84. *Nuclear Resonance Spectra of the Polymorphic Forms of Glycerides.*

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Nuclear resonance spectra have been obtained at temperatures between 20° K and room temperature for a number of fatty acid glycerides in various crystalline modifications. The spectra are discussed in terms of the different types of molecular motion which occur in the various crystalline modifications at room temperature. The method proves to be complementary to infrared spectroscopy. The α_L- can be very readily distinguished from the β_L- and β_L'-forms, and in some cases, where there is a double bond in one of the chains or a significant difference in chain length, all three forms can be classified easily.

MANY long-chain compounds show polymorphism, *i.e.*, exist in more than one crystalline form. The glycerides of the long-chain fatty acids may assume as many as three or four modifications and it is sometimes important in the analysis of natural oils and fats to be able to determine the polymorphic forms of glyceride present.

The crystalline modifications have been studied extensively by *X*-ray [1] and by infrared spectroscopy; [2] the latter is particularly convenient for detecting orthorhombic packing of the hydrocarbon chains but is not so good for distinguishing between triclinic and hexagonal packing.

The hydrogen resonance spectra of a number of glycerides have now shown that the degree of molecular motion in the crystals at room temperature varies with the crystalline modification. These spectra therefore give further insight into the structures of these crystals and provide a method of distinguishing between them.

EXPERIMENTAL

The nuclear magnetic resonance spectra of the polymorphic modifications at the various temperatures were obtained with the apparatus which has been described by Richards and Smith, and by Pratt and Richards.[3]

The glycerides were very kindly supplied by Dr. D. Chapman of Unilever Limited. They were all in the stable polymorphic forms obtained by recrystallization from solvents.

Tristearin and Tripalmitin.—The compounds were received in the β_L-modifications. The

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

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

[3] Richards and Smith, *Trans. Faraday Soc.*, 1951, **47**, 1261; Pratt and Richards, *ibid.*, 1953, **49**, 744.

α-forms were prepared by quenching the melted samples in ice-water. The β_L'-form of tristearin was obtained by melting the sample and allowing it to cool very slowly and to crystallize in a bath at 61°, *i.e.*, several degrees above the m. p. of the α-form (54·5°). The sample was kept at this temperature for 30 min.

The β_L'-form of tripalmitin was obtained in a similar way by cooling the melted sample very slowly and placing it to crystallize in a bath at 52° for 0·5 hr. Nuclear resonance measurements on the samples were carried out at the temperatures indicated in Tables 1 and 2.

TABLE 1. *Line widths.*

Compound	β	β′	α	Sub-α	Sub-β	Temp. (K)
Tristearin	12·9 ± 0·2		6·8 ± 0·1			293°
	14·6 ± 0·3			14·8 ± 0·2		90
				14·3 ± 0·2		20
Tripalmitin	13·0 ± 0·4		6·8 ± 0·3			293
1,2-Distearin		13·5 ± 0·4	5·9 ± 0·1			293
		14·7 ± 0·4		14·8 ± 0·3		90
1,2-Dipalmitin		12·9 ± 0·6	5·2 ± 0·1			293
1,3-Distearin	12·1 ± 0·2	12·0 ± 0·1				293
1,3-Dipalmitin	11·1 ± 0·4	10·8 ± 0·5				293
1-Monostearin	12·7 ± 0·5			13·1 ± 0·2		293
			4·0 ± 0·1			323
1-Monomyristin	12·9 ± 0·4			12·6 ± 0·4		293
			4·3 ± 0·2			303
2-Monopalmitin	11·7 ± 0·6					293
1-Stearodimyristin	11·7 ± 0·2	0·9	6·5 ± 0·2			293
1-Oleodistearin		0·9	0·8			293
		13·4 ± 0·4		10·5 ± 0·3		195
		14·2 ± 0·2		14·0 ± 0·6		90
1-Oleodipalmitin		0·9	0·8			293
		14·2 ± 0·5		14·4 ± 0·2		90
2-Oleodistearin	11·6 ± 0·6		0·8/4·2 ± 0·2		10·4 ± 0·3	293
1-Mono-olein	8·0 ± 0·3	7·5 ± 0·6				293
			9·4 ± 0·8			273
Triolein	11·7 ± 0·2					273

TABLE 2. *Second moments.*

Compound	β	β′	α	Sub-α	Sub-β	Temp. (K)
Tristearin	22·2 ± 0·7		11·1 ± 0·3			293°
	24·7 ± 0·6			24·3 ± 0·2		90
				24·4 ± 1·1		20
Tripalmitin	20·4 ± 1·5		9·8 ± 0·4			293
1,2-Distearin		22·4 ± 0·9	8·1 ± 0·3			293
		25·2 ± 0·4		24·5 ± 0·5		90
1,2-Dipalmitin		20·6 ± 1·1	7·2 ± 0·2			293
1,3-Distearin	20·1 ± 0·7	19·0 ± 0·6				293
1,3-Dipalmitin	18·5 ± 1·3	17·6 ± 0·8				293
1-Monostearin	19·9 ± 1·7			20·0 ± 1·3		293
			4·5 ± 0·1			323
1-Monomyristin	19·7 ± 1·3			19·8 ± 1·4		293
			5·7 ± 1·0			303
2-Monopalmitin	18·2 ± 0·9					293
1-Stearodimyristin	19·1 ± 1·5	15·1 ± 0·4	9·3 ± 0·4			293
1-Oleodistearin		14·9 ± 1·0	0·5 (<1)			293
		20·4 ± 1·4		17·8 ± 1·4		195
		24·7 ± 0·6		24·9 ± 0·9		90
1-Oleodipalmitin		14·3 ± 0·5	0·6 (<1)			293
		24·3 ± 0·9		24·4 ± 0·5		90
2-Oleodistearin	20·2 ± 0·8		0·5/6·6 ± 0·6		16·1 ± 0·5	293
1-Mono-olein	13·1 ± 0·5	12·9 ± 1·4				293
			13·7 ± 1·2			273
Triolein	16·7 ± 0·3					273

1,2-*Distearin and* 1,2-*Dipalmitin*.—Samples of these compounds were received in the β_L'-forms. The lower-melting α_L-forms were obtained by melting the samples and allowing them to crystallize at room temperature.

1,3-*Distearin and* 1,3-*Dipalmitin*.—The β_M'-forms were prepared from the β_M-forms by melting the samples and allowing them to cool slowly to room temperature.

1-*Monostearin and* 1-*Monomyristin.*—The sub-α_L-forms were prepared by melting the β_L-forms and allowing them to crystallize at room temperature. The sub-α_L-form of 1-monostearin changes reversibly into the α_L-form at 47°. The nuclear resonance spectrum of the α_L-form was therefore obtained at 50°. Similarly the transformation between the α_L- and the sub-α_L-form of 1-monomyristin occurs at 24°. To obtain the pure α_L-form it was necessary to melt the glyceride and cool it to 30°, at which the nuclear magnetic resonance spectra were measured.

2-*Monopalmitin.*—This compound only occurs in the β_L-form. The crystals were melted, the melt was allowed to crystallize at room temperature, and the measurements were repeated.

1-*Stearodimyristin.*—The α-form was obtained by quenching the molten β_L-form in ice-water. The β_L'-form was prepared by keeping the α_L-form at 36° for about 10 min. The β_L-form was also regenerated from the melted crystals by maintaining the α_L-form at 47° for 10 min.

1-*Oleodistearin and* 1-*Oleodipalmitin.*—The α_L-forms of these compounds were prepared by melting the β_L'-forms and quenching them in ice-water. Preparation of the sub-α_L-form of 1-oleodistearin was attempted as it probably undergoes transformation at 0° from the sub-α_L- into the α_L-form. The β_L'-form was melted and placed in the sample coil, and the screening can was quickly soldered into position. The assembly was plunged into acetone cooled with solid carbon dioxide in a Dewar vessel at $-12°$. Runs were carried out at $-10°$. The experiment was repeated at $-20°$. The sample was then allowed to warm to 0° and runs were carried out at this temperature. Measurements were also made on both the β_L'- and the α_L-form of 1-oleodistearin at $-78°$.

2-*Oleodistearin.*—The molten β_L-form of this compound was quenched in ice-water. Nuclear resonance measurements were then made at room temperature. This heat treatment would be expected to give a mixture of the α_L- and the sub-β_L-form. The sample was crystallized at 0° by placing the melted sample in the coil, quickly soldering the screening can into position, and plunging the assembly into a Dewar vessel containing ice-water. Measurements were then made at this temperature. The sample was melted and allowed to crystallize at about 30°. The spectra were quickly measured at room temperature. Finally, the sample was melted and then allowed to cool very slowly to room temperature over a period of one week. The spectra were then measured again at room temperature.

1-*Mono-olein.*—The modification obtained by recrystallization from a solvent is believed to be the β_L-form. This was melted, and then quenched in ice-water, and measurements were obtained at room temperature. Under these conditions the β_L'-form should be present. Finally the preparation of the α_L-form was attempted by crystallizing the sample at 0° and making the measurements at this temperature.

Triolein.—This substance is liquid at room temperature. It was cooled in solid carbon dioxide–acetone, soldered into the sample holder, and allowed to come to equilibrium at 0° for the nuclear resonance measurements. According to Ferguson and Lutton [4] the β_L-form should be present at 0°.

RESULTS

The line widths and second moments of the nuclear magnetic resonance recordings given by the different polymorphic forms of the glycerides at various temperatures are summarised in Tables 1 and 2. The values are placed in the various columns according to the type of polymorphic form in which the glyceride is believed to be present from recent *X*-ray and infrared investigations (see below). Each value is the mean of six separate determinations and the standard deviations are included in the Tables.

Some of the recordings have very interesting shapes. Many of the glycerides studied gave a line shape similar to that in Fig. 1. This occurred at room temperature as well as at the lower temperatures. The line shape from the β_L'-form of 1-stearodimyristin is illustrated in Fig. 2.

At room temperature the α_L-form of 1-oleodistearin gave a very narrow line, and repeated conversion among the various modifications and back to the α_L-form always gave identical results. A slow conversion into the β_L'-form was indicated by the appearance of a broader line of second moment 14·9 gauss^2. The overall line shape is illustrated in Fig. 3. Over a period

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[4] Ferguson and Lutton, *J. Amer. Chem. Soc.*, 1947, **69**, 1445.

of a week this broad section became somewhat greater in area. No alteration in the line width of the α_L-line was noticed in this time.

When 2-oleodistearin was melted and then quenched in ice-water and measurements were made quickly at room temperature, a narrow line of the shape shown in Fig. 4 and with a second moment of 6·6 gauss^2 was obtained. After 10—15 min. the line shape had changed to that in Fig. 5 where the broad section had a second moment of 16·1 gauss^2 and the narrow section a second moment of less than 1 gauss^2. These observations could be repeated without difficulty. Such treatment would be expected to give a mixture of the α_L- and the sub-β_L-form of 2-oleodistearin. Similar phenomena were obtained when molten 2-oleodistearin was cooled to 0° and runs were carried out at this temperature. The final line shape was identical with that at room temperature. When the melted sample was allowed to crystallize at about 30° and runs were quickly carried out at room temperature, the final line shape was obtained immediately, with apparently no sign of the line shown in Fig. 4. Finally the line shape of Fig. 5 was obtained when the melted sample was allowed to cool very slowly to room temperature during one week.

FIG. 1.

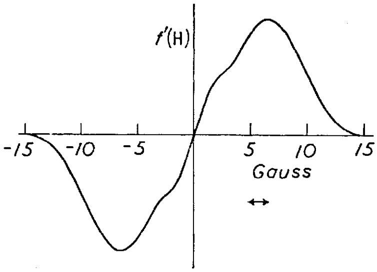


FIG. 2.

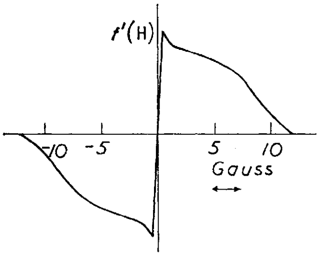


FIG. 3.

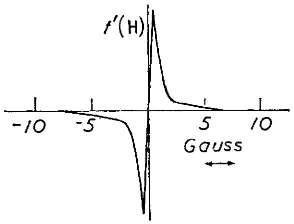


FIG. 4.

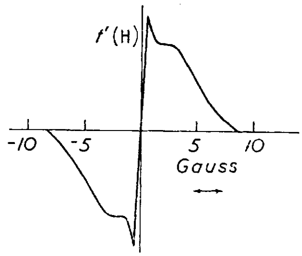
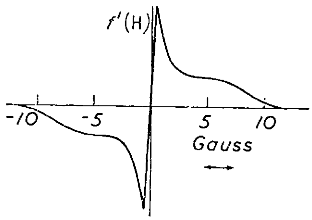


FIG. 5.



Derivative of hydrogen resonance of (FIG. 1) *tristearin in β-form,* (FIG. 2) 1-*stearodimyristin in β′-form,* (FIG. 3) 1-*oleodistearin, mixture of α- and β′-forms,* (FIGS. 4 *and* 5) 2-*oleodistearin* (*see text*).

DISCUSSION

In all our compounds, long hydrocarbon chains constitute the major part of the molecule. The packing of the chains has been shown by *X*-ray [1] and infrared spectroscopic methods [2] to be similar to that which occurs with long-chain hydrocarbons with orthorhombic, triclinic, or hexagonal sub-cells.

The second moment of the proton resonance at low temperatures can be estimated in much the same way as for the pure hydrocarbons.[5] For an infinite chain of rigid CH_2 groups the total second moment would be about 27 gauss^2, but the contribution of terminal methyl groups is usually less than this because of rotational motion even at the lowest temperatures.[6] The CH group of the glycerol also makes a rather smaller contribution and so, although an exact estimate of the expected second moment of a glyceride cannot easily be made, its hydrogen resonance is likely to have a low-temperature value of about 25 gauss^2. The intermolecular contributions in the orthorhombic and the triclinic forms are not significantly different. The line shape is expected to be structureless, but the small second-moment contribution of the methyl groups and of the CH group of the

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[5] Andrew, *J. Chem. Phys.*, 1950, **18**, 607.

glycerol residue may cause the absorption curve to have a weak but narrow component. This is observed in many cases and an example is shown in Fig. 1.

At higher temperatures the hydrocarbon chains are expected to undergo hindered reorientational motion about the chain axis,[5] and when this motion is rapid enough the resulting second moment is reduced. This motion occurs with the long-chain hydrocarbons in the hexagonal forms, and the reduced intramolecular contribution to the second moment is 6·8—11·6/(n + 1) for the hydrocarbon C_nH_{2n+2}.[5] If this formula is applied to a glyceride such as 1,2-distearin ($n = 18$), the intramolecular contribution to the second moment is found to be 6·2 gauss^2. For a hydrocarbon the intermolecular broadening [5] is about 2·6 gauss^2 and this would give a total of 8·8 gauss^2.

If, instead of undergoing hindered reorientation, the chains oscillate about the chain axis, a reduction of the second moment is also expected. The greater the amplitude of oscillation the greater the reduction of second moment [5] and, for example, if the oscillation amplitude is 60°, 45°, or 30° the reduction in second moment is 56%, 43%, or 25% respectively. Reduction of second moment less than that expected for rapid reorientation could therefore be interpreted as arising either from incomplete reorientation (torsional oscillation) of all the chains or from complete reorientation of only part of the chains.

At temperatures not above 90° K all the compounds studied have second moments of 24—25 gauss^2 and thus have " rigid lattices " at these temperatures. At room temperature the β_L-, β'_L-, sub-α_L-, and sub-β_L-forms have large second moments, although they are to varying degrees smaller than the low-temperature values. The results for the individual compounds are discussed in detail below. The α_L-forms, however, all have second moments at room temperature which are much smaller than the low-temperature values, so that there is considerable molecular motion at room temperature. This type of molecular motion occurs in the hexagonal modifications of hydrocarbon crystals and, indeed, the formation of the hexagonal packing itself indicates that the chains have acquired cylindrical symmetry. The low second moment of the α-forms of the glycerides therefore strongly supports the assignment of the hexagonal configuration to the crystal structures. This general conclusion is in accord with recent *X*-ray and infrared measurements.[2]

A great deal of work has been done on the polymorphism of glycerides, using thermal, *X*-ray, and infrared-spectroscopic methods. On the basis of thermal and *X*-ray methods, Malkin [7] postulated that the lowest-melting form was vitreous. This modification, obtained by rapid crystallization, was considered to possess the characteristics of a glass rather than of a true crystal. The difficulty with an *X*-ray investigation, according to Clarkson and Malkin,[8] was that the vitreous and α_M-forms give rise to the same side spacings and it is therefore impossible to state whether or not a specimen giving the α_M-form spacings contains any vitreous material. The infrared method [9] was unable to detect any persistence of the vitreous state in the crystals. None of the crystals gave a spectrum similar to that of the liquid glyceride. The infrared measurements and *X*-ray measurements by Lutton [10] suggest that the lowest-melting form is an α_L-modification with hexagonal packing rather than a vitreous form, whilst the next higher-melting form, designated α by Malkin, was almost certainly not a form with hexagonal packing of the hydrocarbon chains and was thus wrongly designated. The nuclear magnetic resonance spectra support these conclusions, as discussed below.

Tristearin and Tripalmitin.—The ordinary stable crystalline β_L-forms of these glycerides have triclinic packing of the hydrocarbon chains. The second moments at room temperature show that in this modification the chains are not reorienting themselves at

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[6] Richards and Yorke, unpublished work.

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

[8] Clarkson and Malkin, *J.*, 1934, 666; 1948, 985.

[9] Chapman, *J.*, 1956, 2522.

[10] Lutton, *J. Amer. Chem. Soc.*, 1945, **67**, 524.

frequencies greater than 100 kc./sec. The second moments at room temperature are, however, slightly lower (about 2 gauss^2) than the rigid value at low temperatures, and this may be interpreted in terms of reorientation of a few small segments of the chain or as torsional oscillation of the whole chain about its axis. In the case of the tristearin an amplitude of oscillation of about 17° would be required. Tripalmitin, with a second moment of 20·4 gauss^2, evidently has a slightly greater freedom of motion and this is consistent with its lower melting point.

The α_L-forms of tristearin and tripalmitin at room temperature have second moments of 11·1 and 9·8 gauss^2 respectively, close to the value of 9 gauss^2 estimated (see above) for a crystal in which the hydrocarbon chains are freely reorienting about the chain axis. This suggests that the crystal structure is hexagonal and confirms the interpretation of infrared and *X*-ray measurements by Chapman [9] and Lutton.[10] The glycerol residue in the glycerides may hinder the free motion of the hydrocarbon chains slightly and this would explain why their second moments are greater than that estimated for straight-chain hydrocarbons.

The α_L-form in other glycerides is believed [11,12] to be transformed reversibly into a sub-α_L-polymorph at lower temperatures. It is likely therefore that with tristearin at 90° K this transformation has taken place and the sub-α-form, which probably has orthorhombic packing of the hydrocarbon chains, is present.

The β'_L-forms have second moments which are the same as those for the β_L-forms, consistently with the orthorhombic packing attributed to this modification by Chapman [9] on the basis of infrared measurements.

1,2-*Distearin and* 1,2-*Dipalmitin.*—These substances occur in two polymorphic forms only. They also differ from the triglycerides in that the highest-melting form obtained by crystallisation from a solvent probably has orthorhombic packing of the hydrocarbon chains and is classified as β'_L. However, the second moments of this β'_L-form are practically identical with those of the β-forms of tristearin and tripalmitin, and the same conclusions therefore follow with respect to the oscillation of the chains. The second moments of the lower-melting α_L-forms are very close to the value of 9 gauss^2 expected for free reorientation of the chains. This confirms the view that here again the α_L-form has hexagonal packing of the hydrocarbon chains.

1,3-*Distearin and* 1,3-*Dipalmitin.*—The two forms of these substances are classified as β_M and β'_M, but the *X*-ray and infrared measurements [13] indicate that both forms probably have triclinic packing of the chains and differ only in their tilt. The second moments of the β_M and β'_M forms differ by less than 1 gauss^2 for both compounds, and the high values are consistent with triclinic packing in which the chains have some slight freedom of torsional motion.

1-*Monostearin and* 1-*Monomyristin.*—In the β_L-forms the large second moments indicate a triclinic structure similar to that in 1,3-distearin. It is interesting that the second moments of these two compounds are very similar, although the palmitins usually give a slightly lower value than the stearins. This may be connected with the alternating melting points of these compounds.

The sub-α_L-forms also have large second moments, in confirmation of the orthorhombic packing indicated by the *X*-ray short spacings [11] and the doublet at 720 cm.$^{-1}$ in the infrared absorption.[12]

For the α_L-forms, however, the second moments are very small (4·5 at 50° C and 5·7 gauss^2 at 30° C respectively), and in this case it is clear that the chains have considerable freedom of motion, not only about the chain axis. The reduction of second moment from about 9 to about 5 gauss^2 could be caused by some lateral and longitudinal motion of the chains in the crystal. The structure in this form is therefore very probably hexagonal,

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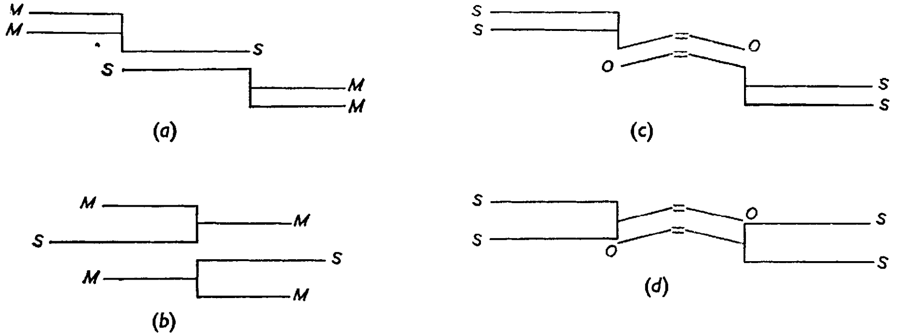
[11] Lutton and Jackson, *J. Amer. Chem. Soc.*, 1948, **70**, 2445.
[12] Chapman, *J.*, 1956, 55.
[13] Chapman, *J.*, 1957, 2715.

as in the previous compounds. It may, however, be that this particular α-modification has some vitreous character.

2-*Monopalmitin.*—The value of 18·2 gauss^2 for the second moment of the ordinary crystalline β_L-form of this substance is as expected and may be compared with the value of 18·5 gauss^2 for 1,3-dipalmitin. 2-Monopalmitin exists only in the β_L-form, because after various thermal treatments the same value of second moment was always obtained.

1-*Stearodimyristin.*—The ordinary crystalline form of this substance is the β_L-modification, in agreement with the second moment of 19·1 gauss^2. The long spacings of the *X*-ray lines[14] indicate, however, that this polymorphic form has a triple-chain-length structure, unlike tristearin and tripalmitin which have a double-chain-length structure. The triple-chain-length structure can probably be represented as in Fig. 6*a*. It has been called a " chair " structure in contrast to the " tuning fork " types of tristearin and tripalmitin. The β'_L-form of 1-stearodimyristin has a double-chain-length structure, however, and can be represented as in Fig. 6*b*. These diagrams are given merely to show the qualitative comparison between the " chair " and " tuning fork " types. The *X*-ray and infrared measurements[15] indicate that the normal orthorhombic packing of the chains occurs in the β'_L-form. The second moment for this modification would have been expected to have been about 18 gauss^2, but in fact it is found to be 15·1 gauss^2. The line shape, which is illustrated in Fig. 2, is also different from that obtained from any β'_L-form above and suggests that it may be made up of two superimposed parts, one of which has a much narrower line width than the other. Inspection of the difference between the triple-chain-length structure of the β_L-form and the double-chain-length structure of the β'_L-form suggests that in the latter the stearic chains (which are four carbon atoms longer than the myristic chains) may not be so well packed as in the β_L-form. Presumably the potential barriers hindering motion of these chains are then lowered enough for part of them to undergo various forms of oscillation which produce a very much narrower line. The second moment of 9·3 gauss^2 for the α_L-form presents no unusual feature. The second moment obtained from samples recrystallised from a solvent and from melting were the same.

FIG. 6. *Packing of hydrocarbon chains in* (*a*) " *triple-chain-length* " *structure,* (*b*) " *double-chain-length* " *structure,* (*c*) 1-*oleodistearin, and* (*d*) 2-*oleodistearin.*



1-*Oleodistearin and* 1-*Oleodipalmitin.*—The normal form of 1-oleodistearin is the β'-modification. This compound gave a line shape and second moment almost identical with those of the β'_L-form of 1-stearodimyristin. Evidently a portion of the molecule undergoes greater motion than the remainder. This form has a triple-chain-length structure and can be represented as in Fig. 6*c*. In this structure the stearoyl chains are closely packed so that reorientation of the hydrocarbon chains is difficult. The oleoyl chains, however, have a double bond which disturbs the regularity of the chains, so that they probably pack less tightly and therefore have greater reorientational freedom. This would explain the line shape observed, which appears to be made up from a narrow and a

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

[15] Chapman, *J.*, 1958, 3186.

broad component. If y is the second moment of the oleoyl chain and the stearoyl chains have the same second moment as in tristearin (22·2) then

$$\text{Observed second moment} = 14{\cdot}9 = \tfrac{2}{3} \times 22{\cdot}2 + \tfrac{1}{3}y \text{ gauss}^2$$

and y has a value of 0·3 gauss ^{2}. This would explain the very narrow line in the spectrum, causing the unusual line shape.

At room temperature the α_L-form gives a very narrow line with a second moment of less than 1 gauss^2. A line width as low as this is rather unusual in a solid and evidently other forms of motion apart from simple rotation are occurring, such as translational motion and flexing of the chains.

Thermal and *X*-ray evidence [16] has been given to show that 1-oleodistearin probably has a reversible sub-α_L- to α_L-transformation at 0° C. The sub-α_L-form was obtained by chilling the melt to low temperatures, but oleodipalmitin showed no sub-α_L-form (although it was not examined below 0° C). After thermal treatment in an attempt to give the sub-α_L-form measurements at $-10°$ and $-20°$ showed the same line shape as above with a strong narrow α_L-line. When the sample was allowed to warm again to 0°, the same line shape was obtained. The persistence of the broad line below 0° shows that either the β'_L-form is still present, or some conversion occurs into the sub-α_L-form which, from the work on 1-monostearin, would also be expected to give a broad line. The persistence of the narrow component below 0°, which implies that a significant amount of α-form remains, may possibly be caused by the low thermal conductivity of the glycerides.

As the temperature is lowered still further, the second moment increases to 17·8 gauss^2 at $-78°$ and reaches the fully rigid value of 24·9 gauss^2 at 90° K. At $-78°$ C the second moment of the melted form is slightly lower (by 2·6 gauss^2) than the β'_L-form.

2-Oleodistearin.—The ordinary crystalline form has the β_L-structure, unlike 1-oleodistearin which occurs in the β'_L-modification. It has a triple-chain-length structure [17] which can be represented as in Fig. 6*d*. The second moment and line shape are very similar to those obtained from the β_L-forms of the other glycerides studied. It therefore appears that, although the double bond confers motional freedom in the orthorhombic packing of 1-oleodistearin and 1-oleodipalmitin, it permits a rigid structure in the triclinic packing of 2-oleodistearin.

When the 2-oleodistearin was melted and then quenched at 0°, the hydrogen resonance at room temperature gave a second moment of 6·6 gauss^2 and a line shape as in Fig. 4 which changed in a few minutes to that of Fig. 5, with a broad component of second moment 16·1 gauss^2 and a very sharp component.

This heat-treatment should give a mixture of α_L- and sub-β_L-modifications, but the packing in the sub-β_L-form is not known.[17]

The observed line shape could be interpreted in two ways. It may be that the original absorption curve (Fig. 4) arises from the α_L-modification (as its second moment of 6·6 gauss^2 is in line with that of the other α_L-forms of glycerides) and that after 15 min. at room temperature some sub-β_L-modification is formed which may give a curve similar to that of the β'_L-form of 1-oleodistearin with the component due to the remaining α_L-form lost beneath it. Alternatively, the initial result may be only a glassy state with a second moment of 6·6 gauss^2, crystallization occurring after 15 minutes at room temperature. The narrow component would then be interpreted as due to the α_L-form (as in 1-oleodistearin and 1-oleodipalmitin) and the broad component as due to the sub-β_L-form.

Repeating these experiments at 0° instead of at room temperature gave similar results. If, however, the sample was melted, allowed to crystallize at 30° C, and then measured immediately at room temperature, the line shape obtained was as in Fig. 5, and there was

[16] Lutton, *J. Amer. Chem. Soc.*, 1951, **73**, 5595.

[17] Lutton, *J. Amer. Chem. Soc.*, 1946, **68**, 676.

apparently no indication of the presence of the form giving the curve of Fig. 4. Unfortunately this does not resolve the ambiguous interpretation of these curves, because either the glassy state may not have been formed under these conditions, or the α_L-form (with m. p. of 22·4°) may not be formed in appreciable quantities under these conditions.

The line shape of Fig. 5 is also obtained if 2-oleodistearin is melted and allowed to cool slowly to room temperature during 10 days, and this treatment has been said to produce the sub-β_L-form.[18]

1-*Mono-olein.*—*X*-Ray and thermal measurements by Malkin and Carter[19] were interpreted in terms of four modifications, but on the basis of other work on glycerides[10] these results would be regarded as due to three forms, α_L, β'_L, and β_L with postulated m. p. of 12·5°, 25°, and 35°, respectively. Hydrogen resonance curves were obtained for the normal form at room temperature and again after two types of heat-treatment which were designed to produce the α_L- and the β'_L-form. In each case the line shape and second moments were identical within experimental error. This means either that only one modification existed under these experimental conditions, or that the degree of molecular motion in the different modifications is remarkably constant. According to Daubert and Lutton,[20] 1,3-diolein occurs only in one form.

Triolein.—The β_L-form of this substance at 0° gave a second moment of 16·7 gauss^2. As in the case of 1-mono-olein, the second moment is lower than that for the β_L-form of the saturated glycerides, and again this may arise from the effect of the double bond on the packing of the chains.

Conclusion.—The nuclear magnetic resonance method proves to be complementary to infrared spectroscopy in the study of the crystalline modifications of the glycerides. The α_L-forms can be very readily distinguished from the β_L- and β'_L-forms, and in some cases, where there is a double bond in one of the chains or a significant difference in chain length, all three forms can be classified easily. The method appears to fail only when all the chains are unsaturated.

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[18] Lavery, *J. Amer. Oil Chemists' Soc.*, 1958, **35**, 418.
[19] Malkin and Carter, *J.*, 1947, 554.
[20] Daubert and Lutton, *J. Amer. Chem. Soc.*, 1947, **69**, 1449.