

## 524. *Infrared Spectra and the Polymorphism of Glycerides. Part III.<sup>1</sup> Palmitodistearins and Dipalmitostearins.*

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Polymorphism of the palmitodistearins and dipalmitostearins has been investigated by means of infrared spectroscopy between 1800 and 650  $\text{cm}^{-1}$ . The transitions have been studied and the packing of the chains deduced.

In previous papers <sup>1</sup> it was deduced that the lowest-melting form of a triglyceride was an  $\alpha$ -form with hexagonal packed chains rather than a vitreous form, whilst the next-highest-melting form designated  $\alpha$  by Malkin <sup>2</sup> was almost certainly not a form with hexagonal packing of the hydrocarbon chains and was thus wrongly designated. These views support the conclusions by American workers <sup>3</sup> from *X*-ray evidence. The present paper extends the infrared spectroscopic study to the polymorphism of 1-palmitodistearin (PSS), 1-stearodipalmitin (SPP), 2-palmitodistearin (SPS), and 2-stearodipalmitin (PSP). Controversy about these glycerides concerns the association of *X*-ray data with melting points, the existence of certain polymorphic forms,<sup>4</sup> and the nomenclature. The last becomes important here, since the stable form of PSP, about which there is agreement over the melting point and *X*-ray data, is designated a  $\beta'$ -form by Lutton *et al.*<sup>4</sup> but a  $\beta$ -form by Malkin.<sup>2</sup>

### EXPERIMENTAL

2-Palmitodistearin, m. p. 67.3°, 2-stearodipalmitin, m. p. 67.5°, 1-palmitodistearin, m. p. 65.0°, and 1-stearodipalmitin, m. p. 62.5°, were prepared by Dr. W. T. Weller of this laboratory by hydrogenation of the disaturated oleo-glycerides <sup>5</sup> at room temperature in the presence of palladised charcoal in ethyl acetate, followed by recrystallisations from solvents.

The infrared spectrometer was a Grubb-Parsons S3 double-beam spectrometer with a rock-salt prism. The spectra were in general obtained between 1800 and 650  $\text{cm}^{-1}$  with capillary thicknesses of the glycerides between rock-salt flats. An infrared cell which could be heated or cooled was used for the investigation of the liquid and for the polymorphic transitions which occur on heating or cooling. Rapid scanning of parts of the spectrum (in particular the 720  $\text{cm}^{-1}$  and the 1250  $\text{cm}^{-1}$  region) during heating or cooling disclosed the transition temperatures. These were confirmed by capillary-tube methods (cf. Lutton *et al.*). The forms obtained by crystallisation from solvent were examined both as Nujol mulls and in potassium bromide discs. The identities of the stable forms were confirmed by m. p. and *X*-ray data.

### RESULTS AND DISCUSSION

Infrared spectra (see Fig. 1) show three polymorphic forms of 1-palmitodistearin (PSS). The lowest-melting form was obtained by quenching the liquid to 0°; its spectrum is

<sup>1</sup> Parts I and II, Chapman, *J.*, 1956, 55, 2522.

<sup>2</sup> Malkin, "Progress in Chemistry of Fats and Other Lipids," Vol. II, Pergamon Press Ltd., London, 1954.

<sup>3</sup> Bailey, Jefferson, Kreeger, and Bauer, *Oil and Soap*, 1945, 22, 10; Filer, Sidhu, Daubert, and Longenecker, *J. Amer. Chem. Soc.*, 1946, 68, 167; Lutton, *ibid.*, 1945, 67, 524.

<sup>4</sup> Malkin and Meara, *J.*, 1939, 103; Carter and Malkin, *J.*, 1939, 577; Lutton, Jackson, and Quimby, *J. Amer. Chem. Soc.*, 1948, 70, 2441.

<sup>5</sup> Chapman, Crossley, and Davies, *J.*, 1957, 1502.

similar in general to that of the  $\alpha$ -form of tristearin,<sup>1</sup> and is similarly designated: in particular there is a single component of the methylene rocking mode at 720  $\text{cm}^{-1}$ . When this form was heated and the spectrum rapidly scanned, a transition was noted to occur at 50.5° to an intermediate-melting form. This behaviour is different from that of the simple saturated triglycerides such as tristearin, where direct transformation from the  $\alpha$ - to the  $\beta$ -form occurs.<sup>1</sup> The spectrum of the intermediate form is in general very similar to that of the  $\beta'$ -form of tristearin and is therefore designated a  $\beta'$ -form: in particular there are two components of the band assigned to a methylene rocking mode at 719 and 720  $\text{cm}^{-1}$ . The bands in the 1250  $\text{cm}^{-1}$  region are not quite as well resolved as those in tristearin. When further heated, this form melted at 61.5°. (This intermediate form was also obtained by crystallisation from ethyl acetate.) The highest-melting form was obtained by slow crystallisation from acetone: its spectrum is similar in general to that of the  $\beta$ -form spectrum of tristearin and is similarly designated; in particular, there is a prominent band at 890  $\text{cm}^{-1}$  and a single component of the methylene rocking mode at 717  $\text{cm}^{-1}$ . These bands are characteristic<sup>2</sup> of the  $\beta$ -forms of tristearin, tripalmitin, and trilaurin. The three forms show a marked change in the intensities of the bands in the 1250  $\text{cm}^{-1}$  region. The spectrum of the  $\beta$ -form shows a pronounced band at 1268  $\text{cm}^{-1}$  with weaker bands round it (perhaps arising from methylene wagging or twisting modes<sup>1</sup>). A similar argument to that used to designate the spectra of the polymorphic forms of tristearin<sup>1</sup> can also be applied to the spectra of this glyceride.

The infrared spectra (Fig. 2) show three forms of 1-stearodipalmitin (SPP). The lowest-melting form was obtained by quenching the liquid to 0°, and its spectrum is similar in general to that of the  $\alpha$ -form of tripalmitin and is similarly designated: in particular there is a single component of the rocking mode at 720  $\text{cm}^{-1}$ . Heating and rapid scanning shows a transition to an intermediate-melting form at 47°, whose spectrum is in general similar to that of the  $\beta'$ -form of tripalmitin<sup>1</sup> and is similarly designated: its methylene rocking mode consists of a doublet at 728 and 718  $\text{cm}^{-1}$ . This form is transformed at 57° into a more stable form which is also obtained by slow crystallisation from acetone. The spectrum of this form is very similar to that of the  $\beta$ -form of tripalmitin. The spectra of the three forms of SPP resemble those of PSS in the 1250  $\text{cm}^{-1}$  region.

This work confirms the conclusions by Lutton *et al.*<sup>4</sup> (based on X-ray evidence and thermal data) that these glycerides can exist in  $\alpha$ -,  $\beta'$ -, and  $\beta$ -forms.

Infrared spectra (Fig. 3) reveal only two forms of 2-palmitodistearin (SPS). The lower-melting form was obtained by quenching to 0° and its spectrum is similar in general (with some slight shifts in frequency of bands in the 1250  $\text{cm}^{-1}$  region) to that of the  $\alpha$ -form of tristearin and is similarly designated. Heating and scanning showed a transition at 50.5° to a more stable form whose spectrum was in general similar to that of the  $\beta$ -forms of other glycerides and is designated  $\beta$ : in particular there is a band at 890  $\text{cm}^{-1}$  and a single band at 717  $\text{cm}^{-1}$ . (The spectrum of the stable crystalline form from solvent was identical with this.) The intensity pattern of the bands in the 1250  $\text{cm}^{-1}$  region, although in general similar to that of the spectrum of the  $\beta$ -form of other glycerides, is a little different from that of SPP or tristearin (see Fig. 4): two bands near 1256 and 1268  $\text{cm}^{-1}$  are of comparable intensity. Since attempts to obtain an intermediate form giving a spectrum similar to that obtained with other  $\beta'$ -forms failed, it must be of a fleeting nature if it exists. This can be compared with the conclusions by Lutton *et al.*<sup>4</sup> (based on X-ray evidence) and by Crowe and Smyth<sup>6</sup> (based on dielectric measurements) that only two forms exist for this glyceride, but Malkin and Meara<sup>4</sup> claim the existence of four forms and give X-ray data for a  $\beta'$ -form.

The infrared spectra (Fig. 4) also reveal only two forms of 2-stearodipalmitin (PSP). This also agrees with the conclusions by Lutton *et al.*<sup>4</sup>, although Malkin and Meara<sup>4</sup> claim four forms also for this glyceride. The lower-melting form was obtained by quenching the

<sup>6</sup> Crowe and Smyth, *J. Amer. Chem. Soc.*, 1951, **73**, 2040.

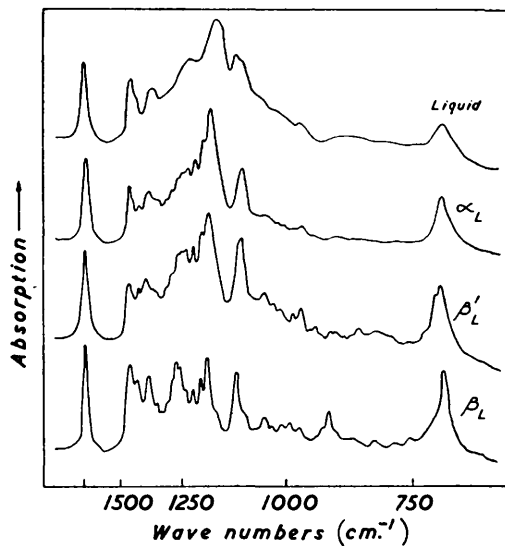
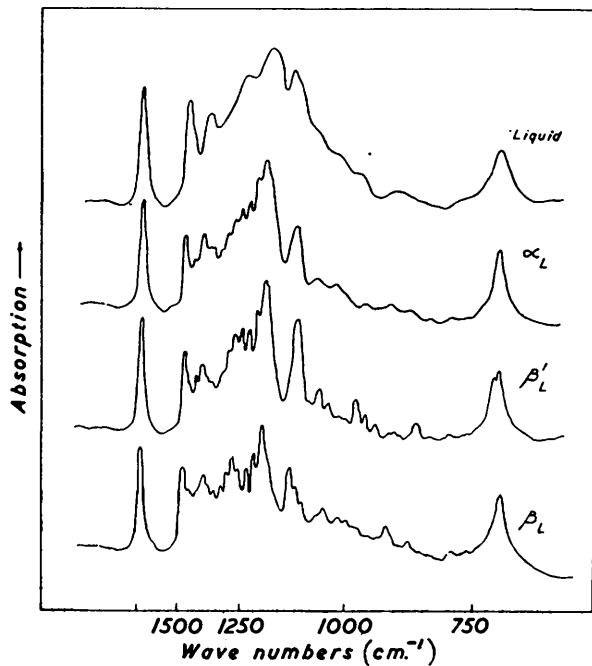
FIG. 1. 1-Palmitodistearin (for  $\alpha_L$ , etc., see p. 2719).

FIG. 2. 1-Stearodipalmitin.



liquid to  $0^\circ$ , but was unusually unstable (cf. Lutton *et al.*, and Crowe and Smyth) in contrast to the stability of the  $\alpha$ -form of SPS (the transition temperature for this form was obtained only by the capillary-tube thrust-in method), and made it difficult to obtain a satisfactory spectrum. The spectrum is in general similar to that of the  $\alpha$ -form of tripalmitin and is similarly designated. The more stable form was obtained by crystallisation from the melt and by slow crystallisation from acetone. The spectrum of this form is similar to, but not

FIG. 3. 2-Palmitodistearin.

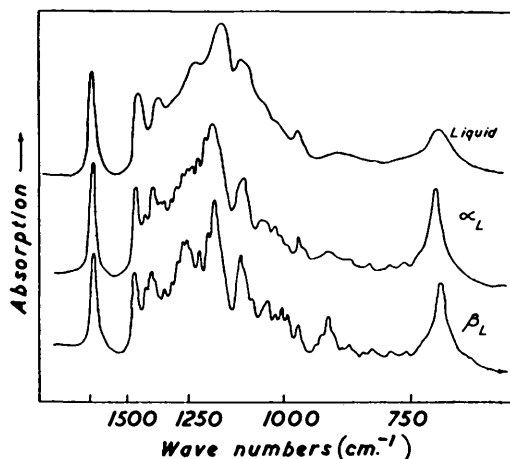
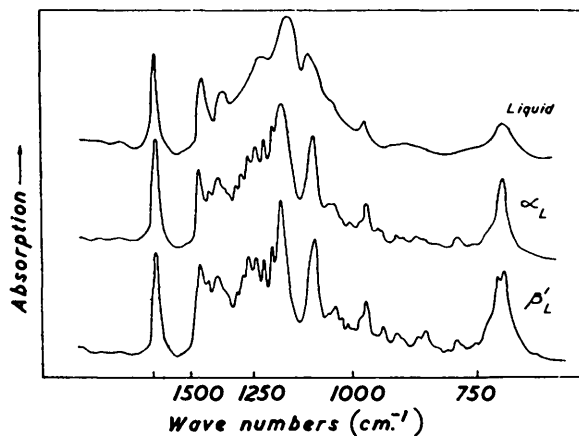


FIG. 4. 2-Stearodipalmitin.



identical with, that of the  $\beta'$ -form of tripalmitin. In particular (as in the spectra of other simple saturated glycerides in their  $\beta'$ -form) the band associated with a methylene rocking mode consists of a doublet at 727 and 719  $\text{cm}^{-1}$ . Also the bands in the 1250  $\text{cm}^{-1}$  region have a different intensity pattern from those occurring in the spectra of forms designated  $\beta$ , and there is no strong band near 890  $\text{cm}^{-1}$  in this spectrum. That the spectrum of the most stable form of this glyceride has similar characteristics to those associated with spectra of the  $\beta'$ -forms of the other saturated glycerides so far examined is of particular interest.

In the first place there can be little doubt that this is the spectrum of a homogeneous

form since it was obtained by very slow crystallisation from solvent, confirming the view that the similar spectra of the  $\beta'$ -forms of other triglycerides which have been obtained by thermal treatment (*e.g.*, that of tristearin, PSS, etc.) are also those of essentially homogeneous forms. Secondly, its *X*-ray pattern shows that it is not an  $\alpha$ -form (it has in fact been noted<sup>2</sup> that the *X*-ray short spacings of this form are practically identical with those of the  $\beta'$ -forms of simple odd-acid glycerides of the same acyl length). Yet the characteristics of this spectrum are the same as those given by the forms of tristearin, tripalmitin, 1-stearodipalmitin, etc., which Malkin would designate as  $\alpha$ -forms. The inconsistency further supports the arguments given previously<sup>1</sup> that these forms are correctly assigned as  $\beta'$ -forms and not as  $\alpha$ -forms. Malkin and Meara<sup>4</sup> in fact designate this form of PSP a  $\beta$ -form since it is the form of highest melting point, whilst Lutton *et al.*,<sup>4</sup> using a nomenclature based on *X*-ray short spacings, designates this a  $\beta'$ -form. The general similarity of the spectrum of this form to the spectra of the  $\beta'$ -forms of other glycerides supports the latter designation.

The existence of two systems of nomenclature, one based on melting points and the other on *X*-ray data, to describe the polymorphic forms of glycerides is confusing. A possible compromise to aid clarification would be to use the suffix M and L (M for Malkin and L for Lutton) in order to give a more precise designation of a particular form. The stable form of PSP could then be referred to as either a  $\beta_M$ - or a  $\beta'_L$ -form. (This suffix is used in the present Figures and Table.)

	PSS	SPP	SPS	PSP
$\alpha_L$ .....	50.5°	47°	50.5°	47°
$\beta'_L$ .....	61.5°	57°	—	67.5°
$\beta_L$ .....	65.0°	62.5°	67.3°	—

The melting point and transition data for the palmitic-stearic glycerides (see Table) agree well with those of Lutton *et al.*<sup>4</sup>

It is now possible to reconsider the basis for the polymorphism of the saturated triglycerides, by considering permissible deductions from infrared spectra and supplementing them with published conclusions from *X*-ray evidence.

Saturated triglycerides so far examined show spectra corresponding to three polymorphic forms. All the spectra show a carbonyl absorption at 1730—1740  $\text{cm}^{-1}$  and two strong bands near 1170 and 1100  $\text{cm}^{-1}$ . The major distinctions between the spectra of the different forms occur in the 1250 and the 720  $\text{cm}^{-1}$  region (other bands in the region 1100—720  $\text{cm}^{-1}$  are nevertheless distinctive). Bands in these two main regions are generally associated with vibrations of the methylene groups, and in particular with wagging (or twisting) and rocking modes respectively.<sup>7</sup>

A comparison of the spectrum of the lowest-melting form ( $\alpha_L$ ) of the saturated triglycerides with the type of spectrum obtained from the  $\alpha$ -forms of alcohols, esters, and hydrocarbons supports the conclusion (also arrived at from the *X*-ray short spacing) that in this form the chains are hexagonally packed (*cf.* Part 2).

In the spectrum of the next-highest-melting form ( $\beta'_L$ ) the band associated with the methylene rocking mode is split into two components at 727 and 719  $\text{cm}^{-1}$ . This is of particular significance. It has been suggested<sup>8</sup> that the existence of a similar doublet in the spectrum of orthorhombic and monoclinic hydrocarbons arises from interactions between adjacent chains in the crystalline phase, which result in an in-phase and an out-of-phase rocking mode. This doublet is observed, however, in the spectra of the crystalline form of many long-chain compounds, and Chapman<sup>9</sup> suggested that it is usually observed when orthorhombic packing of the hydrocarbon chain occurs, owing to similar interaction in the sub-cell. The doublet in the 720  $\text{cm}^{-1}$  region in the spectra of the  $\beta'_L$ -form of the

<sup>7</sup> Brown, Sheppard, and Simpson, *Phil. Trans.*, 1954, **247**, 35.

<sup>8</sup> Stein, *J. Chem. Phys.*, 1955, **23**, 734.

<sup>9</sup> Chapman, 6th Internat. Spectroscopic Colloquium, Amsterdam, May, 1956.

triglycerides suggests that the hydrocarbon chains in this form are packed in the orthorhombic manner.

In the spectrum of the  $\beta_L$ -form of the triglycerides the band associated with the methylene rocking mode is single and at  $717\text{ cm}^{-1}$ . We deduce that in this form the hydrocarbon chains are probably not orthorhombically packed. An X-ray single-crystal structure determination<sup>10</sup> of the stable  $\beta_L$ -trilaurin shows that the hydrocarbon chains in this form have triclinic packing.

In this way we have essentially classified the polymorphic forms of the simple saturated triglycerides into three crystallographic types according to their hydrocarbon-chain packing or, in other words, according to the symmetry of their sub-cells. It is well known that long-chain crystals can be thus described.<sup>11</sup> Thus the  $\alpha_L$ -form has hexagonal sub-cell symmetry, the  $\beta'_L$ -form orthorhombic sub-cell symmetry, and the  $\beta_L$ -form triclinic sub-cell symmetry. This throws light on to the classification of triglycerides by means of their X-ray short spacings proposed by Lutton,<sup>12</sup> since with long-chain compounds the short spacings will be determined primarily by the packing of the hydrocarbon chains. The short-spacing classification is therefore possible because of the underlying symmetry of the sub-cell.

Malkin<sup>2</sup> recently criticised the short-spacing classification on the grounds that all the  $\beta_M$ -forms of certain glycerides give the  $3.8$  and  $4.2\text{ \AA}$  lines. On the present view this means only that the stable form of these glycerides has orthorhombic packed chains. Other long-chain compounds show somewhat similar variation in the packing of the chains in their stable form. *e.g.*, the stable crystalline form for monocarboxylic acids of less than 22 carbon atoms has triclinic packed chains, whilst for molecules of longer chain length the stable form has orthorhombic packed chains.<sup>13</sup> A further criticism<sup>2</sup> that both  $\beta'_M$ - and  $\beta_M$ -forms of 1:3-diglycerides show the  $4.6\text{ \AA}$  line is explained if one argues that both these forms have triclinic packing of the chains and differ only in their tilt.

Lutton's classification extended to 1-monoglycerides<sup>14</sup> leads to a designation sub-alpha. (The X-ray short spacings of this form are very similar to those of the  $\beta'$ -form.) The spectrum of the sub-alpha form<sup>1</sup> shows a doublet at  $719$  and  $727\text{ cm}^{-1}$ , which suggests that the chains in this form are orthorhombically packed. The  $\beta'$ -form of 1-monoglycerides, *e.g.*, 1-monostearin, was considered<sup>1</sup> to have only a single band at  $719\text{ cm}^{-1}$  (an additional band occasionally observed at  $727\text{ cm}^{-1}$  with some samples was attributed to the presence of some sub-alpha form). This conclusion however is incorrect, and re-examination of the spectrum of this form shows that the  $\beta'$ -form also has a doublet at  $727$  and  $719\text{ cm}^{-1}$  (cf. the  $\beta'$ -form spectrum of 1-monostearin<sup>15</sup>). This suggests that there are two closely related forms with orthorhombic packed chains in 1-monoglycerides.

We can conclude that for the glycerides so far examined the infrared spectra show Lutton's short-spacing classification to be reasonable and useful and to be based on sub-cell symmetry. Distortions from the strictly orthorhombic or triclinic type packing are possible, however, which could affect the short spacings, so that caution is needed about its overall generality (cf. Filer *et al.*<sup>16</sup> on an apparent anomaly with 1-stearyl 2-acyl 3-decanoyl glycerides).

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<sup>10</sup> Vand and Bell, *Acta Cryst.*, 1951, **4**, 465.

<sup>11</sup> Daniel, *Adv. Physics*, 1953, **2**, 457.

<sup>12</sup> Lutton, *J. Amer. Oil Chem. Soc.*, 1950, **27**, 276.

<sup>13</sup> Von Sydow, *Arkiv Kemi*, 1956, **9**, 231.

<sup>14</sup> Lutton and Jackson, *J. Amer. Chem. Soc.*, 1948, **70**, 2445.

<sup>15</sup> Chapman, *Nature*, 1955, **176**, 216.

<sup>16</sup> Filer, Sidhu, Chen, and Daubert, *J. Amer. Chem. Soc.*, 1945, **67**, 2085.