646. *Infrared Spectra and the Polymorphism of Glycerides. Part IV.*[1] *Myristopalmitins and Myristostearins.*

By D. Chapman.

The polymorphism of some myristo-palmitins and -stearins has been investigated by infrared spectroscopy between 1800 and 650 cm.$^{-1}$, and data on the transitions have been obtained.

This paper extends our infrared spectroscopic studies [1, 2] to the polymorphism of 2-myristodistearin, 1-stearodimyristin, 2-myristodipalmitin, and 1-palmitodimyristin. These glycerides have been previously examined by Malkin *et al.*[3] and by Lutton *et al.*[4] who used thermal and *X*-ray techniques. Of these glycerides, the first is of particular interest since, unlike most other saturated triglycerides which have only three polymorphic forms, it is reported to have an additional fourth form [4] (designated β′-4). Malkin *et al.*[3] did not report this form, although they noted four melting points.

Experimental

2-Myristo-distearin and -dipalmitin, and 1-stearo- and 1-palmito-dimyristin, were prepared (by Dr. W. T. Weller of this laboratory) by refluxing 1 : 3-distearin, 1 : 3-dipalmitin, 1-monostearin, and 1-monopalmitin respectively with a small excess of myristoyl chloride (prepared from myristic acid, setting point 53—59°) in purified chloroform–pyridine for some hours. They were finally recrystallised a number of times from ethanol and acetone.

The infrared spectrometer was a Grubb-Parsons S.3 double-beam spectrometer with a rock-salt prism. The spectra were obtained between 1800 and 650 cm.$^{-1}$ with capillary thicknesses of the glycerides between rock-salt flats. A cell which could be heated or cooled was used for investigating the polymorphic transitions, and to obtain the spectra of the glycerides in the liquid state. Rapid scanning of parts of the spectrum (in particular the 1250 and 720 cm.$^{-1}$ regions) during heating or cooling disclosed the transition temperatures (which are in good agreement with those given by Lutton *et al.*[4]); these were confirmed by capillary-tube methods. The forms obtained by crystallisation from solvent were examined both as Nujol mulls and in KCl discs: *X*-ray data on all the polymorphic forms were also obtained, and are in good agreement with those given by Lutton *et al.*[4]

The α_L-forms were obtained by quenching the melt to 0°, the β'_L-forms by warming the α_L-form to the transition temperature and also by rapid crystallisation from light petroleum or alcohol; the β_L-forms were obtained by heating the β'_L-forms to the transition temperature or by keeping them at this temperature for some time, and also by slow crystallisation from, *e.g.*, acetone.

Discussion

The polymorphic forms of the triglycerides previously examined by the infrared spectroscopic method have given spectra which can be classified into three main types.[1] Whilst the spectra within a certain type vary slightly from one glyceride to another, notably in the 1250 cm.$^{-1}$ region, each type has a certain " family " appearance. This supports a similar classification of these glycerides [5] on the basis of their *X*-ray short spacings, such a classification being possible because of the general constancy of packing of the hydrocarbon chains in the different forms. Forms designated[1] α_L are considered to have hexagonal packed chains; β'_L-forms probably have orthorhombic packed chains, and β_L triclinic packed chains.

The spectra of the myristo-palmitins and -stearins show that the polymorphic forms of these glycerides (apart from the higher intermediate form of 2-myristodistearin) fit this classification. The β_L-forms show a single band at 718 cm.$^{-1}$ and a prominent band at

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[1] Part III, Chapman, *J.*, 1957, 2715.

[2] Chapman, *J.*, 1956, 55, 2522.

[3] Malkin and Meara, *J.*, 1939, 103; Carter and Malkin, *J.*, 1939, 577.

[4] Jackson and Lutton, *J. Amer. Chem. Soc.*, 1949, **71**, 1976.

[5] Lutton, *J. Amer. Oil Chemists' Soc.*, 1950, **27**, 276.

890 cm.$^{-1}$, similar to those of other saturated glycerides previously designated β_L, *e.g.*, tristearin. (This is despite the fact that the stable β_L-forms of 2-myristodipalmitin and 1-palmitodimyristin are of double-chain-length structure whilst the β_L-forms of the two stearo-analogues have the triple-chain-length structure.) The α_L-forms show a single band at 720 cm.$^{-1}$, whilst the β'_L-forms show a doublet at 726 and 719 cm.$^{-1}$. These also are similar to those of the corresponding forms of other saturated triglycerides.[1,2]

FIG. 1.

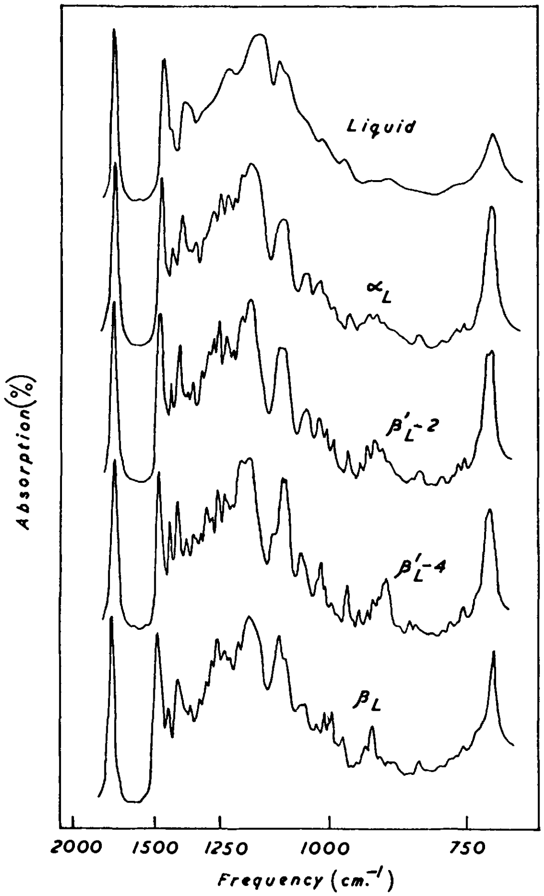

FIG. 2.

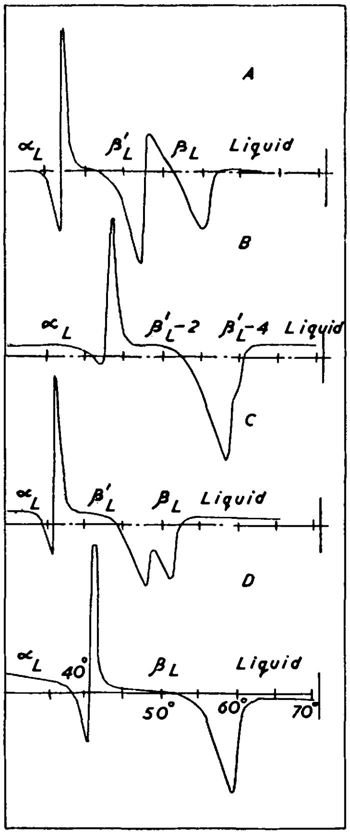

FIG. 1. *Infrared spectra of polymorphic forms of 2-myristodistearin.*

FIG. 2. *Differential heating curves of (A) 1-stearodimyristin, (B) 2-myristodistearin, (C) 1-palmitodimyristin, and (D) 2-myristodipalmitin.*

There are other differences between the spectra of the polymorphic forms of each glyceride, notably in the intensity patterns in the 1250 cm.$^{-1}$ region. The spectra of each of the β_L-forms of these glycerides show small differences from each other in this region. The major bands are similar to those observed in other triglycerides, *e.g.*, the β_L- forms have a strong band between 1730 and 1740 cm.$^{-1}$ and two strong bands near 1170—1180 and 1100 cm.$^{-1}$.

Owing to the rapidity of the intermediate transition in 2-myristodipalmitin, only the spectra of two forms α_L and β_L could be obtained, although there was slight evidence for the intermediate transition, *e.g.*, a fleeting asymmetrical broadening of the 720 cm.$^{-1}$ band before the transition to the β_L-form. (This can be compared with the behaviour of the homologous glyceride, 2-palmitodistearin, where only two forms were observed.[3])

The spectrum of the higher-melting intermediate form of 2-myristodistearin (see Fig. 1) is different from that of the β′-2 form. One outstanding feature is that a band at 1193 cm.$^{-1}$ becomes as strong as that at 1174 cm.$^{-1}$. The spectrum also shows that the band at 720 cm.$^{-1}$ is asymmetrically broadened on the high-frequency side, indicating the presence of a doublet not clearly resolved; and a strong band at 886 cm.$^{-1}$ is present. When further heated, this form melts (when held at 50—60° for some time it changes into the stable β-3 form). Lutton[5] designates the intermediate form as β'_L-4. The long spacing is greater than that of the β′-2 form and the short spacings also differ. This form, however, fits Lutton's *X*-ray short-spacing classification.

Since the doublet in the 720 cm.$^{-1}$ region for the β'_L-4 form is not clearly resolved we may predict that the interchain distances in this form are perhaps greater than in the β'_L-2 forms since the extent of the splitting depends on the interaction forces. It may be, however, that the chains are packed only approximately in the orthorhombic manner. The relation of the packing of long-chain compounds to the appearance of the 720 cm.$^{-1}$ band has been discussed elsewhere.[6]

Whilst four forms are found for 2-myristodistearin the spectra are consistent with the conclusions of Lutton *et al.*[4] rather than those of Malkin *et al.*[3], in that they do not suggest that one of them is vitreous. Deductions analogous to those given previously for other saturated triglycerides[1] can be made about the spectra and their relation to crystal forms.

APPENDIX

A differential calorimeter has been recently shown to be valuable for studying commercial fats[7a] and pure glycerides.[7b] The present glycerides have been studied with this apparatus and the resultant heating curves are shown in Fig. 2. The glyceride was melted and quenched in ice, placed in the calorimeter at a temperature some 10° below that of the lowest-melting form, and heated at a rate of 1·1° per minute until finally molten. (The temperatures given on the curves are accurate within ±1·5°.)

When 1-stearodimyristin is heated, some melting of the α_L-form occurs, followed by rapid evolution of heat and transition into the β'_L-form. When further heated, this form melts, gives out heat, and is transformed into the stable β_L-form. This in turn melts and finally becomes liquid. Thus three forms are observed and there is no evidence for an intermediate form having m. p. 52°.

When 2-myristodistearin is heated, a small amount of melting of the α_L-form occurs, followed by rapid evolution of heat and transition into the β'_L-2 form. This form melts and is transformed very rapidly into the β'_L-4 form which when further heated melts and becomes liquid. (The stable β_L-form is obtained only after some hours at 50—60°.)

With the 1-palmitodistearin, some melting of the α_L-form occurs, followed by rapid transition into the β'_L-form. When further heated this form melts and is transformed into the β_L-form. On being further heated this melts and becomes liquid.

When 2-myristodipalmitin is heated, some melting of the α_L-form occurs, followed by evolution of heat and transition into the stable β_L-form. This in turn melts and becomes liquid. No evidence for a β'_L-form is observed.

Malkin[8] has recently emphasised the use of heating and cooling curves for the study of the polymorphism of glycerides. It is evident that the differential calorimeter will play an important rôle in many future studies.

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[6] Chapman, *J.*, 1957, 4489.

[7] (*a*) Hannewijk and Haighton, (*b*) Lavery, *J. Amer. Oil Chemists' Soc.*, in the press.

[8] Malkin, " Progress in the Chemistry of Fats and other Lipids," Vol. II, Pergamon Press Ltd., London, 1954.