942. *Infrared Spectra and the Polymorphism of Glycerides. Part V.** 1 : 2-*Diglycerides.*

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The polymorphism of some 1 : 2-diglycerides has been investigated by means of infrared spectroscopy between 3500 and 670 cm.$^{-1}$. The spectra are discussed in terms of the packing of the hydrocarbon chains in the crystals and are compared with that of the 1 : 3-isomer.

INFRARED spectroscopy has recently been applied to the study of the polymorphism of a variety of long-chain compounds including alcohols, esters, and glycerides.[1,2] It is here applied to the study of the polymorphism of some 1 : 2-diglycerides. Howe and Malkin[3] previously examined these glycerides by thermal and *X*-ray methods. It is of interest to see whether the spectra of these forms fit the general pattern already found for other types of glycerides, and to contrast the spectra with those of the 1 : 3-isomers.

EXPERIMENTAL.

The 1 : 2-diglycerides (laurin, myristin, palmitin, and stearin) were made by Mr. I. P. Freeman[4] of these laboratories. A sample of 1 : 2-dilaurin was also kindly presented by Dr. T. Malkin of Bristol University.

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* Part IV, *J.*, 1958, 3186.

[1] Chapman, *J.*, 1956, 53, 2522; 1957, 2715.

[2] Chapman, 6th Internat. Spectroscopic Colloquium Symp., Amsterdam, 1956.

[3] Howe and Malkin, *J.*, 1951, 2663.

[4] Freeman and Pierce, unpublished work.

Experimental details were similar to those described in the earlier papers.[1] *X*-Ray results on the most stable form of each glyceride were in good agreement with those given by Howe and Malkin.[3] Two polymorphic forms were observed for each glyceride. Crystallisation from solvents gave the higher-melting forms. Re-solidification from the melt gave the lower-melting form. Holding the lower-melting form for many hours near its m. p. converted it into the higher-melting form.

Thermal data for the 1 : 2-diglycerides (Table) are in good agreement with those given by Howe and Malkin.[3]

Melting points.

	$\alpha_L = \alpha_M$	$\beta_L' = \beta_M$		$\alpha_L = \alpha_M$	$\beta_L' = \beta_M$
Dilaurin	19·7°	38·2°	Dipalmitin	49·7—50°	61°
Dimyristin	37·1	51·7	Distearin	59·9	71

RESULTS AND DISCUSSION.

The spectra of the liquid and of each of the polymorphic forms of the four 1 : 2-diglycerides were obtained. Apart from the 1250 cm.$^{-1}$ region where the number of bands present increased with increasing chain length, the spectrum of a particular form bears a marked " family " resemblance to those of its homologues. Only the spectra of the liquid and the crystalline forms of 1 : 2-distearin are therefore discussed in detail (see Fig. 1).

Liquid State.—The spectrum is rather typical of that obtained from other glycerides in the liquid state. Prominent bands occur at 3407, 1743, 1463, 1418, 1374, 1240, 1166, 1116, 1097, 1054 and 720 cm.$^{-1}$.

Crystalline Forms.—First form. Solidification from the melt gives the first crystalline form, whose bands occur at 3385 and 1740 cm.$^{-1}$. The band previously at 1418 cm.$^{-1}$ shifts to 1416 cm.$^{-1}$ and that originally at 1166 shifts to 1178 cm.$^{-1}$. A series of bands occur in the 1250 cm.$^{-1}$ region, at 1342, 1329, 1309, 1290, 1272, 1253, 1234, 1214, and 1194 cm.$^{-1}$ spaced about 18 cm.$^{-1}$ apart. These bands probably arise from CH_2 wagging vibrations.[5] Strong bands also occur at 1104, 1062, and 1045 cm.$^{-1}$. The band at 720 cm.$^{-1}$ is single and increased in intensity.

When this form was heated to 59° and the spectrum scanned, the material was observed to melt and the spectrum of the liquid form was again obtained.

Second form. Crystallisation from solvent gave the second form, whose spectrum shows many differences from that of the first. Prominent bands occur at 3468, 1733, and 1709 cm.$^{-1}$. The band at 1416 cm.$^{-1}$ in the spectrum of the first form now shifts to 1423 cm.$^{-1}$. The bands in the 1250 cm.$^{-1}$ region have the same frequencies (within experimental limits) as for the first form, but the relative intensities of the bands are greatly altered. A doublet occurs at 1109 and 1092 cm.$^{-1}$, a strong band at 1066 cm.$^{-1}$, and weak bands at 1042, 1028, 958, 873, 886, 842, 810, and 758 cm.$^{-1}$. There are two components at 729 and 719 cm.$^{-1}$.

The spectrum of 1 : 3-distearin in its crystalline form is also shown in Fig. 1. The remarkable difference between the spectra suggests that the isomeric configuration of unknown diglycerides of this type may be easily deduced by means of their infrared spectra.

A line diagram showing the bands in the 1250 cm.$^{-1}$ region of the four glycerides is shown in Fig. 2. As is observed with anhydrous sodium soaps there is an empirical relation between the number of bands and the length of the aliphatic chain, *viz.*, the number of bands is equal to half the number of carbon atoms in the chain. Further, the frequency difference between the band of highest frequency and the next lower band is always less than the frequency difference between the other bands. This may be related tentatively to the presence of the α-methylene group, where the influence of the carbonyl group is greatest. The frequency difference between the remaining bands is approximately constant for each glyceride.

The lowest-melting forms of these glycerides have been designated[3] α-forms. Their infrared spectra support this designation, by analogy with the spectra of the α-forms of hydrocarbons, alcohols, and esters.[2] There is moreover a strong general resemblance

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[5] Sinclair, McKay, and Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2570; Chapman, *J.*, 1958, 784.

between this type of spectrum and that of the lowest-melting form of saturated triglycerides, recently designated [1] an α_L-form. Two components occur at 729 and 719 cm.$^{-1}$ in the spectrum of the higher-melting form, as in the spectra of the forms previously designated β_L' for saturated triglycerides and monoglycerides, confirming the significance of the general classification.[1] (The main *X*-ray short spacings are at 3·8 and 4·2 Å; cf. Lutton.[6])

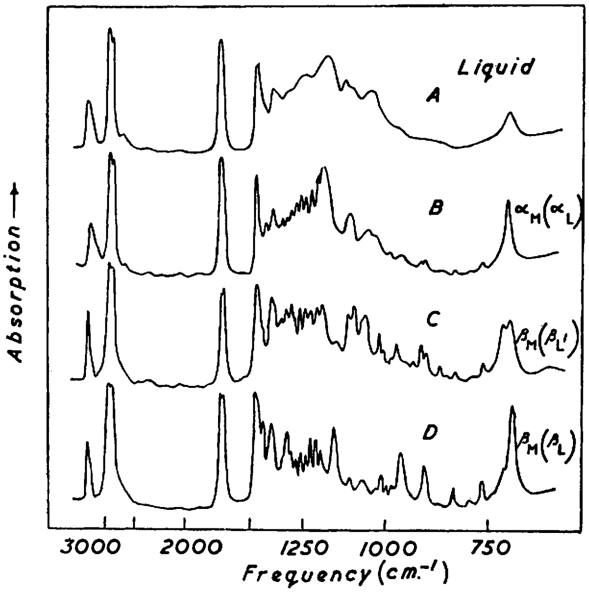

FIG. 1. *Infrared spectra of* (*A*, *B*, *C*) 1 : 2-*distearin and* (*D*) 1 : 3-*distearin.*

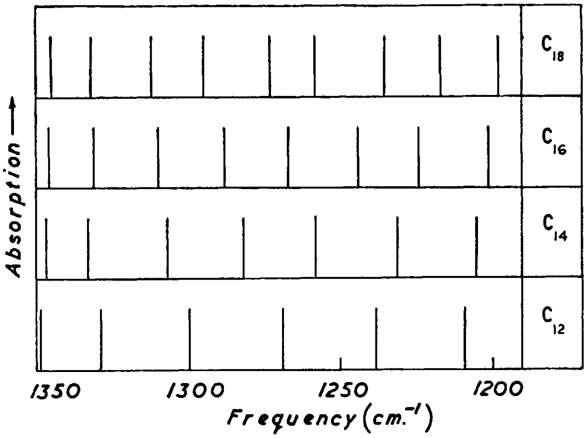

FIG. 2. *Line diagrams of infrared spectra of triglycerides in the* 1250 *cm.*$^{-1}$ *region.*

We can deduce that the hydrocarbon chain packing in the $\alpha_L(\equiv \alpha_M)$-form of the 1 : 2-diglycerides is hexagonal, whilst in the $\beta_L'(\equiv \beta_M)$-form the chains are very probably packed predominantly in the orthorhombic manner as is common with many long-chain hydrocarbons and other long-chain crystals.[7] This contrasts with the polymorphism of 1 : 3-diglycerides where both main crystal forms appear to have the hydrocarbon chains packed in the triclinic manner (cf. the single band at 717 cm.$^{-1}$ in the spectrum of 1 : 3 distearin).

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[6] Lutton, *J. Amer. Oil Chemists' Assoc.*, 1950, **27**, 276.
[7] Chapman, *J.*. 1957, 4489.