It is probable that a second-order transition occurs with triglycerides, *e.g.*, when tristearin or trimargarin in the liquid state is quenched to

a low temperature at about  $-70^\circ$  a reversible phase change occurs on warming to  $-50^\circ$  which probably corresponds to the onset of reorientation of the long chains (25, 57).

Thermodynamic studies of pure glycerides would be valuable for studying the various phase transitions and the molecular motion which occurs with these compounds.

### III. EXPERIMENTAL METHODS FOR EXAMINATION OF POLYMORPHISM

Any determination which is dependent on crystal structure inherently provides a further method for its study and there are now a wide variety of techniques available. The methods commonly applied are briefly described and their limitations for the study of glycerides assessed.

#### A. CAPILLARY MELTING POINT

Many of the early studies of polymorphism of glycerides were carried out by means of capillary melting point determinations and it is quite a good method for determining the melting point of transitory forms. The method was first described by Timmermans (106). The sample is placed in a small thin-walled capillary and then thrust into a bath of known temperature. If the sample melts, similar samples are thrust into the bath at lower temperatures until a temperature is discovered at which the sample barely melts. Suitably applied, this method can be useful in determining the number of polymorphic forms which occur with a particular glyceride.

The method is, however, time consuming, requires patience, and transition points can be missed. The poor thermal conductivity of glycerides sometimes can lead to mixtures of forms being present, *e.g.*, when a capillary is immersed in a cold bath the inner core of the material is protected by a solid outer core and may cool relatively slowly. No information is provided by this method about detailed internal crystal structures.

#### B. COOLING AND HEATING CURVES

Considerable use has been made of cooling and heating curves to study phase transformations. Nicolet (90) was the first to obtain cooling curves for triglycerides and Malkin has used both cooling and heating curves quite extensively in his work. The technique used by Malkin (83) is given:

About 0.75 to 1 g. of specimen is placed in a thin-walled test-tube of about 9.5–12.6 mm. diameter and fixed by a cork in a tube of about three times this diameter to act as an air jacket. This is placed in a Dewar vessel which may contain air, water, ice, or a freezing mixture to give any desired cooling or heating gradient. A copper-constantan thermocouple fixed centrally in the specimen was attached to a Cambridge

thread recording instrument which marks a chart on a revolving drum every half minute. The chart can be read to  $0.25^{\circ}$ .

The type of curve obtained depends on the previous history of the sample and upon the heating or cooling gradient; *e.g.*, if the heating gradient is too small transformations may occur (because of the inherent instability of the form) before the capillary melting point has been reached.

The method has the disadvantage that the breaks in the curves may not be well delineated and can therefore be misleading. The use of differential techniques for improving the delineation of thermal transitions has been described by Haighton and Hannewijk (51). The glyceride is placed in a copper block which is heated at a constant rate. Before and after melting there is a constant difference in temperature between the glyceride and its surroundings. On melting, the temperature of the fat will be below that of the surroundings and when an exothermic transition occurs, above its surroundings. These differences are recorded and give rise to differential heating curves which can be characteristic of a particular glyceride.

The differential method is particularly useful, since automatic records can be obtained rather easily and small transitions revealed and a variety of treatments of the sample can be studied conveniently. The accurate determination of the transition temperature sometimes can be difficult, however. Differential cooling apparatus for the study of glycerides has not yet been described but would be useful.

#### C. MICROSCOPE METHODS

A considerable amount of work has been carried out using simple microscope techniques, but the information is widely scattered. The use of heating and cooling stages combined with polarizing techniques is convenient for studying phase transitions and the dynamics of crystallization, particularly since only thin films of the glycerides are needed. Unfortunately, partly because different crystal habits can exist with glycerides for the same polymorphic form, the technique has limitations. It is a valuable supplementary technique to X-ray and thermal methods.

#### D. DILATOMETRY

Dilatometry or the measurement of volume change with temperature is a convenient method for examining polymorphism and has been applied to many glycerides. The apparatus required is simple and inexpensive and the technique is particularly useful for measuring slow transformations at a selected temperature. Some transitions may, however, be too rapid for this technique. A further difficulty arises from the effects of vacuole formation. This occurs particularly when a liquid fat is solidified in one polymorphic form and

transforms into another without melting. The method does not provide any direct detailed information about the internal crystal structure. It is a supplementary technique to the X-ray and spectroscopic methods.

#### E. DIELECTRIC STUDIES

Dielectric measurements as a function of temperature are useful for studying polymorphism where molecular motion occurs in one or more of the forms. The technique is limited to the study of compounds containing dipoles. The measurements are made with an impedance bridge and have to be made at different frequencies. Impurities in only small amounts can give misleading results. Glycerides as well as other long chain compounds have been examined by this technique at frequencies of 50, 5, and 0.5 kc. and dipole orientational freedom observed in various forms indicating segment or molecular mobility (32, 33, 34).

#### F. X-RAY DIFFRACTION PATTERNS

The use of X-ray diffraction patterns is the most direct and can be the most informative technique for studying polymorphism. (From the diffraction pattern the number of polymorphic forms present for a given molecule can be deduced, and changes and transformations followed.) The complete structure of a particular polymorphic form can also in principle be obtained. The latter, however, depends on the production of adequate single crystals and this can be a considerable limitation. (A single crystal study of trilaurin has been published (115) and work on monoglycerides briefly described (3). Further work is in progress (64) using the heavy atom technique on di- and triglycerides.)

The greatest amount of work to date has been carried out using the powder-photograph technique.

From the diffraction patterns, changes and transformations can be followed. With long chain compounds, because of the large difference between the width of the molecules and the length, the observed spacings on X-ray powder photographs fall conveniently into two groups corresponding to long and short spacings. The long spacings are related to the distance between the planes formed by the methyl or polar groups and the short spacings are related in some way to the cross-sectional arrangement. The long spacing for a particular form is usually a linear function of the number of carbon atoms. The short spacings are practically independent of the chain length.

The variation in the geometry of triglyceride from compound to compound gives rise to major variations in crystal structure in the long-chain direction. Thus a long spacing may include one, two, three, or four segments not necessarily of equal length but in general corresponding with the lengths of constituent fatty acid chains. The number of segments has been referred to as "the chain-length multiplicity."

The powder photograph technique is extremely convenient for studying polymorphism but it has some limitations. These include (a) the difficulty of obtaining diffraction patterns at low temperatures as continuous recording variable temperature cameras are not, as yet, generally available; (b) the necessary exposure times can generally be so long that transformation of unstable forms can occur during the exposure; (c) long spacings may be sometimes difficult to determine; and (d) short spacings of different forms may have some lines in common.

#### G. INFRARED SPECTROSCOPY

The spectrum of a molecule in the fundamental region 2 to 15  $\mu$  shows the presence of a number of bands which can be correlated with the functional groups present in the molecule, while other bands correspond to skeletal vibrations. Because of this, infrared spectroscopy has been used to a considerable extent both to obtain information of the functional groups present in unknown molecules and also to act as a "fingerprint" for the molecule. When the molecules are in the crystalline state the infrared spectrum is influenced by the particular crystal structure involved so that modifications of the spectrum now occur. This means that polymorphic changes are reflected by spectral changes. This technique has been applied to the study of the polymorphism of long-chain compounds (18); *e.g.*, the spectra of long-chain alcohols show significant differences corresponding to the two main polymorphic forms in which these molecules occur.

The technique has the advantages that only thin samples are required for an adequate spectrum, both amorphous and crystalline material can be examined, rapid scanning and graphical recording enable spectra to be obtained while heating and cooling the sample. A form existing for only a few seconds can sometimes be detected. Detailed information about the internal crystal structure sometimes can be obtained. The technique is, however, complementary to the X-ray single crystal technique. It never can provide the detailed information of a single crystal structure determination but can, and frequently does, provide more information than that given by use of the powder technique. It is, for example, particularly useful for studying changes in hydrogen bonding with mono- and diglycerides. The use of polarized infrared radiation can also help to provide some detailed crystal structural information.

#### H. NUCLEAR MAGNETIC RESONANCE

This spectroscopic technique makes use of the absorption of electromagnetic radiation in the region between 1 and 100 Mc./s. It arises from the resonant absorption of energy by atomic nuclei when they are placed in a strong magnetic field and subjected to a

radio frequency field. Such resonance is confined to nuclei which have a magnetic moment and a spin angular momentum. The resonant frequency is proportional to the field strength. For protons in a field of 10,000 gauss the resonant frequency is 42.6 Mc./s.

The basic apparatus is as described. A specimen of volume about 1 cc. is enclosed in a glass vial, a small coil of wire is wound on the specimen, and it is then inserted between the poles of a magnet which provides a strong, stable, and uniform magnetic field.

A radio frequency voltage is applied to the coil at the n.m.r. frequency. The nuclei absorb energy from the electromagnetic field within the coil, and this is detected either by placing the specimen coil in an arm of a radiofrequency bridge (the additional resistive loss in the coil displaces the balance of the bridge) or by making the specimen coil the inductance of a tuned circuit of an oscillator (the resistive loss at resonance reduces the amplitude and is thereby detected). The magnetic field is swept through the resonant condition by passing current at a low frequency through an auxiliary coil mounted on the magnetic pole. The steady magnetic field may be provided by either an electromagnet or a permanent magnet of field strength usually between 5 and 10 kgauss. Accurate work requires a very uniform and stable field. For work with solid specimens a uniformity of a few parts in  $10^5$  over the specimen volumes is sufficient.

The technique is valuable for studying polymorphic forms where rotational freedom or reorientation occurs. It has been used to study the hexagonal or  $\alpha$ -forms of long chain paraffins (4). It is sensitive, the threshold frequency for detection of the motion is usually a few kc./s. It has advantages over the dielectric method; *e.g.*, the method can be applied to polar and non-polar molecules. From the measurement of the spectrum and its temperature dependence the existence and nature of the motion can be deduced while the kinetics of the motion can be determined from the spin-lattice relaxation time. The temperature dependence of the spectra of the polymorphic forms of a number of glycerides have recently been examined (26) but as yet no relaxation-time measurements have been reported.

#### I. ELECTRON DIFFRACTION

The use of electron microscopy allied with electron diffraction is potentially a powerful tool for relating the crystal habit to the internal crystal structure of polymorphic forms. Little work has as yet been published on glycerides using this combination. Electron diffraction is similar to X-ray diffraction, but the interaction by electrons is greater and the wave length of the radiation shorter. This means that electron diffraction patterns can be obtained from individual crystals less than one micron in diameter with only a few seconds exposure and that the diffraction pattern

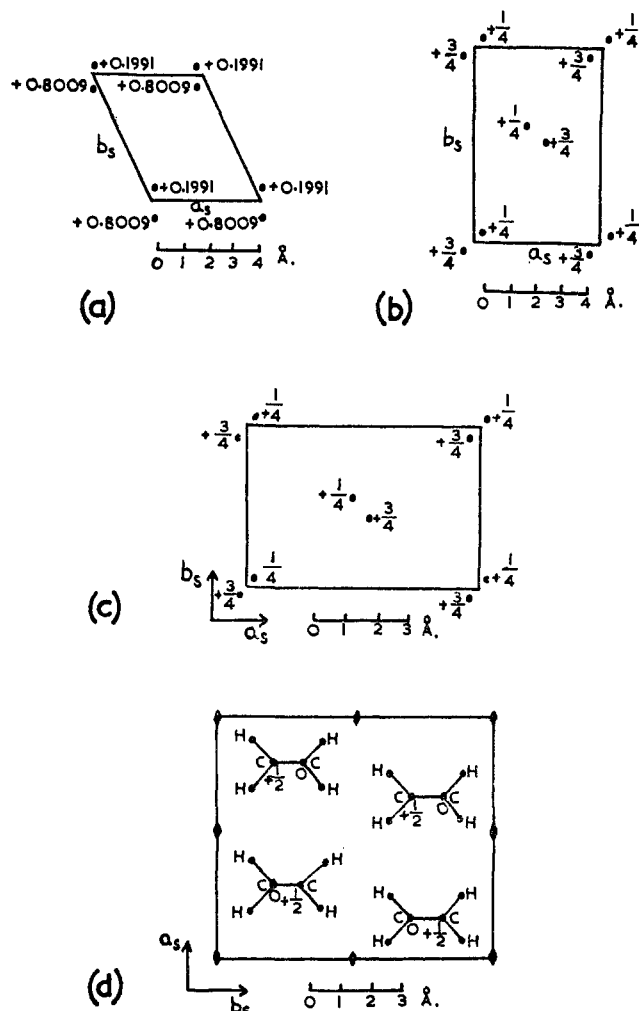


FIG. 3.—Types of sub-cell packing: (a) triclinic  $T||$ , (b) orthorhombic  $O\perp$ , (c) orthorhombic  $O'\perp$ , (d) orthorhombic  $O||$  (after von Sydow).

remains sharp for much smaller crystalline dimensions. Only tiny quantities of material are required. Limitations to the application of glycerides include the heating effect of the electrons and the fact that only basal plane reflections are usually readily observed.

#### J. MECHANICAL RESONANCE DISPERSION

A technique which has not yet been applied to the polymorphism of glycerides but which would seem well worth-while exploring is that of mechanical resonance (48), in which dynamic shear compliance measurements are made by means of electromagnet transducer equipment. A pair of samples is clamped between metal surfaces and sheared by a sinusoidally varying stress in a direction perpendicular to the static clamping stress. The storage compliance  $J'$  and the loss compliance  $J''$  are determined;  $J'$  is a measure of the elastic response or energy stored per cycle while  $J''$  is proportional to the viscous part of the response or energy loss per cycle. The technique has been applied to vinyl and ethyl

stearate and the measurements were shown to depend critically on the particular crystalline modification examined.

#### IV. CRYSTALLIZATION BEHAVIOR OF LONG CHAIN COMPOUNDS

In order to examine the polymorphism of glycerides and to see it in its correct perspective, it is important to review briefly the crystal forms which occur with other long chain compounds, *i.e.*, those compounds containing polymethylene chains of about ten carbons or more particularly with simpler molecules such as paraffins, alcohols, and esters.

In recent years (35) a considerable interest has been exhibited in the general crystallization behavior of these long chain compounds (111, 112) and a number of single crystal structure determinations have now been made (9, 103, 115). With such compounds the molecular end groups whether they be methyl or polar groups associate with each other to form planes. The distances between the planes in the crystal correspond to integral multiples of the molecule or chain length. In many cases tilting of long chain axes with respect to end-group planes occurs. Polymorphism can occur because of this, the different polymorphic forms being associated with different angles of tilt. The polarity and geometry of the molecule determines whether the long spacing corresponds to single or multiple chain lengths. The long chains are often parallel to each other, but crossed chain forms also may occur particularly with polar molecules such as soaps and amines (98, 113), and polymorphism may arise in this way.

Because the van der Waals energy is insensitive to a slight change of the mutual orientation of the chain planes of the neighboring molecules, a large number of structures with minor differences of lattice energy can exist. Various types of chain packing have been reported and when the long chains are parallel to each other a classification is possible (87, 114) using the concept of a sub-cell. Schoon (99) made the original suggestion that monoclinic structures may be derived from the orthorhombic merely by translation of each chain by an integral multiple of the repeat distance along the chain. The periodicity of the chain gives rise to a small unit of repetition in space within the main cell; this is a sub-cell. The sheets of end groups are regarded merely as faces of a sub-cell, sub-crystal. With normal fatty acids only two types of sub-cell occur (103) the common orthorhombic,  $O\perp$  and the triclinic,  $T||$ . The orthorhombic  $O\perp$  sub-cell is shown in Fig. 3b. The four  $CH_2$  groups of the cell are arranged according to the space group  $Pbnm$ . There are two hydrocarbon chains per cell and the chains have every second chain plane perpendicular to the other planes. The orthorhombic packing is found in a variety of long chain compounds, *e.g.*, paraffins (110), polythene (9). The

triclinic  $T||$  sub-cell was first described by Vand and Bell. It contains two  $CH_2$  groups and belongs to the space group PI. It is shown in Fig. 3a. All zig-zag planes are parallel and there is one chain per sub-cell. This chain packing exists in paraffins (89), the A and A' forms of fatty acids (103) and in the most stable form of trilaurin (115). Two other orthorhombic type chain packings have been observed with branched chain fatty acids (2) but apparently are very rare. These are the  $O'\perp$  type and the  $O||$ . In the former the sub-cell has shape identical with the common orthorhombic type, but equivalent chains make the closest approach in the  $b$ -direction of  $O'\perp$ , whereas they are closest in the  $a$ -direction of the  $O\perp$  type (see Fig. 3). The  $O'\perp$  type is found only in 2-D-methyloctadecanoic acid. The orthorhombic  $O||$  type is found only in (-)-2-methyl-2-ethyleicosanoic acid (104) but may also exist in  $\alpha$ -sodium stearate hemihydrate. The sub-cell has the symmetry  $P2_12_12_1$  and contains eight  $CH_2$  groups. The chain planes are all parallel in this packing. The volume per  $CH_2$  group is slightly larger than that of the other orthorhombic types for comparable chain lengths.

It should be emphasized that the common types of packing are the orthorhombic  $O\perp$  and the triclinic  $T||$  and that the symmetry of the sub-cell is not necessarily the same as the main unit cell.

The production of a particular form depends upon the temperature, the number of carbon atoms, and the purity (91); *e.g.*, the lower even-membered paraffins have triclinic packed chains  $T||$ , while  $C_{28}$  and  $H_{58}$  and higher members have orthorhombic packed chains  $O\perp$ ;  $C_{26}H_{54}$  may crystallize in forms with either packing (101). The latter is observed to be particularly important—the very existence of a particular form can depend completely on the presence or on the absence of impurities. Even at a fixed temperature different forms can appear by changing the method of crystallization by using different solvents. Transition points can be depressed and the temperature range over which the hexagonal lattice occurs extended. The hexagonal and orthorhombic lattices are well known to accommodate solid solution formation.

The hexagonal packed form was first observed by Muller (88) with paraffins of chain length greater than 22 carbon atoms and it was inferred that the molecules rotated about their long axes, which are perpendicular to the basal plane. Below the transition point the molecules stop rotating and settle into a new lattice. This is orthorhombic for the odd and triclinic for the even numbered hydrocarbons. Other long chain molecules exhibit this hexagonal form, *e.g.*, alcohols, ethyl esters, the form being recognized by a single short spacing of  $\sim 4.2$  Å. on the X-ray powder photograph (76). This form, generally called alpha and often indicated by the symbol  $\alpha$ -, always occurs in these compounds just below

the melting point. Various theories concerning the molecular rotation which occurs in hydrocarbons and long chain alcohols have been presented (54, 62).

#### V. NOMENCLATURE OF GLYCERIDES

The nomenclature for designating the different polymorphic forms of glycerides in recent times has been extremely confusing, because of the fact that the same symbols have been used with different association with polymorphic form by different workers. The nomenclature of Malkin (83) is based on melting points; the highest melting form is called  $\beta$ , the intermediate melting forms marked with a prime ( $\beta'$ ,  $\beta''$ ) and the form having a single X-ray short spacing of  $\sim 4.1$  Å. is designated  $\alpha$ - or alpha. The lowest melting form for triglycerides is said by this author to be vitreous. Lutton, on the other hand (72), uses X-ray data as a basis for his nomenclature, as is shown in Table I.

TABLE I  
LUTTON NOMENCLATURE FOR GLYCERIDE FORMS

Form	Short spacing pattern characteristics
Alpha	A single strong line corresponding to approximately 4.15 Å.
Beta prime	Usually two (but occasionally more) strong lines corresponding to approximately 4.2 and 3.8 Å.
Beta	A strong (usually strongest) line corresponding to approximately 4.6 Å.

It may be noted that presumably in order to try to prevent confusion the full name is written by Lutton, *e.g.*, alpha rather than  $\alpha$ - and beta prime rather than  $\beta'$ -, but confusion nevertheless has occurred. The subtlety of this has apparently not always been obvious, and when the terms are spoken they are, of course, the same. In addition to these terms and to designate an alpha form having long spacings equivalent to two lengths of fatty acid chains the term alpha-2 is used and similarly beta-3 to indicate triple chain length structures, *etc.*

The existence of these two alternative schemes of nomenclature leads to unusual situations; *e.g.*, the highest melting form of 2-stearodipalmitin is referred to correctly as beta or  $\beta'$  (pronounced beta-prime) depending upon the author or on which side of the Atlantic one is writing. The present author suggested (20) that the use of a suffix M or L would be useful in order to give a more precise designation of a particular form and the short symbol  $\alpha$ - for alpha,  $\beta'$ - for beta prime, and  $\beta$ - for beta could otherwise be retained. Hence the highest melting form of 2-stearodipalmitin can be referred to as either a  $\beta_M$ - form or a  $\beta'_L$ -form without resultant confusion. This method is used wherever possible throughout this review.

Both systems have their limitations. The weakness of the Malkin scheme (apart from the introduction of

a vitreous form now considered non-existent; see later discussion) is that it does not give any indication of marked crystal similarities between one family of glycerides and another. On the other hand, the scheme of Lutton while revealing crystal similarities almost certainly oversimplifies the variations possible in glyceride crystal structures. It is also at present becoming rather cumbersome and terms such as sub-alpha, sub-A-beta, sub-B-beta, and super alpha-1 are used. Furthermore it is not clear how far crystal similarities are being picked out and indicated in the nomenclature. The hydrocarbon chain packing in the sub-alpha form is almost certainly the same (common orthorhombic) as in the  $\beta'_L$  form of the triglycerides, yet the nomenclature does not indicate this. One might ask whether the chain packing in the super-alpha form is similar to the alpha or the sub-alpha modification. The nomenclature gives no clue to this.

The new types of sub-cell or chain packing observed with amides, soaps, and branched chain fatty acids (see earlier discussion) makes one very cautious in attempting to provide a simple nomenclature based on crystal structure to cover the enormous variation possible in all glycerides. The introduction of yet another system of nomenclature at present would however be unwise, and the use of one or other of the two systems with the suffix M or L seems the best at this stage. Indeed if the nomenclature based on X-ray data is regarded as an approximation and used as such it can be useful.

## VI. POLYMORPHISM OF SATURATED TRIGLYCERIDES

### A. MONOACID TRIGLYCERIDES

Although this group of glycerides probably is the most complete homologous series of glycerides that has been studied, it is around these compounds that most disagreement and controversy has raged (53, 72, 83). Disagreement centers on the association of X-ray diffraction patterns with melting point, the existence of a vitreous form, and the precise number of forms possible for these compounds.

With regard to the latter, most workers in the field now generally agree that an early claim (118) for the occurrence of seven polymorphic forms for glycerides such as tristearin is incorrect. With pure monoacid saturated triglycerides only three, or at best four, distinct X-ray patterns have ever been observed.

#### 1. The Main Controversy

The disagreements in this field can be illustrated best by considering the polymorphism of tristearin (see Table II).

Malkin claims on the one hand (83) that this compound has four melting points between 54.5° and the final melting point, while Lutton on the other hand claims (72) that there are only three. Both workers

TABLE II  
X-RAY AND MELTING DATA FOR TRISTEARIN ACCORDING TO  
MALKIN AND LUTTON

Tristearin m.p., °C.	Malkin		Lutton	
	X-Ray short spacing, Å.	Name	X-Ray short spacing, Å.	Name
54.4	Diffuse 4.15	Vitreous	4.15	Alpha ( $\alpha$ )
65.0	4.15	$\alpha$	3.8 and 4.2	Beta prime ( $\beta'$ )
70.0	3.8 and 4.2	$\beta'$	—	—
72.0	4.6	$\beta$	4.6	Beta ( $\beta$ )

find three distinct X-ray powder patterns but unfortunately associate them with different melting forms. Indeed it is only with the highest melting form that there is agreement on association of X-ray powder patterns.

On reference to Table II we can see that Malkin claims that the form melting at 54.5° gives a *diffuse* short spacing at 4.15 Å. and calls it a vitreous form stating it to be not fully crystalline and having some characteristics of a glass. Lutton, on the contrary, says that this form gives a *sharp* single spacing at 4.15 Å. and concludes that the form is crystalline and analogous to the  $\alpha$ -forms of hydrocarbons and other long chain compounds.

One can appreciate that with the fogging on the film from general X-ray scattering the decision as to whether a line is sharp or diffuse can be a matter of individual judgment.

Malkin claims that it is the next highest melting form at 65° which is associated with the powder pattern having a sharp single short spacing at 4.15 Å. and that this is the crystalline  $\alpha$ -form. He points out that only small amounts of this form need be present in a predominantly vitreous form and yet give rise to a sharp X-ray diffraction pattern and thus lead to erroneous conclusions.

One might expect that the correction association of the X-ray pattern with short spacings of 3.8 and 4.2 Å. and melting point would be a comparatively easy matter to decide. However, one of the short spacings is close to that of the lower melting form and transitions can occur before the capillary melting point is reached. The average time for an adequate exposure on the X-ray equipment is moreover quite long and during this time such a transition may occur.

Both workers have repeated their original observations but also unfortunately their original arguments.

Malkin supported the correctness of his experimental work with a number of points: (a) The  $\alpha$ -form is distinguished from the vitreous only by the presence of sharp lines due to long spacings. It is to be remembered that there is no sharp dividing line between the crystalline and the non-crystalline state. With very small units the X-ray diffraction becomes more diffuse. As the layer structure falls below a certain size the



long spacings disappear, a diffused short spacing still persists, owing to lateral diffraction by the hydrocarbon chains, which does not necessarily depend on a layer structure.

(b) When the most stable form of a triglyceride is obtained from solvent it has a higher melting point (say  $72.0^\circ$ ) than the form (regarded by Lutton as the most stable form) obtained by thermal transformation (say  $70^\circ$ ). With a pure compound, the same crystallographic form cannot have two different melting points.

(c) Consideration of the methyl group packing in long chain crystals leads to an association of alternation of the melting points of an homologous series with the tilting of the hydrocarbon chains; *i.e.*, where the melting points alternate the hydrocarbon chains are tilted and where they are non-alternating the chains are vertical (77). As the long spacings associated with the short spacings at 3.8 and 4.2 Å. are consistent with tilted and not vertical chains, this pattern cannot be associated with a series of non-alternating melting points as Lutton would have it.

Arguments put forward against these points were:

(a) The problem is not whether a form actually crystalline is called a glass but what properties are truly associated with the lowest melting point. The form is moreover not a glass in the usual sense anyway: it has (1) a sharp melting point, (2) discontinuity in specific volume on melting, (3) discontinuity in heat content on melting, (4) anisotropy, (5) sharp diffraction lines not in the position of the typical diffuse lines of a liquid fat.

(b) A pure long chain compound can give rise to a spread in melting level according to the degree of stabilization of the form (see later discussion).

(c) The relationship between alternation and tilting of hydrocarbon chains (77) is only a theory (due to Malkin). If the experimental facts show the theory to be not completely valid, so much the worse for the theory.

American workers (7, 46) other than Lutton also considered that Malkin had mistakenly associated X-ray diffraction pattern with melting points. Against this, however, Russian workers (96) have supported Malkin in his claim for the existence of a vitreous form for glycerides, adducing optical evidence to do so. Since the same considerations apply to all the triglycerides including simple saturated, mixed saturated, and unsaturated in character, a massive deadlock occurred in this field which has lasted for some years, and has been further confused by the use of the two alternative systems of nomenclature already discussed.

This deadlock was at last broken by the introduction of a new technique for studying the polymorphism of glycerides, namely, infrared spectroscopy (15). A study of the various spectral changes observed with the polymorphic forms of hydrocarbons, ethyl esters and alcohols (18) showed infrared spectroscopy to be useful for studying polymorphism. Marked changes occurred

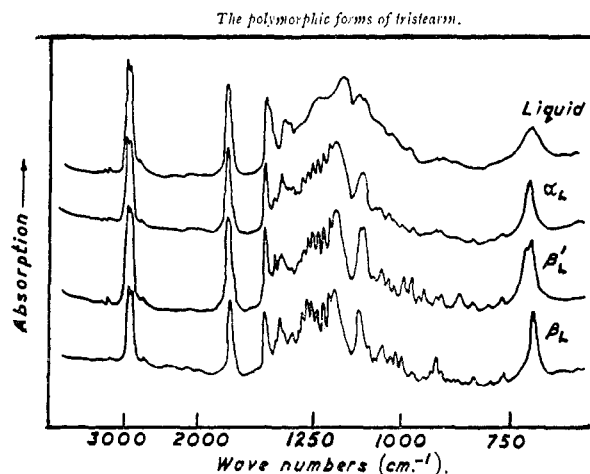


FIG. 4.—The infrared spectra of the polymorphic forms of tristearin (by kind permission of the Chemical Society).

between one polymorphic form and another. Certain significant similarities were also apparent between the spectra of related forms from one class of long chain compound to another. Thus when these molecules were obtained by thermal treatment in the hexagonal  $\alpha$ -form (rotator form) a strong single band was observed in the infrared spectrum at  $720\text{ cm.}^{-1}$  corresponding to the main  $\text{CH}_2$  rocking mode. The spectra of the more stable crystalline forms (non-rotator forms) showed usually a doublet for this mode at 727 and  $719\text{ cm.}^{-1}$  of approximately equal intensity, although occasionally with certain hydrocarbons only a strong single band at  $717\text{ cm.}^{-1}$  was observed.

When the technique was applied to triglycerides, *e.g.*, tristearin, three distinct spectra were obtained, Fig. 4; this may be compared with the three distinct X-ray diffraction patterns obtained for this compound. The form obtained by quenching the melt to room temperature or ice temperature gave a spectrum not typical of that obtained with molecules in a glass or vitreous form such as alcohols and alkyl halides (11). Definite evidence of crystallinity was observed particularly in the  $1250\text{ cm.}^{-1}$  region where a regular series of bands occurs arising from  $\text{CH}_2$  wagging or twisting modes. Furthermore, as with the spectra of the  $\alpha$ -forms of the other long chain compounds, the main  $\text{CH}_2$  rocking mode was a single band at  $720\text{ cm.}^{-1}$ . By rapid scanning of the spectrum and continuous recording this form was observed (spectroscopically) to melt and transform into a form giving a new and distinct spectrum. This spectrum was identical with that of the form obtained by solvent crystallization.

This observation clearly showed that the form melting at  $54.5^\circ$ , *i.e.*, the lowest melting form, was not a vitreous form, had spectral similarities to the  $\alpha$ -forms of other long chain compounds, was crystalline, and was correctly designated as an  $\alpha$ -form by Lutton. Furthermore, the transition of the  $\alpha$ -form to the stable  $\beta$ -

form without the appearance of an intermediate form had been observed spectroscopically just as the same transition had been observed by Lutton using X-ray diffraction patterns.

On cooling the melt to a temperature a degree or two above  $54.5^\circ$  and rapidly scanning the spectrum, the intermediate form was observed to crystallize out, giving the third distinct spectrum. As with the spectra of the non-rotator or more crystalline forms in this spectrum, the main  $\text{CH}_2$  rocking mode is a doublet at 726 and 719  $\text{cm}^{-1}$ . By comparison with the spectrum of the  $\alpha$ -form, the relative intensity of the bands in the 1250  $\text{cm}^{-1}$  region changes and new bands appear. Again spectroscopically this form was observed to melt at  $65^\circ$  and transform into a form having a spectrum identical with that of the solvent crystallized material, *i.e.*, the  $\beta$ -form.

As the doublet at 726 and 719  $\text{cm}^{-1}$  is related to the packing of the hydrocarbon chains in a particular way, *i.e.*, in the orthorhombic  $\perp$  manner (see later discussion) this showed that the form melting at  $65^\circ$  could not possibly be a hexagonally packed or  $\alpha$ -form and was therefore correctly designated a  $\beta'$ -form in agreement with Lutton.

The spectrum of the stable  $\beta$ -form was different from the spectra of the other forms. The relative intensities of the bands in the 1250  $\text{cm}^{-1}$  region are different; there is a strong band at 890  $\text{cm}^{-1}$  absent in the other spectra and now the main  $\text{CH}_2$  rocking mode is single at 717  $\text{cm}^{-1}$ .

When the homologous members of the series were examined, it was seen that similar spectra were observed for the same polymorphic form of these members. Thus the lowest melting form of trimyristin, tripalmitin, and tribehenin were all very similar, only the number of bands in the 1250  $\text{cm}^{-1}$  region changing with the change in chain length. The number of bands for an even number of carbon atoms is equal to half the number of carbon atoms in the chain as with anhydrous sodium soaps (22). In each case only a single band is observed at 720  $\text{cm}^{-1}$ . Similarly, the  $\beta'$ -forms showed a family similarity with a doublet in the 720  $\text{cm}^{-1}$  region and also the  $\beta$ -forms which all showed the unusual intensity pattern in the 1250  $\text{cm}^{-1}$  region, the band at 890  $\text{cm}^{-1}$ , and a single band at 717  $\text{cm}^{-1}$ .

Further confirmation of the correctness of this conclusion was observed when intercomparison was made with the spectra of the polymorphic forms of other triglycerides, particularly with the triglyceride 2-stearodipalmitin (20). Here the spectrum of the most stable form obtained by solvent crystallization has markedly similar spectral characteristics to that of the intermediate form of tristearin (m.p.  $65^\circ$ ). If Malkin were correct this would mean that very similar spectra were obtained from the  $\alpha$ -form of tristearin and the  $\beta$ -

form of 2-stearodipalmitin. Significantly the strong X-ray short spacings of this form are at 3.8 and 4.2 Å. and using the Lutton nomenclature it would be designated a  $\beta'$ -form as is the intermediate form of tristearin. Similar confirmatory spectroscopic evidence is obtained with other glycerides (*cf.* the 1,2-diglycerides).

As well as the spectroscopic method providing a new criterion for the polymorphic forms of the glycerides, a detailed study of the relationship between the appearance of the band in the 720  $\text{cm}^{-1}$  region and the hydrocarbon chain packing in the long chain compounds was used to provide a better understanding of the basis of the polymorphism of glycerides. A band assigned to the main  $\text{CH}_2$  rocking mode usually occurs in the 720  $\text{cm}^{-1}$  region in compounds containing a paraffinic chain  $-(\text{CH}_2)_n\text{CH}_3$  where  $n > 3$ , but the band is associated with an essentially planar *trans* configuration.

By considering the sub-cell of the long chain crystals it was possible to correlate the appearance of the band to the packing in the sub-cell and to understand the reason for the various appearances (21). The single band at 720  $\text{cm}^{-1}$  is correlated with hexagonal packed chains. The reason for only one band being observed at this position in this form was related to the fact that only one chain per primitive sub-cell occurs and that the interchain distance in this form is very large. (For hexatriacontane the distance is 4.86 Å. in the liquid (114) and 4.85 Å. in the hexagonal form.) The doublet of near equal intensity 727 and 719  $\text{cm}^{-1}$  was correlated with common orthorhombic  $\text{O}\perp$  packed chains. The doublet is attributed to interaction between neighboring chains (102) there being two chains per sub-cell. The single band at 717  $\text{cm}^{-1}$  was correlated with triclinic  $\text{T}\parallel$  packed chains, the single band being related to only one chain per sub-cell and its shift in position (from the unperturbed position at 720  $\text{cm}^{-1}$ ) related to the change in the internal potential energy function of the molecule due to the equilibrium field of the crystal, this in turn being due to the van der Waals forces operative in the sub-cell.

This correlation extends over long-chain esters, fatty acids, hydrocarbons, and alcohols. By relating these considerations to the simple saturated triglycerides the polymorphic forms were classified into three crystallographic types according to their hydrocarbon chain packing or the symmetry of their sub-cells. Thus the  $\alpha_L$ -form has hexagonal sub-cell, the  $\beta'_L$ -form orthorhombic  $\text{O}\perp$  sub-cell and the  $\beta_L$ -form triclinic  $\text{T}\parallel$  sub-cell symmetry. This throws light on to the triglycerides by means of their X-ray short spacings proposed by Lutton. The short spacing classification is possible because of the underlying symmetry of the sub-cell.

Further support for these considerations has been provided by a recent discussion (75) of the relationship between X-ray short spacings and hydrocarbon chain

TABLE III  
COLLECTED DATA ON THE THREE MAIN CRYSTALLOGRAPHIC FORMS FOR MONOACID TRIGLYCERIDES

	$\alpha_L$ -form	$\beta'_L$ -form	$\beta_L$ -form
Melting	Sharp melting point non-alternating	Sharp melting point non-alternating	Sharp melting point alternating
X-Ray diffraction	Sharp diffraction line at 4.1 Å.	Strong short spacings at 3.8 and 4.2 Å.	Strong short spacing near 4.6 Å.
Chain packing	Hexagonal	Orthorhombic; probably monoclinic crystal	Triclinic; also triclinic crystal
Dilatometric data (6) (tristearin) g./ml. (-38°)	Least dense (1.014)	Intermediate density (1.017)	Greatest (1.043)
Heat of fusion (28)	38.9 cal. per g.	Undetermined	54.5 cal. per g.
Dielectric behavior. (33) (tristearin)	Different from that with glass (2.684) at 52°	—	(2.340) at 65.1°
Infrared spectrum	Characteristic spectrum evidence of considerable crystallinity; single band at 720 cm. <sup>-1</sup>	Characteristic spectrum. Doublet at 727 and 719 cm. <sup>-1</sup>	Characteristic spectrum; single band at 717 cm. <sup>-1</sup>
N.m.r. spectrum	Considerable proton mobility; second moment of the line width is similar to that obtained with hydrocarbons in their rotator form. <i>i.e.</i> , 11.1 for tristearin	Slight degree of proton mobility as in the $\beta_L$ -form	A slight degree of proton mobility; second moment for tristearin 22.2 (293°K.)

packing in long chain crystals. It should be emphasized that the classification into three types is related not to the crystal symmetry but to the sub-cell symmetry or hydrocarbon chain packing of the glyceride.

Quite clearly all the evidence shows that rejection of Malkin's interpretation of his X-ray data produces (a) consistency of pattern of infrared spectra of the triglycerides with those of other long chain compounds, (b) an internal consistency of the pattern of infrared spectra of one type of triglyceride to another, and (c) consistency of X-ray and infrared data. Conversely, acceptance of Malkin's interpretation produces inconsistency of spectral characteristics within the glycerides themselves and also with other long-chain compounds.

Other evidence confirms this work. The molecular motion in paraffins was studied by n.m.r. spectroscopy and a reduction in the second moment observed when the molecules were in the hexagonal packed ( $\alpha$ -) form (4). This corresponds to hindered reorientational motion about the chain axis. The reduced intramolecular contribution to the second moment is  $6.8 - 11.6/(n + 1)$  for the hydrocarbon  $C_nH_{2n+2}$ . If this formula is applied to a glyceride where  $n = 18$  the intramolecular contribution to the second moment is 6.2 gauss<sup>2</sup>. The intermolecular contribution is some 2.6 gauss<sup>2</sup>, and an expected total second moment of  $\sim 8.8$  gauss<sup>2</sup> is predicted. With tristearin and tripalmitin the second moments at room temperature show that in the most stable  $\beta_L$ -form the chains are not reorienting themselves at frequencies greater than 100 kc./s. Reorientation of a few small segments of the chain or a torsional oscillation of the whole chain about its axis is occurring since this value is slightly lower than the rigid value at low temperatures (22.2 gauss<sup>2</sup> at 293 and 2.47 gauss<sup>2</sup> at 90°K. for tristearin). The second moments of the

lowest melting forms are 11.1 (tristearin) and 9.8 gauss<sup>2</sup> (tripalmitin), close to the value of  $\sim 9$  gauss<sup>2</sup> estimated for a crystal in which the hydrocarbon chains are freely reorienting about the chain axis, confirming that the crystal structure of the lowest melting form is hexagonal. The fact that the second moments are a little higher than the corresponding paraffins is considered to be due probably to a slight hindrance of the free motion of the hydrocarbon chains due to the glycerol residue (26).

Dielectric studies of tristearin and tripalmitin (33) also show that orientational freedom occurs in the lowest melting  $\alpha$ -form of these compounds. The dielectric constant is lower than that of the liquid but high enough to show orientational freedom.

Microscope investigations of these glycerides are unfortunately not too definitive in that a variety of crystal habits may occur for the same basic crystal form. An examination (93) of the lowest melting form, however, shows that it exhibits strong birefringence inconsistent with this form being glassy or vitreous.

A further recent interesting fact is that a study of the kinetics of crystal nucleation in some normal alkane liquids, *e.g.*,  $C_{16}H_{34}$ ,  $C_{17}H_{36}$ ,  $C_{18}H_{38}$ ,  $C_{24}H_{50}$ , and  $C_{32}H_{66}$ , shows that such molecules have very weak glass-forming tendency, which is attributed to the hypothesis of nucleation of small segments of molecules (107).

Information relating to the properties of the three main forms of the even monoacid triglycerides is collected in Table III.

The unfortunate consequence of Malkin's error is that it is perpetuated in all of his work on triglycerides. This means that a large part of the work requires re-examination. In some cases the correct association of X-ray and melting data may be comparatively easy to make; in other cases it will be more difficult. The

TABLE IV  
 X-RAY AND MELTING DATA FOR THE MONOACID TRIGLYCERIDES

	-Melting points, °C.-			Long			Short								
	$\alpha_L$	$\beta'_L$	$\beta_L$	$\alpha_L$	$\beta'_L$	$\beta_L$	$\alpha_L$	$\beta'_L$	$\beta_L$						
Tristearin	54	64	73.1	50.6	47.2	45.0	4.2	3.8s	4.22s	3.7m	3.9m	4.6s	5.3m		
Tripalmitin	44.7	56.6	66.4	45.6	42.6	40.6	4.2	3.8s	4.22s	3.7m	3.9m	4.6s	5.3m		
Trimyristin	33	46.5	57.0	41.2	37.6	35.8	4.2	3.8s	4.22s	3.7m	3.9m	4.6s	5.3m		
Trilaurin	15	35.0	46.4	35.6	32.9	31.2	4.2	3.78s	4.18vs	3.7m	3.9m	4.6s	5.3m		
Tridecylin	-15	18.0	31.5	—	—	26.8	4.2	—	—	3.7m	3.9m	4.6s	5.3m		
Trimargarin	50	61.0 (62.5)	64.0	48.5	43.7	43.5	4.2	3.79s	4.02w	4.19s	4.37w	3.65m	4.0m	4.6s	5.3m
Tripentadecylin	40.0	51.5 (53.0)	54.0	42.9	39.1	38.9	4.2	3.81s	4.12s	4.3s	—	3.65m	4.0m	4.6s	5.3m
Tritridecylin	25.0	41.0 (42.5)	44.0	37.7	34.2	34.1	4.2	3.85m	4.04w	4.26s	4.43w	3.65m	4.0m	4.6s	5.3m
Triundecylin	1.0	26.5 (29.0)	30.5	33.0	29.5	29.6	4.2	3.88s	4.25s	4.52w	—	3.65m	4.0m	4.6s	5.3m

correct associations of X-ray data and melting points for the even-members are shown in Table IV. The corrected associations for the odd-members also are given with the suspect additional melting points given in parentheses. Further work is required with the odd-members.

### 2. Additional Forms

While there is little doubt about the incorrect association by Malkin of X-ray data and melting point with the simple saturated triglycerides, the question still remains as to how many polymorphic forms are possible with these compounds. It is an experimental fact observed by many authors that the stable form obtained from solvent has a higher melting point than the same form obtained by thermal transformation, yet the X-ray powder photographs are often the same.

An attempt to provide a rationalization of microscope data, melting point, and X-ray data for tristearin is shown in Table V.

TABLE V

THE RELATIONSHIP OF THE SEVEN FORMS OF TRISTEARIN USING MICROSCOPY WITH X-RAY DATA (93)

Weygand and Gruntzig symbol	Probable X-ray pattern	Microscope appearance <sup>a</sup>	M.p. for tristearin, °C.
I C	$\beta_L$	Beta rhombs	71.0
I B	$\beta_L$	Beta spherulites	70.5
I C	$\beta_L$	Often alpha mosaic may be hazy	69.5
II A	$\beta'_L$	Bright beta prime	65.5
II B	$\beta'_L$	Dull to bright beta prime	65.0
II C	$\beta'_L$	Dull beta prime	65.0
III C	$\alpha_L$	Alpha mosaic	55.0

<sup>a</sup> Note—beta crystals have oblique extinction; beta prime crystals have parallel extinction and spherulites positive and/or negative; alpha crystals have spherulite elongation always negative.

Attempts have been made to explain the variation in melting point by considering variations in crystalline size and crystalline perfection. It is certainly true that small particles of the same substance may have different properties from larger particles of the same substance, such as lower melting point, higher solubility. Very thin layers of tristearin can give a lower melting point than thicker layers. The large differences

of 2 or 3° seem rather high to be explained on this basis. The effect of variation of chain alignment or of the methylene groups within the chain may provide the basis for a better explanation. Comparison has been made with similar behavior in polymers (72), but there is as yet no accepted explanation for this behavior.

There is however experimental evidence for a further form of the simple triglycerides. The presence of this form was first observed in some behenyl mixed triglycerides (57) and subsequently in tristearin. It transforms reversibly from the  $\alpha_L$ -form at low temperature ( $-50^\circ$ ) without melting. Its short spacings were similar to those of the  $\beta'_L$ -form ( $\sim 3.7$  and  $4.2 \text{ \AA}$ .) and it was designated a sub-alpha (sub- $\alpha_L$ -form). With tristearin a diffuse darkening in the  $3.8 \text{ \AA}$ . region was observed at  $-50^\circ$ . Malkin threw doubt on the correctness of this interpretation, pointing out that at such low temperatures ice condenses on the specimen giving rise to a spacing in this region (83).

A phase change was confirmed, however, by means of infrared spectroscopy. If the glyceride is obtained in the  $\alpha_L$ -form in an evacuated low temperature cell and the temperature lowered, the specimen remains generally the same although bands narrow and sharpen. As the temperature approaches  $-50^\circ$  to  $-70^\circ$  the main  $\text{CH}_2$  rocking mode in the  $720 \text{ cm.}^{-1}$  region gradually changes from a single band to a doublet. The doublet is similar to that observed with the spectrum of the intermediate  $\beta'_L$ -form and the chains in this sub- $\alpha_L$ -form are probably orthorhombically packed. This spectral change was observed with other triglycerides such as trimargarin and 1-oleodistearin (25). It is analogous to the changes observed with 1-monoglycerides (15, 16). Examination of differential heating curves of the triglycerides reveals no heat changes in the  $-70$  to  $-50^\circ$  region. Examination of curves showing the variation of dielectric constant with temperature for the  $\alpha_L$ -form shows a region of anomalous dispersion consistent with a phase change taking place. The dispersion behavior is similar to that observed with the sub- $\alpha$ -form of monoglycerides. When n.m.r. measurements are made on the  $\alpha_L$ -form of tristearin the second moment is observed to be  $11.1 \pm 0.3$  at  $293^\circ\text{K}$ . and  $24 \pm 0.2$  at  $90^\circ\text{K}$ . showing a considerable reduction in

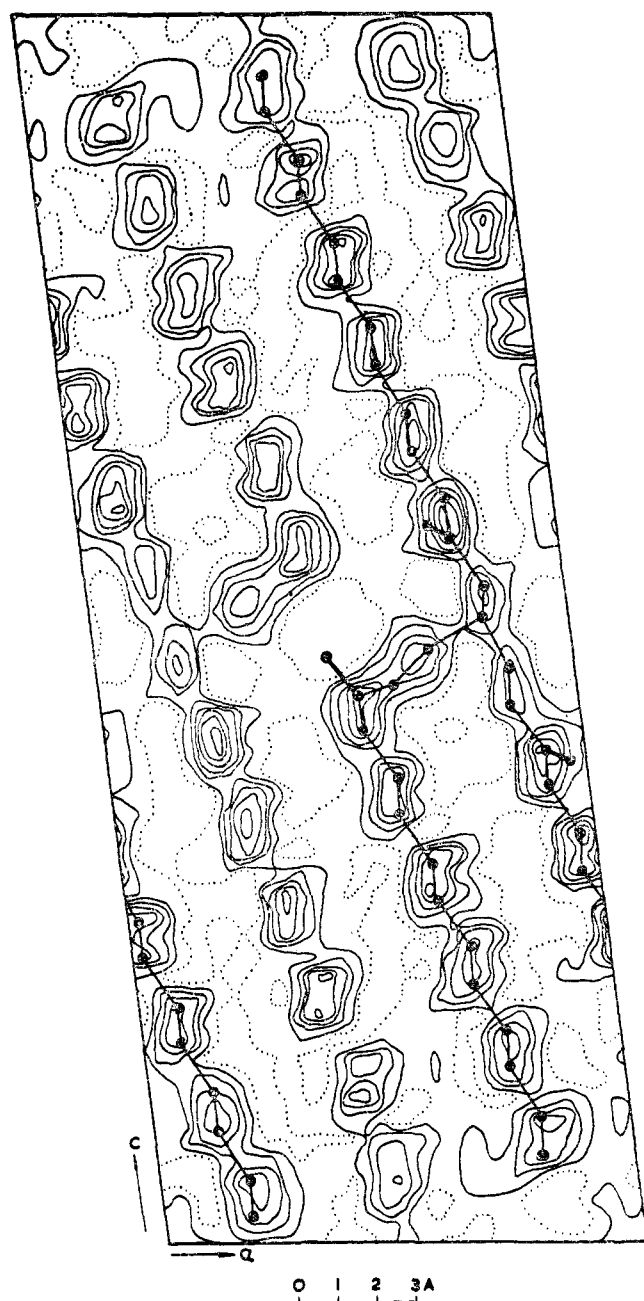


FIG. 5.—The arrangement of trilaurin in the crystal lattice [after Vand (116)].

proton mobility. (The second moment for the stable  $\beta_L$ -form at this temperature is  $24.7 \pm 0.6$ .) The infrared and n.m.r. data indicate that as the temperature is lowered the chains rotate less rapidly and pack together more tightly.

### 3. X-Ray Structure of the $\beta_L$ -Form

Single crystal data are available only for the  $\beta_L$ -form of trilaurin (115). This shows that the unit cell is triclinic and that it contains two molecules per unit cell. The sub-cell is also triclinic and contains two  $\text{CH}_2$  groups per unit cell. The angle of tilt between the

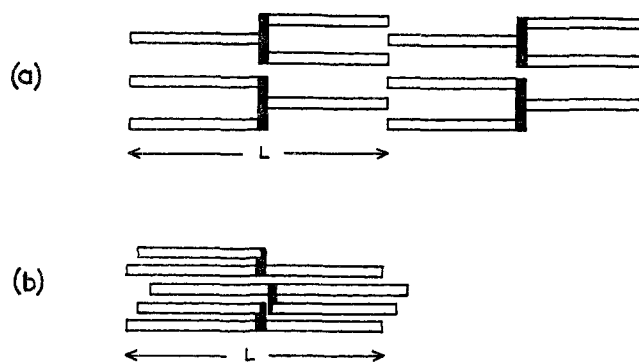


FIG. 6.—(a) Tuning fork arrangement; (b) correct arrangement.

chains and the  $ab$ -plane of the main unit cell is  $62^\circ 7'$ , in good agreement with the angle predicted from the long spacing of the even series of triglycerides ( $61^\circ 35'$ ).

The general manner of arrangement of the glycerides in the lattice (116) is shown in Fig. 5. This shows that the glyceride packs in a type of tuning fork configuration but rather different from that conventionally accepted. The central and one of the two extreme alkyl groups are along the same axis. Two glyceride molecules pack in such a way that the third remaining alkyl groups also lie along an axis parallel to the first. It can be seen from this arrangement that the structure resembles very much that of a long chain hydrocarbon, the perturbation from the presence of the glyceryl residue being made rather small in its effect. It can be appreciated from this structure why the crystallization behavior is similar to that of long chain paraffins.

The structure enables better insight to be made into the interpretation of the long spacings than has been previously made with simple saturated triglycerides. The long spacings of these glycerides commonly have been associated with a double structure with reversed tuning forks (handle beside prongs) as shown in Fig. 6a. This is not correct, however, and the same long spacing is obtained with the structure shown in Fig. 6b. Similar reexamination can be made of the interpretation of the long spacings of mixed saturated triglycerides, but it is rather dangerous to try to predict too much detail from long spacing data alone. Further single crystal studies are essential. A full X-ray single crystal study of the  $\beta'_L$ -polymorphic form of the simple saturated triglycerides would be particularly valuable.

### 4. The Polymorphic Transitions of the Saturated Monoacid Triglycerides

The present picture of the polymorphic transitions which occur with saturated monoacid triglycerides is: A triglyceride, *e.g.*, tristearin, on being cooled from the melt to below room temperature crystallizes in a form in which the long hydrocarbon chains are hexagonally packed with chains normal to the basal plane and

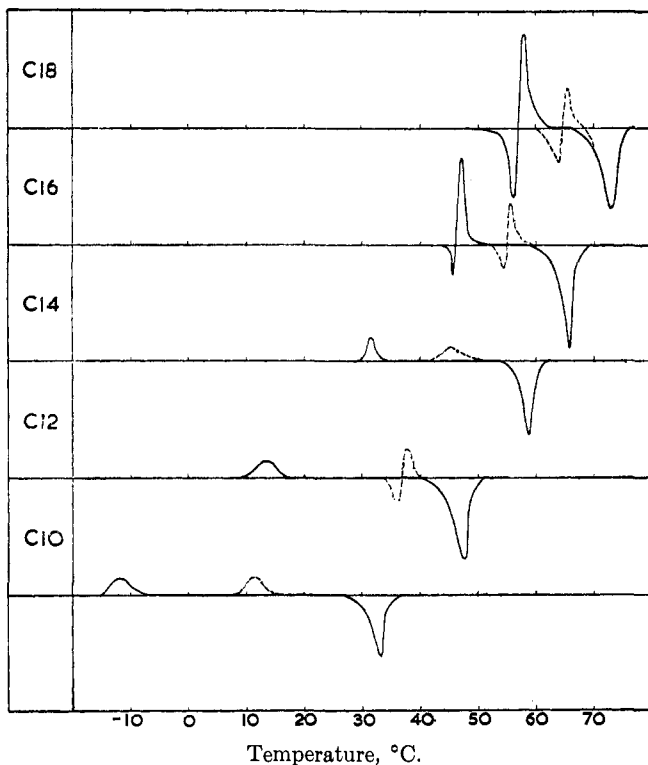


FIG. 7.—Differential heating curves for tristearin and homologs (27) (exothermic up, endothermic down): dotted curve shows  $\beta'_L \rightarrow \beta_L$  changes; full curve shows  $\alpha_L \rightarrow \beta_L$  changes.

in which the chains can rotate in a manner analogous to that observed in the rotator form of hydrocarbons. Essentially in the undercooled liquid the hydrocarbon chains have arranged themselves parallel over small distances and this has extended over more than say a hundred molecules to form an  $\alpha_L$ -nucleus. The terminal groups move into a single plane as far as possible. The molecules in this form do not fit into each other very tightly and the entropy decrease in the formation of an  $\alpha_L$ -nucleus is considerably less than in the formation of the more densely packed  $\beta_L$ -nucleus. The formation of an  $\alpha_L$ -nucleus is hence much more easily undergone than that of the more stable modifications. This form gives rise to X-ray short spacings near 4.2 Å, and a characteristic infrared spectrum with a single band at 720  $\text{cm}^{-1}$ .

If the  $\alpha_L$ -form is further cooled, the long chains rotate more slowly and pack more tightly. X-Ray short spacings at 3.8 and 4.2 Å are now observed and a doublet is formed in the infrared absorption spectrum near 727 and 719  $\text{cm}^{-1}$ . The transition is a gradual one and is reversible. The packing of the chains probably is common orthorhombic,  $O \perp$  with the chains normal to the basal plane.

On heating the  $\alpha_L$ -form to its melting point (with very pure saturated triglyceride) a rapid transformation occurs with evolution of heat to the most stable form, the  $\beta_L$ -form. There is now a strong X-ray short spacing

at 4.6 Å, and a single band in the infrared spectrum at 717  $\text{cm}^{-1}$ . The hydrocarbon chains are now triclinically packed  $T \parallel$  and tilted to the basal plane. (With some mixed saturated triglycerides transitions can occur directly from the  $\alpha_L \rightarrow \beta'_L \rightarrow \beta_L$  form.)

If alternatively the liquid melt is cooled to a temperature a few degrees above the melting point of the  $\alpha_L$ -form and held at this temperature until crystallization occurs, the intermediate  $\beta'_L$ -form is produced. This form has X-ray short spacings at 3.8 and 4.2 Å, and a distinctive infrared spectrum with bands near 727 and 719  $\text{cm}^{-1}$  in the 720  $\text{cm}^{-1}$  region. The hydrocarbon chains probably are packed in the common orthorhombic  $O \perp$  manner and tilted with respect to the basal planes. (The crystal structure probably is monoclinic.) On heating to the melting point of this form some melting occurs and evolution of heat and a transition into the stable  $\beta_L$ -form. These transitions are demonstrated (27) for tristearin and its homologs in Fig. 7.

The melting points are lower and transformation rates are faster as the chain length is decreased. A variety of pathways are available for the formation of stable  $\beta_L$ -crystals depending upon the particular glyceride and the conditions. The stable  $\beta_L$ -form also is obtained readily from solvent.

With the odd numbers of the series, *e.g.*, trimargarin, the transitions are similar but the  $\beta'_L$ -form appears to be rather more stable and can be obtained relatively easily by heating the  $\alpha_L$ -form. The stable  $\beta_L$ -form is obtained from solvent and only slowly by heating. A sub- $\alpha_L$ -form has been detected with these compounds by infrared spectroscopy and analogous spectra for  $\alpha_L$ -,  $\beta'_L$ -, and  $\beta_L$ -forms to those observed with the even numbers obtained. These glycerides, however, require a full reexamination before anything more definite can be said about their behavior.

#### B. DIACID TRIGLYCERIDES

The diacid triglycerides, while having behavior similar to the simple saturated triglycerides, vary quite considerably depending upon the chain length of the acids concerned and upon their symmetrical or unsymmetrical nature. A considerable amount of work has been done on the polymorphism of the mixed saturated glycerides by Malkin and his associates (12, 13, 79, 80, 81). Different groups of glycerides shown have been examined, *e.g.*

- (a)  $C_{12}C_{10}C_{12}$  .....  $C_{18}C_{16}C_{18}$   
 (b)  $C_{10}C_{12}C_{10}$  .....  $C_{16}C_{18}C_{16}$   
 (c)  $C_{10}C_{12}C_{12}$  .....  $C_{18}C_{15}C_{18}$   
 (d)  $C_{12}C_{10}C_{10}$  .....  $C_{18}C_{16}C_{18}$

Diacid triglycerides where the acids differ by more than two carbon atoms, *e.g.*,  $C_{10}C_{14}C_{10}$ ,  $C_{16}C_{12}C_{16}$ , also have been studied (13, 81). It is unfortunate that the vitreous form is assumed to occur in all of them, so

that an incorrect association of melting point and X-ray data has taken place. While in some cases the correction of this error may be straightforward, such may not be so in other cases. This problem is seen where a re-examination of some of these glycerides already has been made, and is illustrated in Table VI with the mixed triglycerides of palmitic and stearic acids. Different associations of X-ray pattern and melting form are made, different melting points are observed, and there are differences in long spacing data.

TABLE VI

A COMPARISON OF DATA RELATING TO THE MIXED TRIGLYCERIDES OF PALMITIC AND STEARIC ACID

	-M.p., °C. (Malkin)-			-M.p., °C. (Lutton)-			
	Vitr.	$\alpha_M$	$\beta'_M$	$\beta_M$	$\alpha_L$	$\beta'_L$	$\beta_L$
1-Stearo-dipalmitin (SPP)	46.5	55	59.5	62.5	47.4	57.7-61.7	62.7
1-Palmito-distearin (PSS)	50	57	61	65	50.6	61.1-65.0	62.5°
2-Stearo-dipalmitin (PSP)	49	59	65	68	46.5	68.6	—
2-Palmito-distearin (SPS)	50	56	64	68	51.8	—	68.5
		Long spacings (Malkin)			Long spacings (Lutton)		
		$\alpha_M$	$\beta'_M$	$\beta_M$	$\alpha_L$	$\beta'_L$	$\beta_L$
1-Stearo-dipalmitin (SPP)		47.8	43.9	42.5	47.6	43.8	42.1
1-Palmito-distearin (PSS)		48.8	44.7	46.5	48.5	45.1	44.7
2-Stearo-dipalmitin (PSP)		50.2	44.7	43.2	46.65	42.75	—
2-Palmito-distearin (SPS)		50.5	47.5	44.2	49.2	—	43.1

It can be seen that 2-stearodipalmitin can exist in four polymorphic forms according to one group (80) but only two according to the other group (70), as is also the case with 2-palmitodistearin. An infrared spectroscopic investigation (20) confirmed the conclusions of the latter workers. (The existence of a third form for 2-palmitodistearin may, however, be related directly to the presence or absence of small impurities.)

The strong X-ray short spacings for the most stable form of the glycerides in group (b) are the same as those of the intermediate  $\beta'_L$ -form of tristearin, which probably indicates that for these glycerides the most stable forms crystallize with common orthorhombic  $O \perp$  rather than triclinic  $T \parallel$  packed chains. By analogy with tristearin, the form is designated a  $\beta'_L$ -form. The infrared spectrum of a member of this series, 2-stearodipalmitin, in its most stable form shows spectral resemblance to the spectra of the  $\beta'_L$ -form of tristearin and tripalmitin. A doublet occurs for the main  $CH_2$  rocking mode in the  $720 \text{ cm.}^{-1}$  region.

The considerable individuality shown by quite closely related isomers of the  $C_{16}$  and  $C_{18}$  saturated acids is shown in Table VII.

Dielectric measurements on some of these glycerides have been made (34). The dielectric properties and

TABLE VII

POLYMORPHIC BEHAVIOR OF CLOSELY RELATED ISOMERS OF PALMITIC AND STEARIC ACIDS (70)

Glyceride	Forms
1-Stearodipalmitin (SPP)	$\alpha_L$ , $\beta'_L$ , and $\beta_L$ ( $\beta_L$ -stable)
1-Palmitodistearin (PSS)	$\alpha_L$ , $\beta'_L$ from melt; $\beta_L$ from solvent ( $\beta'_L$ and $\beta_L$ equally stable)
2-Stearodipalmitin (PSP)	$\alpha_L$ , $\beta'_L$
2-Palmitodistearin (SPS)	$\alpha_L$ , $\beta_L$ , ( $\beta'_L$ -possibly)

dispersion characteristics of the  $\alpha_L$ -form were observed to be similar to that of the  $\alpha_L$ -forms of tristearin and tripalmitin showing molecular freedom occurred. The sharpness of the  $\alpha_L$ -solidification point of this glyceride aroused the comment that this could not possibly correspond to a glassy form.

The infrared spectra of these compounds are very similar to those of tristearin and tripalmitin, differing from them in the  $1250 \text{ cm.}^{-1}$  region. The polymorphic modifications show a single band at  $720 \text{ cm.}^{-1}$  for the  $\alpha$ -forms, a doublet at  $727$  and  $719 \text{ cm.}^{-1}$  for the  $\beta'_L$ -forms, and bands at  $890$  and  $717 \text{ cm.}^{-1}$  for the stable  $\beta_L$ -forms.

Other triglycerides also have been reexamined (56)—2-myristodistearin, 2-myristodipalmitin, 1-stearodimyristin and 1-palmitodimyristin—and corrections made. While three forms are observed rather than four (including a vitreous form) for three of these glycerides, 2-myristodistearin was found to occur in four forms. The four forms, however, do not include a vitreous form. The additional form is designated a  $\beta'_L$ -4 form on the basis of its similarity in short spacings to the  $\beta'_L$ -forms but it has a long spacing consistent with a chain length multiplicity of four. Infrared spectroscopy and differential heating curves have confirmed the general conclusions of this work (23).

Four forms also are observed with 1-stearodilaurin:  $\alpha_L$ -2,  $\beta'_L$ -2,  $\beta'_L$ -3, and  $\beta_L$ -3 (69). When the chain length difference is two or less usually three forms are observed, but with greater chain length difference the polymorphism becomes more complex. Close similarity between mixed triglycerides occurs when the chain length differences within the similar glycerides are equal as with 2-myristodipalmitin and 2-palmitodistearin. The behenyl mixed triglycerides, 2-behenyldipalmitin, 2-behenyldistearin, 1-palmitodibehenin, and 1-stearodibehenin, also have been examined (57). While their behavior is somewhat similar to that of the mono-acid saturated triglycerides, the behenyl glycerides all show a great stability for the  $\beta'_L$ -form, and with some of them the stable  $\beta_L$ -forms could not be obtained from the melt. The glyceride 1-palmitodibehenin crystallizes from solvent in a  $\beta'_L$ -form, this being its most stable form. A sub- $\alpha$  form is also clearly observed with these compounds (see Table VIII).

The polymorphism of glycerides containing both long:

TABLE VIII  
 X-RAY AND THERMAL DATA OF SOME PHENYL TRIGLYCERIDES (57)

	M.p., °C.			Long spacings				Short spacings						
	$\alpha_L$	$\beta'_L$	$\beta_L$	Sub				Sub- $\alpha_L$						
				$\alpha_L$	$\alpha_L$	$\beta'_L$	$\beta_L$	$\alpha_L$	$\beta'_L$	$\beta_L$	$\beta_L$			
2-Behenylidistearin (SBS)	56.0	64.0	70.6	—	53.2	49.4	75.1	—	—	4.14	4.18vs	3.78s	4.58s	3.78vs
2-Behenyldipalmitin (PBP)	47.4	61.5	66.6	—	50.0	46.0	70.4	—	—	4.14	4.19vs	3.76s	4.58s	3.79vs
1-Palmitodibehenin (BBB)	55.9	66.1	—	58.9	57.4	52.4	—	4.2s	3.72m	4.15	4.20vs	3.78s	—	—
1-Stearodibehenin (SBB)	61.3	71.5	73.5	61.4	59.1	53.3	54.6	4.2s	3.77m	4.15	4.20vs	3.78s	4.59s	3.87s 3.70s

TABLE IX

## MELTING POINTS OF TRIACID TRIGLYCERIDES AND LONG AND SHORT SPACINGS OF TRIACID TRIGLYCERIDES

The asterisk indicates those glycerides in which the associations of forms I and II with  $\beta_L$  and  $\beta'_L$ -forms appear to be incorrect.

	Melting points, °C.			Long		Short	
	I	II	III	$\beta$	$\beta'$	$\beta$	$\beta'$
C <sub>18</sub> -C <sub>10</sub> -C <sub>14</sub>	52.5	50.1	14	57.3	—	3.82vs 4.3m 4.62s 4.82m 5.18s 5.35m	—
C <sub>18</sub> -C <sub>10</sub> -C <sub>12</sub>	52.0	47.0	33.4	62.4	43.3	3.82vs 4.34m 4.62vs 5.2m	3.82s 4.11s 4.29vs
C <sub>18</sub> -C <sub>14</sub> -C <sub>12</sub>	49.5	45.5	27.5	59.6	40.1	3.82vs 4.32s 4.61vs 4.82s 5.02m 5.42m	3.81vs 4.26vs 4.45m
C <sub>18</sub> -C <sub>10</sub> -C <sub>12</sub>	—	41.8	22.3	54.9	—	3.82vs 4.6vs 5.28m	—
C <sub>18</sub> -C <sub>16</sub> -C <sub>10</sub> *	50.0	46.5	26.1	38.5	59.0	3.85vs 4.14vs 4.33s 4.82m 5.35m 5.55m	3.76s 3.86s 4.22vs 5.14m
C <sub>18</sub> -C <sub>14</sub> -C <sub>10</sub> *	45.0	42.0	21.5	56.1	54.3	3.83vs 4.2vs 4.45s 5.6s	3.73s 3.84s 4.05s 4.19s 4.45s 4.58s
C <sub>18</sub> -C <sub>12</sub> -C <sub>10</sub> *	44.0	40.0	14.5	35.6	53.0	3.81s 4.19vs	3.83s 4.16vs 4.29s 4.46s
C <sub>16</sub> -C <sub>14</sub> -C <sub>12</sub>	49.0	44.0	37.0	35.7	—	3.74s 3.83s 4.57vs 5.08m 5.33m	—
C <sub>14</sub> -C <sub>12</sub> -C <sub>10</sub> *	37.0	34.0	22.0	33.4	—	3.82s 4.13vs 4.33vs 4.6m	—

and very short chains exhibit unusual properties. The glycerides 1-stearodiacetin, 1-palmitodiacetin, 1-stearodipropionin, 1-stearo-, and 1-palmitodibutyryn have been examined and the unusual stability of the  $\alpha_L$ -form of these glycerides observed (59). The  $\alpha_L$ -form of the dibutyroglycerides appears to be indefinitely stable between its melting point and a sub- $\alpha_L$ -transformation. The glyceride 1-stearodiacetin normally solidifies into a soft waxy polymorphic form ( $\alpha_L$ -form) from the melt which transforms reversibly into a sub- $\alpha_L$ -form on cooling. The  $\beta_L$ -form is obtained from solvent. The  $\alpha_L$ -form of this glyceride can be stretched to some 200–300 times (42, 117); the highest melting form does not exhibit this property (117). The dilatometric properties of 1-palmitodiacetin, 1-palmito-, and 1-stearodibutyryn have been reported and some polymorphic transformation points observed which had been missed by earlier workers (44).

A study of the glycerides 2-aceto-, 2-butyro-, and 2-caproyldistearin and -dipalmitin has been made using thermal and X-ray data (58). These glycerides were found to exhibit marked individuality to behavior although the glycerides having in common a given acyl short chain behave similarly. Three of the compounds exhibit an  $\alpha_L$ -1-form (2-butyrodistearin and -dipalmitin and 2-caproyldistearin). The long spacing is compatible only with a single palmito or stearo chain. All of these glycerides exhibit a sub- $\alpha_L$ -form. Particularly unusual is the observation of a super- $\alpha_L$ -form. This is a polymorphic modification having the characteristic short spacing near 4.2 Å. with a melting

point 10–12° higher than the  $\alpha_L$ -form. This was observed with 2-butyrodistearin and -dipalmitin. The caproyl glycerides show a multiplicity of  $\beta_L$ -type forms. Thus 2-caproyldistearin exhibits sub-A- $\beta_L$ -forms, sub-B- $\beta_L$ -forms, as well as a  $\beta_L$ -form.

The abnormal behavior of these glycerides is attributed to the relatively large role played by the carbonyl portions of the short acyl groups compared with the poly-methylene chains. These glycerides need further examination, particularly to obtain additional information on the peculiar super- $\alpha_L$ -form.

It seems clear that the nomenclature is becoming particularly cumbersome with these glycerides, matching of course the greater complexity of their polymorphic behavior.

## C. TRIACID TRIGLYCERIDES

The m.p. data for a series of triacid triglycerides have been reported (29, 100). The chain lengths extend from C<sub>10</sub> . . . C<sub>18</sub>. Three forms are observed, but X-ray data for only two forms are reported. The two forms were called  $\beta'$ - and  $\beta$ -forms and it was observed that the  $\beta'$ -form could be obtained readily from solvent. A selection of the data is given in Table IX. It was suggested that forms I and II correspond to  $\beta$ - and  $\beta'$ -forms.

Examination of the data suggests that the reported correspondence of forms I and II to  $\beta_L$ - and  $\beta'_L$ -forms may not be correct with the 1-stearyl-2-acyl-3-caproyl-glycerides (these are marked with an asterisk in the table). Instead, it seems that 1-stearyl-2-palmityl-3-



TABLE X  
MELTING AND X-RAY DATA FOR UNSATURATED SIMPLE TRIGLYCERIDES

	Melting points, °C.			Long spacings				Short spacings					
	$\alpha_L$	$\beta'_L$	$\beta_L$	$\alpha_L$	$\beta'_L$	$\beta_L$	$\alpha_L$	$\beta'_L$		$\beta_L$			
Triolein	-32	-12	4.9	45.2	45.8	43.3		4.35	3.87	5.28	4.57s	3.97	
										3.84	3.71		
Trielaidin	15.5	37(?)	42	—	—	44.1		—	—	5.3	4.6s	3.9	
Trierucin	6	17(25)	30	—	54.7	51.1		4.53	4.28	3.88	5.24	4.6s	4.03
											3.84	3.7	
Tibrassinidin	43	50	59	59.3	—	53.6		—	—	—	5.3	4.6s	3.9
											3.7	3.7	

caprylglyceride can exist in two  $\beta'_L$ -forms rather than a  $\beta$ - and  $\beta'$ -form as shown. (There is nothing extraordinary about a long chain compound existing in two forms having orthorhombic or approximately orthorhombic packing.) Also the triglyceride 1-stearyl-2-lauryl-3-caprylglyceride appears to have its X-ray diffraction patterns in the wrong order. The typical  $\beta'_L$ -diffraction pattern is here designated as a  $\beta$ -form. The diffraction pattern associated with the  $\beta'$ -form of 1-stearyl-2-myristyl-3-capryl on the other hand has a strong short spacing at 4.58 Å, while the pattern associated with the  $\beta$ -form has strong spacings at 3.83vs, 4.2vs (and 4.45vs).

Whether the correspondence of these forms is or is not correct, it is clear that further work is required with the triacid triglycerides.

#### D. UNSATURATED TRIGLYCERIDES

Glycerides containing unsaturated acids have very similar polymorphic behavior to that of the saturated glycerides. Those containing *trans* unsaturated acids are thought to be very similar in behavior and structure to glycerides of the corresponding saturated acids. Those containing *cis* groups have a tendency to crystallize in a way which gives rise to long spacings indicative of a triple chain length structure. The controversy over the existence of a vitreous form and the association of X-ray diffraction pattern and melting point also exists with these compounds (83).

##### 1. Simple Triglycerides

Little additional work has been reported on these compounds since the earlier review by Malkin (83). What is considered to be the correct association of X-ray pattern and melting point is shown in Table X. Further work may be required for trierucin where four melting points are given but only three distinct X-ray diffraction patterns are observed, and tibrassinidin where three melting points are observed but only two distinct X-ray patterns.

The infrared spectra of the polymorphic forms of trielaidin and triolein have been published (25). With trielaidin the spectra of two forms were obtained corresponding to an  $\alpha_L$ - and  $\beta_L$ -form. A single band is observed at 722  $\text{cm}^{-1}$  in the spectra of the  $\alpha_L$ -form and at 718  $\text{cm}^{-1}$  in that of the  $\beta_L$ -polymorphic form. The

relative intensities of the bands in the 1250  $\text{cm}^{-1}$  region change in an analogous manner to that observed with the saturated triglycerides. In the spectrum of the  $\alpha_L$ -form of triolein a single band is observed at 723  $\text{cm}^{-1}$ , in the  $\beta'_L$ -form at 729 and 722  $\text{cm}^{-1}$ , and in the  $\beta_L$ -form a single band at 722  $\text{cm}^{-1}$ . This is rather analogous to the saturated triglycerides and may be indicative that part of the chains still pack predominantly in a manner similar to these glycerides. The X-ray short spacings are to some extent consistent with this interpretation (41).

##### 2. Unsaturated Mixed Triglycerides

A considerable amount of work has been carried out in recent years on these glycerides mainly because of their practical importance in confectionary fats such as cocoa-butter. The variety of results obtained on nominally the same compounds are disturbing and must be related to variations in the purity of the compounds examined. The effect of acyl migration occurring at some stage of the synthesis of the compounds may explain partly some of the differences.

Daubert and Clarke (36) used cooling and heating curves to examine the 2-oleo disaturated glycerides of capric, lauric, myristic, palmitic, and stearic acids and suggested there were four polymorphic forms; later X-ray data for some of the glycerides also were reported (46). A later investigation of 2-oleodimyrstin, dipalmitin, and distearin then led to the proposal that there were five forms for these glycerides, but this total included a vitreous form (82). Further examinations were made (63, 66, 74) of 1-oleo disaturated glycerides, oleodipalmitin, distearin, palmitostearin, and steopalmitin as well as 2-oleopalmitostearin, using capillary melting point, X-ray photography, differential heating apparatus and with some of the glycerides dilatometry. The number of possible polymorphic forms for these glycerides is still, however, in doubt and there is wide diversity of melting point data (see Table XI) showing this for 2-oleodistearin and 2-oleopalmitostearin. Further work is required on these glycerides provided some adequate check on purity can be devised.

The most stable forms of the 2-oleo and 1-oleo disaturated glycerides have different crystal structures. The short spacings for the 2-isomer are consistent with

TABLE XI  
THE VARIATION IN MELTING DATA FOR SOME  
2-OLEOGLYCERIDES

	2-Oleodistearin				Landmann Feuge. Lovegren (63)
	Daubert and Clark (36)	Malkin & Wilson (82)	Lutton (72)	Lavery (66)	
Form I	22.3	23.0	22.4	22.4 T	22.8
Form II	29.8	29.5	—	—	30.0
Form III	37.0	37.0	35	36.8	37.7
	37.6		36.2		
Form IV	41.6	41.6	—	41.5	—
Form V	—	43.5	44.3	—	42.8
	2-Oleopalmitostearin				
Form I			18.2	20.8	18.2
Form II			?	—	24.5
Form III			33	30.7	33.0
Form IV			38	35.5	37.4

it being a  $\beta_L$ -form, while for the 1-isomer they are consistent with it being a  $\beta'_L$ -form. The long and short spacings are given in Table XII for the most stable forms of the isomer of oleodistearin and oleodipalmitin. The long spacings for all the isomers appear to be consistent with a triple chain length structure (72).

TABLE XII  
LONG AND SHORT SPACINGS FOR THE MOST STABLE FORMS OF  
SOME 2-OLEO- AND 1-OLEODISATURATED GLYCERIDES

	Long spacing	Short spacing
2-Oleodistearin	64	4.59s 3.68 4.02ms 3.79ms
1-Oleodistearin	70.8	4.06s 3.79ms 4.64m 4.39m
2-Oleodipalmitin	60.2	4.56 vs 4.05m 3.73 m 5.40w
1-Oleodipalmitin	65.0	4.30s 3.78 vs 4.68m

The infrared spectra of two polymorphic forms of 1-oleodistearin, of four forms of 2-oleodistearin (18), and of the most stable forms of 1-oleo- and 2-oleodipalmitin have been recorded (25). The spectra of the  $\alpha_L$ -forms of these glycerides are similar to those of the simple saturated triglycerides. The main  $\text{CH}_2$  rocking mode is a single band at  $720 \text{ cm}^{-1}$ . The spectra of the most stable forms of the 1-oleo isomers have spectral similarity to those of the  $\beta'_L$ -forms of the simple monoacid saturated triglyceride. A doublet occurs near  $727$  and  $719 \text{ cm}^{-1}$  in these spectra. The spectra of the most stable forms of the 2-oleo isomers have spectral similarities to the  $\beta_L$ -forms. A band occurs at  $890 \text{ cm}^{-1}$  and the main  $\text{CH}_2$  rocking mode is a single band at  $717 \text{ cm}^{-1}$ . This is consistent with the X-ray short spacings and suggests that despite the presence of the *cis* group in the molecule the hydrocarbon chains are packed in the common orthorhombic  $\text{O}\perp$  manner for the 1-oleo isomer but in the triclinic  $\text{T}\parallel$  manner for the 2-isomers. It is of interest that a strong band at  $690 \text{ cm}^{-1}$  attributed to a vibration of the *cis* group occurs in the spectrum of the 2- but not the 1-isomer. When the  $\alpha_L$ -form of 1-oleodistearin is cooled to  $0^\circ$  and spectra obtained, the single band at  $720 \text{ cm}^{-1}$  is

observed to split into a doublet at  $727$  and  $719 \text{ cm}^{-1}$  consistent with the occurrence of a sub-alpha (or sub- $\alpha_L$ -form) for this glyceride. The change is reversible.

An examination using n.m.r. measurements of the oleodisaturated glycerides showed interesting behavior. The line shape of the  $\beta'_L$ -form suggested that it was made up of two superimposed parts, one of which has a much narrower line width than the other. This was considered to be due to the greater reorientational freedom of the oleoyl chains compared with the saturated chains, possibly because the packing is less tight for the former. On this basis if  $y$  is the second moment of the oleoyl chain and the stearoyl chain has the same second moment as in tristearin

$$\text{obs. second moment} = 14.9 = 2/3 \times 22.2 + 1/3y \text{ gauss}^2$$

then  $y = 0.3 \text{ gauss}^2$  corresponding to the very narrow line observed. At room temperature the  $\alpha_L$ -form gives a very narrow line with a second moment of less than  $1 \text{ gauss}^2$ , which is consistent with considerable motion occurring including translation and flexing of the chains. As the temperature is lowered the second moment increases to  $17.8 \text{ gauss}^2$  at  $-78^\circ$  and  $24.9 \text{ gauss}^2$  at  $90^\circ$ .

When the 2-oleodistearin was examined the second moment of the stable  $\beta_L$ -form was observed to be similar to that of the  $\beta_L$ -forms of other glycerides examined. (This is in contrast to the second moment of the stable form of the 1-oleodistearin.) On melting and quenching to  $0^\circ$  a second moment of  $6.6 \text{ gauss}^2$  was observed. This changed in a few minutes into a line shape consisting of a broad component with a sharp line superimposed as with the  $\beta'_L$ -form of the 1-oleo isomer. The interpretation of this was not certain but it was suggested that this line shape corresponded to the formation of a sub- $\beta_L$ -form.

A dielectric study of this glyceride showed that the stable  $\beta_L$ -form had a lower dielectric constant than the sub- $\beta_L$ -form and that the low temperature dispersion of the  $\alpha_L$ -form was less pronounced than with 2-oleoyl-dipalmitin (34).

Short chain unsaturated glycerides such as 1,2-diaceto-3-olein and 1,2-dibutyro-3-olein recently have been examined and thermal and dilatometric data obtained (43, 49) but no X-ray data.

## VII. DIGLYCERIDES

### A. 1,3-DIGLYCERIDES

The polymorphism of simple 1,3-diglycerides was first investigated by Malkin, Shurbagy, and Meara (79), who suggested that these compounds are similar to the triglycerides and exist in  $\alpha_M$ -,  $\beta_M$ -, and  $\beta'_M$ -forms. They also considered that a discontinuity occurred in the even homologous series. Other authors (8) found only two forms which they termed  $\beta_L$ -a- and  $\beta_L$ -b-forms on the basis of the X-ray short spacings

TABLE XIII  
 MELTING AND X-RAY DATA FOR 1,3-DIGLYCERIDES (8)

M.P., °C.	—Long spacings—		—Short spacings—								
	$\beta_L$ -a	$\beta_L$ -b	$\beta_L$ -a		$\beta_L$ -b						
Distearin	78.2	50.2	4.61vs	3.90s	3.71s+	2.55w+	4.59vs	4.14w	3.74vs	2.52w	2.44w
Dipalmitin	72.9	44.7	4.60vs	3.88m	3.72s+	2.50m	2.33w	4.58vs	3.75vs	2.45m	
Dimyristin	66.5	40.6	4.58s	3.91m	3.73s	2.53w	2.44w	4.55s	3.74s		
Dilaurin	56.8	35.4	4.48s	3.89m	3.68s	3.39w		4.55m	3.70s		
								2.75w	2.50w	2.41w	2.30w

for the series dilaurin to distearin. They found no evidence for the occurrence of an  $\alpha_L$ -form. The  $\beta_L$ -a-form was characterized by short spacings 4.6, 3.9, and 3.7 Å. and  $\beta_L$ -b-form by spacings of 4.6 and 3.75 Å. These authors did not agree that a discontinuity occurred in the even homologous series. The  $\beta_L$ -a-form usually is the first form obtained from the melt but it transforms to  $\beta_L$ -b near its melting point. Both forms are obtainable from solvent, high purity favoring the  $\beta_L$ -b-type. Although they exhibit different stability, both are considered to have the same melting points.

Disagreement still exists with these glycerides. Malkin suggests (55, 83): (a) that an  $\alpha_M$ -form exists and gives definite melting points; (b) that the two stable forms have different melting points, *e.g.*, dilaurin 54° and 56.5°; (c) that the X-ray short spacings for the stable forms can be classified into three groups a, b, and c. The a-type is observed with the  $\beta_M$ -forms of all odd acid diglycerides and the  $\beta'_M$ -forms of dipalmitin and distearin; the b-type with the  $\beta'_M$ -forms of all diglycerides except dipalmitin and distearin and the c-type with the  $\beta_M$ -forms of all even acid diglycerides (*i.e.*, a discontinuity does occur with the  $\beta'$ -forms of the even diglycerides). Note that the c-type corresponds to the  $\beta_L$ -b-type of pattern. (d) The fact that both the  $\beta'_M$ - and  $\beta_M$ -forms of the diglycerides give rise to diffraction patterns with a strong spacing at 4.6 Å. shows the difficulty of attempting to classify the polymorphic forms of glycerides according to the type of short spacing.

While a judgment on this classification into three types would require an examination of the original diffraction photographs, an examination of the quoted data shows that such a distinction rests on very slender evidence. The X-ray short spacings for the even-acid diglycerides is said to fall into two groups. Thus while tristearin has short spacings at 4.6s, 3.88s, and 3.68s, dimyristin, on the other hand, of supposedly a different type, has spacings at 4.64s, 3.88m, 3.68s, and 3.53vw. The data for dimyristin given by the other group of workers (8) are 4.58s, 3.91m, 3.73s, 2.53w, and 2.24w.

The data considered to be the most reliable are given in Table XIII for the even-acid diglycerides.

An infrared spectroscopic examination of some even-acid diglycerides (17) showed that two very similar spectra are obtained for the forms corresponding to the  $\beta_L$ -a- and  $\beta_L$ -b-forms. No evidence for the  $\alpha_L$ -form

was observed. Both spectra showed the main  $\text{CH}_2$  rocking mode to be a single band at 717  $\text{cm}^{-1}$ . It was pointed out that there is no inconsistency in the application of the Lutton nomenclature to these glycerides since both forms probably have triclinic T|| packed chains and are correctly designated  $\beta_L$ -forms.

The spectrum of the  $\beta_L$ -form obtained from solvent shows two carbonyl frequencies and two hydroxy frequencies, consistent with the hydrogen bonding being different for one carbonyl group than the other. A recent X-ray single-crystal structure of the 1,3-diglyceride and 3-thiododecanoic acid supports this and shows that the hydrogen bond links from the hydroxyl group of the one molecule to a carboxylic oxygen in a neighboring molecule. The repetition in the structure is such that one carboxylic oxygen always participates in the hydrogen bond while the other carboxylic group never does so. The two carbon chains are oppositely directed but are *not* parallel (64). Nuclear resonance spectra of the two forms of the 1,3-diglycerides (26) show that both forms have similar second moments ( $\sim 20$  gauss<sup>2</sup>) and the chains undergo only slight freedom of torsional motion. Additional evidence confirming the absence of an  $\alpha_L$ -form with these diglycerides was obtained by a study of the variation of the dielectric constant with temperature for distearin and dipalmitin (33.)

X-Ray studies of mixed chain 1,3-diglycerides such as 1-aceto-3-stearin show differences in polymorphic behavior. This glyceride exists in three polymorphic forms  $\alpha_L$ , sub- $\alpha_L$ , and the most stable form is a  $\beta'_L$ -form. The infrared spectrum of the stable form of 1-aceto-3-palmitin shows a doublet near 720  $\text{cm}^{-1}$  analogous to that observed with the  $\beta'_L$ -form of saturated simple triglycerides.

Some unsaturated diacid diglycerides have been examined, *e.g.*, 1-stearyl-3-olein, and found to exhibit rather individualistic behavior (37). Thermal and dilatometric data have been reported recently (49) on other diglycerides such as 1-butyro-3-olein, 1-aceto-3-olein, and 1,3-diolein. Three forms were found for the latter compound, in contrast to earlier investigators (14, 37). The diglycerides 1-stearyl-3-elaidin and 1-oleyl-3-elaidin also have been examined (60). The former showed two  $\beta_L$ -type forms while the latter showed one.

## B. 1,2-DIGLYCERIDES

The polymorphism of 1,2-diglycerides has been investigated by thermal and X-ray methods (55) and they are shown to exist in two modifications  $\alpha_M$  and  $\beta_M$ . The material from solvent is in the  $\beta_M$ -form; on melting it resolidifies at the  $\alpha_M$  melting point. The transition  $\alpha_M \rightarrow \beta_M$  is very slow. These glycerides also have been examined by thermal and infrared spectroscopy (24). By analogy with the short spacings of the polymorphic forms of other glycerides the forms are designated  $\alpha_L$ - and  $\beta'_L$ -forms; see Table XIV. The  $\alpha$ -

TABLE XIV

MELTING AND X-RAY DATA FOR THE 1,2-DIGLYCERIDES

	Melting points, °C.		Long spacings		Short spacings			
	$\alpha_L$	$\beta'_L$	$\alpha_L$	$\beta'_L$	$\alpha_L$		$\beta'_L$	
Distearin	59.9	71	54.5	48.3	4.12	3.81s	4.05vs	4.27m
Dipalmitin	47.7	61	49.3	43.5	4.10	3.76s	4.03vs	4.27m
	- 50							
Dimyristin	37.1	51.7	44.4	38.8	4.12	3.82s	4.06vs	4.31m
Dilaurin	19.7	38.2	39.2	34.1	4.13	3.79s	4.0vs	4.31m

form has spectral similarities to that of the  $\alpha_L$ -form of the simple saturated triglycerides. The  $\text{CH}_2$  rocking mode is a single band at  $720 \text{ cm.}^{-1}$ . The  $\beta'_L$ -form gives rise to a doublet at  $729$  and  $719 \text{ cm.}^{-1}$  similar to that observed with the  $\beta'_L$ -forms of the triglycerides. From this it was deduced that the hydrocarbon chains are packed hexagonally and orthorhombically, respectively, in the two forms. From the presence of two carbonyl stretching frequencies in the spectrum of the  $\beta'_L$ -form it is suggested that the carbonyl oxygens are hydrogen bonded to different extents. Nuclear resonance spectra of the two forms show that the second moment of the line width of the  $\beta'_L$ -forms is practically identical with those of the  $\beta'_L$ -forms of tristearin and tripalmitin ( $\sim 22$  and  $21 \text{ gauss}^2$ , respectively). The second moments of the  $\alpha_L$ -forms are close to the value of  $9 \text{ gauss}^2$  expected for free reorientation of the hydrocarbon chains.

## VIII. POLYMORPHISM OF MONOGLYCERIDES

## A. 1-MONOGLYCERIDES

The first report (47) of the double melting of 1-monostearin and palmitin was in 1920. In 1930, a systematic study of the even-acid 1-monoglycerides from monolaurin to monostearin was carried out and they were shown to exist in two distinct forms (97). The work was extended by Malkin and Shurbagy (78) who found three modifications for the 1-monoglycerides from monodecain to monostearin. These were a low melting  $\alpha_M$ -form and two higher melting modifications,  $\beta'_M$  and  $\beta_M$ . The X-ray pattern of the  $\alpha_M$ -form shows only one strong side spacing at  $4.12 \text{ \AA}$ . Lutton and Jackson (70) also examined some 1-monoglycerides and suggested that the  $\alpha_L$ -form is reasonably stable

down to a lower transition temperature at which point it changes reversibly into a new crystalline modification, sub- $\alpha_L$ , giving a distinctive set of short spacings. Some differences in the long spacings also were observed. A similar nomenclature to that used for the triglycerides was adopted, *i.e.*

Sub-alpha (sub- $\alpha_L$ )	A single strong short spacing at $4.15 \text{ \AA}$ . with other medium lines at $3.9, 3.75,$ and $3.55 \text{ \AA}$ .
Alpha ( $\alpha_L$ -form)	A single strong short spacing at $4.15 \text{ \AA}$ .
Beta-prime ( $\beta'_L$ -form)	A strong short spacing at $4.15 \text{ \AA}$ . and at $3.65 \text{ \AA}$ ., a medium line which is the strongest between $4.2$ and $2.6 \text{ \AA}$ .
Beta ( $\beta_L$ -form)	A strong short spacing at $4.55 \text{ \AA}$ . and the highest melting form

Large unexplained density differences were observed for slowly and rapidly chilled sub- $\alpha_L$ -forms.

Malkin (83) did not agree with some of the conclusions of this work, repeated that the  $\alpha_M$ -form was only stable near the melting point, and he stated that the sub- $\alpha_L$ -form was a semi-vitreous solid rather than a crystalline modification. The reversible character of the sub- $\alpha_L$ -to  $\alpha_L$ -form also was doubted.

An infrared spectroscopic examination (15, 16) showed that the  $\alpha_L$ -form was stable down to a lower transition temperature and changed into a form giving a spectrum of a crystalline modification, the sub- $\alpha_L$ -form. A doublet occurs in the  $720 \text{ cm.}^{-1}$  region at  $727$  and  $719 \text{ cm.}^{-1}$ . The reversible nature of the sub- $\alpha_L$ -to the  $\alpha_L$ -modification was also confirmed. The bands in the spectrum of the sub- $\alpha_L$ -form were rather broad and suggestive of some orientational freedom. The spectra of the  $\beta'_L$ - and  $\beta_L$ -forms gave bands which were narrow and sharp and typical of some crystalline materials without orientational freedom. The spectrum of the  $\beta'_L$ -form was at first thought to have only a single band at  $719 \text{ cm.}^{-1}$  but further work showed that a doublet occurs at  $727$  and  $719 \text{ cm.}^{-1}$  as with the  $\beta'_L$ -form of other glycerides. It may be that the  $\beta'_L$ - and the sub- $\alpha_L$ -form have common orthorhombic  $\text{O} \perp$  packed chains while the  $\beta_L$ -forms have triclinic  $\text{T} \parallel$  packed chains as with the triglycerides. The infrared spectrum of the most stable form of the optical active isomer of the monoglyceride L-1-monostearin shows that the chain packing is probably orthorhombic  $\text{O} \perp$  as with the  $\beta'_L$ -form of the racemic monoglyceride.

The changes in hydrogen bonding for the glyceride in the liquid state through the variety of polymorphic forms can be determined from the spectra. The carbonyl stretching frequency shifts from  $1706 \text{ cm.}^{-1}$  in the liquid, to  $1721 \text{ cm.}^{-1}$  in the  $\alpha_L$ -form,  $1730 \text{ cm.}^{-1}$  in the sub-alpha form, and  $1736 \text{ cm.}^{-1}$  in the  $\beta$ -forms. The OH stretching frequency shifts to lower frequencies in the order liquid  $\rightarrow \alpha_L \rightarrow$  sub-alpha  $\rightarrow \beta'_L \rightarrow \beta_L$ . This is taken to indicate that the hydrogen bonding is increasing in this order but that the bonding is occurring

preferentially between hydroxyl groups rather than between hydroxyl and carbonyl groups.

Nuclear magnetic resonance measurements of 1-monoglycerides (26), *e.g.*, 1-monostearin, show that the sub- $\alpha$  form gives rise to a large second moment  $\sim 20$  gauss. The  $\alpha_L$ -form, however, gives rise to rather small second moments, 4.5 at  $50^\circ$  and 5.7 at  $30^\circ$ , showing that for this form the chains have considerable freedom of motion not only about the chain axes. Some lateral and longitudinal motion of the chains seems to occur. The second moment for the stable  $\beta_L$ -form is 19.9 gauss<sup>2</sup>.

Dielectric studies show similar effects (32). The dielectric constant increases normally in the liquid until the freezing point of the  $\alpha$ -form is reached; at this point it increases sharply. Just below the  $\alpha \rightarrow$  sub- $\alpha$  transition point the dielectric constant is still reasonably high, indicating considerable orientational freedom in this form, but the frequency dependence of the dielectric constant and the conductivity decrease rapidly below the transition temperature. The abnormally high conductivities of the  $\alpha$ -forms were suggested to be the result of the transfer of protons through the sheets of hydroxyl groups in the crystals. The dielectric constants of the stable  $\beta$ - and  $\beta_L$ -forms are low enough for them to be considered as non-rotators while in the sub- $\alpha$ -form the dipole orientation process is probably segment orientation. Thermal and X-ray data relating to the 1-monoglycerides are given in Tables XV and XVI.

It is of interest that the  $\alpha_L$ -forms show additional weak lines compared with other glycerides. This observation may be related to the large amount of

freedom of the hydrocarbon chains in this form detected by the n.m.r. measurements. The sub- $\alpha_L$  to  $\alpha_L$  change can be followed readily by dilatometry (71). The density of the stable  $\beta_L$ -form is between that of the  $\alpha_L$ - and the sub- $\alpha_L$ -forms.

Some recent X-ray single crystal studies on mono-glycerides have been reported (3). Optically active 1-monoglycerides are said to exist in four polymorphic forms. Crystallization from solvents gives rise to two stable modifications both with orthorhombic  $O \perp$  chain packing. Further details concerning these studies will be useful in relating the crystallization of these compounds to those of the di- and triglycerides.

A recent investigation of 1-monolein using the capillary tube method has indicated (49) that it exists in three forms and not four as suggested by an earlier investigation (14).

## B. 2-MONOGLYCERIDES

These glycerides appear to be free of polymorphism and the same form is obtained from solvent and by cooling the melt (36, 46). The lines at 4.60s, 4.4vs, and 3.9vs seem to be common to the various homologs. It will be noted that a strong line occurs at 4.6 Å. It is possible that the hydrocarbon chains pack here in a manner analogous to that of the  $\beta_L$ -form of 1-monoglycerides. Infrared spectra have been reported and show distinctive differences from the stable forms of the 1-monoglycerides (16). Only a single band occurs in the 720 cm.<sup>-1</sup> region. Nuclear magnetic resonance measurements show that the second moment for 2-monopalmitin is 18.2 gauss<sup>2</sup>. Thermal and X-ray data relating to these forms are shown in Table XVII. The melting points are some  $10^\circ$  lower than the corresponding 1-monoglyceride and the long spacings are much smaller.

TABLE XV  
LONG SPACINGS AND THERMAL POINTS FOR THE  
1-MONOGLYCERIDES (78)

	Thermal points				Long spacings			
	Transition to $\alpha_L$	$\alpha_L$	$\beta'_L$	$\beta_L$	Sub- $\alpha_L$	$\alpha_L$	$\beta'_L$	$\beta_L$
Decoic	8	27	49	53	...	37.2	32.9	32.9
Undecoic	3	36.5	52	56.5	...	40.2	35.2	35.2
Lauric	15	44	59.5	63	...	43.2	37.3	37.3
Tridecoic	9	50	61	65	...	46.2	39.6	39.6
Myristic	24	56	67.5	70.5	...	...	41.5	41.5
Penta-decoic	17	62	69	72	...	51.3	43.8	43.8
Palmitic	34 (39)	66.5	74	77	(45.5)	(45.6)	45.8	45.8
Hepta-decoic	28	70	74.5	77	...	...	48.2	48.2
Stearic	47.5 42 (49°)	74	79	81.5	50.3	58.3 (50)	50.0	50.0

TABLE XVI  
CHARACTERISTIC SHORT SPACINGS FOR 1-MONOPALMITIN AND  
1-MONOSTEARIN (71)

Sub- $\alpha_L$	$\alpha_L$	$\beta_L$	$\beta_L$
4.14vs	4.64w	4.14vs	4.55
3.92m	4.18vs	3.87vw	4.37s
3.75m	3.99vw	3.65w+	3.86s+
3.56m	3.81w	3.30w	3.74w.

TABLE XVII

MELTING AND X-RAY DATA FOR 2-MONOGLYCERIDES (83)

	M.p., °C.	Long spacing	Short spacings
Monostearin	75.2	43.9	3.86, 4.43, 4.60
Monopalmitin	69.0	40.4	3.88, 4.42, 4.60
Monomyristin	61.3	36.2	3.92, 4.42, 4.60
Monolaurin	51.0	32.8	3.96, 4.40, 4.58
Monocaprin	40.2	29.4	4.07, 4.38, 4.58

## IX. SUMMARY OF GLYCERIDE CRYSTALLIZATION BEHAVIOR

### A. GENERAL COMPARISON

In a discussion covering the crystallization of the different types of glycerides, *i.e.*, mono-, di-, and triglycerides, it is readily appreciated that similar polymorphic behavior should not be expected to arise merely because they are all derivatives of glycerol. Any similarity in behavior which we observe is de-

terminated by the fact that hydrocarbon chains are common to all of them and that with fairly long chains they tend to dominate the crystallization processes. For a given chain length the balance of polar and non-polar forces involved differs from a triglyceride to a diglyceride and a monoglyceride and this must receive consideration when we compare their behavior. If we examine only fairly long chain derivatives, say greater than ten carbon atoms, then we might expect to have similarities in crystallization behavior, but with shorter chain lengths where the polar properties are becoming more important less similarity will be expected. We can instance the amides and soaps where unusual crossed chain packing is observed although parallel chain packing is the more usual behavior. When we remember the complicated polymorphic behavior of the paraffins depending upon chain length, upon even or odd number of carbons, upon temperature and solvent, we should not be surprised to find the polymorphic behavior of the glycerides to be at least as complex.

Without more definite X-ray single crystal data one must be extremely cautious in picking out similarities in crystal form between one glyceride and another and from one type to glyceride to another, particularly if they are based only on X-ray powder photography short spacings.

The infrared spectroscopic data alone are also inadequate. The doublet observed in the  $720\text{ cm.}^{-1}$  region and associated with common orthorhombic  $O\perp$  packing also is observed when the hydrocarbon chains are packed in the rather rare orthorhombic  $O'\perp$  type sub-cell (the sub-cells have identical shape but some symmetry elements are interchanged with respect to identical axes) although this doublet is at  $726$  and  $717\text{ cm.}^{-1}$ . The single band in the  $720\text{ cm.}^{-1}$  region usually near  $717\text{ cm.}^{-1}$  associated with triclinic  $T\parallel$  packed chains also is observed with the rare type of sub-cell; the orthorhombic  $O\parallel$  type in which the chain planes are strictly parallel to one another (1) also is observed with crossed chain structures (21).

However when both the X-ray data and the infrared data are taken into consideration it is clear that the two support each other so well that one must conclude that similarities can indeed be picked out. Essentially the  $\beta_L$ -forms are considered to have triclinic  $T\parallel$  packed chains, the  $\beta'_L$ -forms to have orthorhombic  $O\perp$  packed chains, and the  $\alpha_L$ -form to have hexagonal packed chains. The sub- $\alpha_L$ -forms are also considered to have orthorhombic  $O\perp$  chains, but the chains are vertical to the basal plane whereas they are usually tilted with the  $\beta'_L$ -forms. (It must be emphasized that this is only an approximation and that this says nothing of the symmetry of the actual crystals.) If we use this approximation we should not be surprised to find a glyceride having two forms with triclinic packed chains of different tilt and hence two  $\beta_L$ -forms or two forms with

orthorhombic packed chains of different tilts, hence two  $\beta'_L$ -forms. The n.m.r. results show how the molecular mobility can vary from one  $\alpha_L$ -form to another, again emphasizing that such a designation implies similarity and not identity of behavior. Deductions based on long spacing data must also be considered with considerable caution at present and it already has been seen how with the monoacid saturated triglycerides such deductions can be in error.

It now seems certain that exceptions to the simple classification of Lutton will be observed when complete structures are determined. The variety of sub-cells observed with the long branched chain fatty acids makes one realize that the over-all generality of the classification is bound to fail when it is applied to the enormous variations possible with glycerides. At the present stage of development of structural determinations of glycerides the classification is still useful as an approximation, particularly with the limited chain length range of the glycerides at present examined.

#### B. CRYSTALLIZATION FROM SOLVENTS

The crystal modification obtained from solvent is usually the most stable form, but occasionally a less stable modification is obtained, sometimes by variation of the solvent and sometimes by varying the speed of crystallization. This occasionally has aroused comment (45, 46), yet the behavior is also observed with other long chain compounds, *e.g.*, the even-membered saturated monocarboxylic acids where rapid crystallization gives the C-form, and slow crystallization favors formation of A or B forms except when the solvent molecules are strong dipoles. The solvent effect probably is due to the variation in vapor pressure. A solvent of high vapor pressure will vaporize more quickly than one with lower vapor pressure, thereby varying the rate of crystallization. If one phase has a higher rate of formation than another it can be formed by rapid crystallization even if it is less stable.

It is of interest that the  $\beta'_L$ -form of tristearin sometimes has been observed when the glyceride is crystallized from paraffin oil (105).

#### C. PURITY OF GLYCERIDES

The large differences in behavior noted by various groups of observers on what are nominally the same compounds emphasizes the importance of having some criterion for determining the purity of the glycerides concerned. It is well known that the existence or absence of a particular crystal modification with paraffins can depend on the presence of tiny amounts of impurities (less than 10%). The same must be true with glyceride polymorphism yet there are no adequate methods for determining their purity. The mixed saturated and unsaturated glycerides are particularly difficult in view of the possibility of acyl migration occurring during

synthesis (31). The use of chromatographic and enzymatic techniques and, with sufficiently volatile materials, mass spectroscopy may help in this matter.

#### X. APPLICATIONS OF POLYMORPHISM

The characterization of naturally occurring compounds is usually rather difficult and this is true of oils and fats. Polymorphic behavior can, however, assist this identification. A number of melting points corresponding to those of a glyceride is more conclusive than a single value, as also is true for other physical data such as X-ray pattern or infrared spectrum. For example, while the infrared spectrum of a molecule frequently has been likened to a fingerprint and has been used to assist unique identification of many simple molecules, glycerides may give a regular "handful of fingerprints." Polymorphic study has already been useful for determining a number of glycerides in natural fats (72), including 2-oleodistearin (84) and 2-oleodipalmitin (73, 85), and various isomers of palmitic and stearic acids (84, 94). A great deal of work has been carried out on the polymorphic behavior of cocoa butter because of its importance in chocolate manufacture. The lowest melting form is said to be a glassy or vitreous form (5, 108) and a critical assessment of the polymorphism seems to be required. The identification of the major glyceride of cocoa butter followed from the fact that two closely related isomers such as 1-oleo- and 2-oleo-disaturated glycerides, *e.g.*, 2-oleodistearin and 1-oleodistearin, have different crystallographic stable forms ( $\beta'_L$  and  $\beta_L$ , respectively), hence giving rise to considerable difference in X-ray patterns and infrared spectra (19). The needs of a rapidly increasing world population will make research work on oils and fats and related compounds of increasing importance. The curious crystallization and melting behavior of glycerides will be relevant to much of this work.

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