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Infrared spectra of monoacid triglycerides

with some applications to fat analysis



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Abstract

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Methods for characterization of fatty products and for the detection of foreign fats are discussed.

The polymorphism of triglycerides as apparent from melting behaviour, X-ray diffraction, electron diffraction and infrared spectroscopy is reviewed.

Infrared spectra between 1500 and 400 cm^{-1} of even and odd triglycerides are given: from C_7 to C_{22} of the α , β' and β forms at -180° and of the liquid forms at room or elevated temperature; from C_2 to C_6 of the liquid form at -180° and room temperature.

The majority of strong and medium bands of the solid state spectra are assigned to molecular vibrations. Some deuterated compounds have also been studied.

The concept 'diathesis' is introduced to describe the intramolecular behaviour as apparent from vibrational spectra. The length of the fatty acid chains can be concluded from the spectra.

Some applications for the detection of beef tallow in milk fat and in lard are mentioned.

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Foreword

The development of the instrumental methods of spectrophotometry and gas-liquid chromatography in the last two decades allowed a complete and rapid determination of the fatty acid composition of fats and oils and gave a tremendous impulse to fat chemistry and fat analysis. In the beginning of this new period, however, expectations for the use of infrared spectrophotometry in this field were not very high. Except for *trans*-unsaturated compounds, natural fats of different origin are similar in structure, so that their infrared spectra would not differ significantly. At that time, therefore, spectrophotometric and chromatographic methods were hardly used in fat research because of the expense and complexity of apparatus.

Developments in the field of solid state spectra, in the sixties, in particular the work of Chapman, gave a new dimension to the infrared analysis of fatty products. His work has helped considerably to sort out confusions about crystalline forms of triglycerides. He was able to determine the structure of natural fat components by infrared-spectrophotometry where other methods had failed.

The author of this book pursued this subject and completed it in such a way that we now have at our disposal a list of infrared spectra of all monoacid triglycerides from triacetin up to tribehenin in their various phases, either liquid or crystalline. Special attention has been paid to the assignment of the absorption bands in infrared spectra of solid state triglycerides to definite molecular vibrations. This had already been done for long chain molecules as hydrocarbons, but not for triglycerides. Recently little has been published about vibrational analysis of more complex compounds. This might be caused by a 'brain drain' to other fields of interest, especially nuclear magnetic resonance and mass spectrometry, or because much basic information was already available and new knowledge could only be achieved by laborious and minute investigations.

At the Netherlands Government Dairy Station (Rijkszuivelstation) at Leiden the problem of the detection of foreign fat in milk fat and of the adulteration of natural fats in general has been studied for about sixty years. The main reason for this interest is the guarantee given by the Netherlands Government for the genuineness of exported dairy products. During the first half of this century there was no comprehensive system for the analysis of natural fats. Often the composition of an unknown mixture of fats could not be determined completely and with certainty, as a consequence of which adulterations could not always be proved. For the detection of adulteration the analysis of the minor constituents of fats in the unsaponifiable fraction: the sterols, was chosen in this institute around 1910. These compounds often show more distinc-

tive characteristics than the fatty acid composition of the glycerides themselves. Investigations in this institute on sterol technique were described by Den Herder, Roos, Riemersma and Copius Peereboom, showing several specific ways for detection on estimation of adulteration.

From the data gathered in the study, it should become possible to test fats, such as milk fat and lard, for adulteration with beef tallow, which cannot be detected by the sterol method. Specially made mixtures of these fats have been analysed satisfactorily; good prospects, however, still have to be confirmed by further investigations taking into account the influences of origin and seasonal variability.

I trust that De Ruig's book 'Infrared spectra of triglycerides; with some applications to fat analysis' will provide food control authorities, trade and industry with some new possibilities for testing fats. The author's contribution to the understanding of infrared spectra of triglycerides, both by experiments and theoretical consideration, is worthy of the attention of scientists in this fields.

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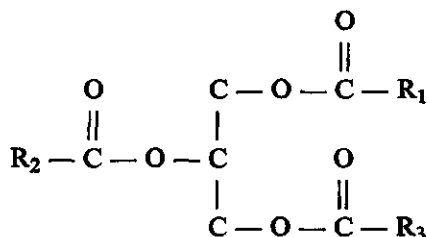
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1 Introduction

1.1 Natural fats

Natural edible fats and oils are substances of animal or vegetable origin. As early as 1823 Chevreul established that they were composed of glycerol esters of fatty acids. Nowadays fats are known to consist of about 95% triglyceride, with the general formula



where R_1 , R_2 and R_3 are hydrocarbon chains, which can be either saturated or unsaturated, straight or branched. Free acids, monoglycerides, and, more rarely, diglycerides, may also be present. In the 'unsaponifiable matter' there are smaller or larger proportions of sterols, fatty alcohols, hydrocarbons, phosphatides, colouring matters, and other minor components.

In general the term 'fats' refers to materials which are solid, and the term 'oils' for those which are liquid at room temperatures. As this is not a rigid distinction, I will use the term 'fats' and 'fatty products', to include both. Differences in the market value of natural fats can tempt people to mix relatively expensive fats with lower-priced fats. Reliable and sensitive analytical detection methods can be helpful to withstand these temptations. From the controller's viewpoint these methods are even required.

The problem whether or not fats are mixed with fats of other origin is not equally important for all fats. For those used as raw materials in manufacturing complex nutritive fats, such as margarine and shortenings, nature and purity are less important than their properties. On the contrary, much value is attached to the purity of milk fat, which should not be mixed with other fats in milk products, such as butter, butter oil, cheese, condensed milk and dried milk. Olive oil, cocoa butter and lard should also be free from foreign fats.

1.2 Classical characteristic values

The analysis of fats and the detection of foreign fats are strengthened on the one hand by the great natural variability in the composition of the same kind of fat and on the other hand by the similarity of different fats. In the early stages of fat analysis knowledge of chemical composition and structure of fats was limited and the analytical equipment was restricted. Yet indications about the character of the fats were needed. Over the years a number of so called 'characteristic values' were found to distinguish fats and to detect the admixture of foreign fats. Among these the following are mostly used.

The *Reichert-Meissl-Wollny value* (R.M.W.) indicates water-soluble volatile fatty acids in saponified matter (in milk fat mainly butyric acid, further caproic and caprylic acid).

Similarly the *Polenske value* indicates water-insoluble volatile fatty acids (caproic and higher).

The *saponification value* (S.V.) measures the chain length of fatty acids, whereas the *iodine value* (I.V.) indicates the degree of unsaturation.

The *refractive index* depends both on chain length and unsaturation.

The genuineness of lard can be demonstrated by the *Bömer value*, defined by

$$B.V. = S_g + 2(S_g - S_f)$$

where

S_g = melting point of the saturated fraction insoluble in diethyl ether of the glyceride and

S_f = the melting point of the fatty acids thereof.

A number of characteristic values for some well known fats are collected in Table 1.

Table 1. Characteristic values of several natural fats (AOCS, 1946).

	RMW value	Polenske value	Saponification value	Iodine value	Refractive index (40°)	Unsaturated acids (%)
Milk fat	26 -34	1.5- 3.7	210-232	26 - 40	1.453-1.457	33-42
Beef tallow	< 1	-	190-200	33 - 47	1.450-1.458	40-51
Lard	< 1	-	190-203	53 - 68	1.448-1.460	59-68
Cocoa butter	0.2- 1.5	0.5	192-200	32 - 40	1.456-1.458	41-48
Coconut oil	6 - 8	14 -18	248-264	7.5- 10.5	1.448-1.450	6-10
Palmkernel oil	4 - 7	9 -12	243-255	14 - 23	1.449-1.452	13-19
Palm oil	< 0.5	< 0.5	196-202	45 - 56	1.453-1.459	48-58
Olive oil	< 1	< 0.5	190-196	79 - 90	1.460-1.464	83-91
Soyabean oil	< 1	< 1	189-195	127 -138	1.465-1.470	82-90
Rapeseed oil	< 1	< 0.5	168-180	97 -108	1.464-1.468	90-98

To detect foreign fats, it has turned out to be successful to investigate the unsaponifiable matter instead of the glycerides itself. Animal fats are accompanied by cholesterol, whereas there are phytosterols (e.g. β -sitosterol, campesterol, stigmasterol) in vegetable oils.

By analysis of the sterols animal fats can be distinguished from vegetable fats and the presence of vegetable fat in animal fat can easily be shown. As some vegetable fats also contain cholesterol, the reverse is not the case. And of course the problem of the detection of animal fat in other animal fat is not at all solved by this method. This problem is still of interest for fat chemists.

1.3 Modern analysis of fats

Modern analytical methods have resolved the composition and structure of fatty products. The fatty-acid composition could be determined by gas-liquid chromatography, for which the triglycerides are first converted into methyl esters. Nowadays also the triglyceride composition can be determined by this technique.

The crystal structure of solid glycerides has been analysed successfully by X-ray diffraction, and very recently also by electron-diffraction methods (cf. Chapter 2). Also other modern, mostly instrumental, methods of analysis have been applied to fat analysis. Among these are differential-thermal analysis, thin-layer chromatography, ultraviolet and infrared spectroscopy, nuclear-magnetic resonance and mass spectroscopy. One of the main tasks of the present-day investigators is to 'translate' the classical characteristic values into data obtained by these modern techniques.

As this publication is concerned with infrared-spectroscopic investigations, how this technique is applied to fat chemistry will be discussed in Section 1.5.

1.4 Standard methods

Very careful instructions for analysis are needed as the result, particularly the determination of the classical characteristic values, is often affected by procedure. Conventions and legislation also promote international standard methods.

A number of international bodies are working on standardization of methods. Among these are IUPAC¹, Codex Alimentarius Committee², Committee of Government Experts on the Code of Principles³, the ISO⁴, and the IDF⁵. Standard methods are also published by several national bodies as e.g. AOCS⁶ and DGF⁷.

Methods of analysis are also described in a number of standard books on fat chemistry (E.g. Boekenooen, 1964, 1968; Bailey, 1950, 1951; Brink & Kritchevsky, 1968; Hilditch & Williams, 1964; Kaufmann, 1958; Mehlenbacher, 1960; Williams, 1966; Wolff, 1968).

Monographs are published in the series Progress in the chemistry of fats and other lipids (Holman, 1952f).

Methods for the detection of foreign fats in milk fat have been reviewed by Roos (1963).

1.5 Infrared spectroscopy of fats

When infrared spectroscopy became available as an easy and simple analytical technique, it was applied to the investigation of fatty products. As the infrared spectrum is highly specific for a distinct compound, it is a useful tool for identification. The main bands due to vibrations of functional groups have been assigned and are applied to detection of e.g. monoglycerides, epoxy compounds, branched chains, etc. by a number of authors. Also problems as the autoxidation of unsaturated oils have been studied.

Results are reviewed amongst others by Wheeler (1954), O'Connor (1955, 1956, 1961), O'Connor et al. (1955), Chouteau (1961), Chapman (1965b) and Freeman (1968). The AOCS Instrumental Techniques Committee deals with advances in analytical applications (O'Connor, chairman, 1970).

An important application is the determination of *trans*-unsaturated products. This started with the observation of Rasmussen, Brattain and Zucco (1947) that a strong band at 967 cm^{-1} appears to be due to a *trans* C=C group. A tentative standard method has been published by the AOCS (1961). Recently a rapid alternative method is reported (Allen, 1969). It is possible to distinguish between isolated *cis*- and *trans*-unsaturation, and even between various forms of conjugated *cis-trans*-unsaturation. Adulterations of butterfat can be detected by using these differences (Bartlet, pers. comm., Bartlet & Chapman, 1961; De Ruig, 1968).

Much information can be obtained from solid-state spectra about the nature and composition of triglycerides, including the crystalline structure, chain length, and whether an even or odd triglyceride is present (cf. chapters 2, 5 and 7). Chapman et al. (1957) showed with solid-state spectra that the major component of cocoa butter consists of 2-oleo-palmitostearin, and not 2-palmito-oleostearin as was previously assumed, whereas the latter is the major disaturated glyceride in lard.

At the Netherlands 'Government Dairy Station' an examination of natural fats with infrared spectroscopy indicated that a further fundamental study of infrared

1. International Union of Pure and Applied Chemistry.
2. Joint FAO/WHO Food Standards Programme; Codex Alimentarius Commission: Codex Committee on Fats and Oils (CX/FO), Codex Committee on Methods of Analysis and Sampling (CX/MAS),
3. Joint FAO/WHO Committee of Government Experts on the Code of Principles concerning Milk and Milk Products and associated Standards.
4. International Organization for Standardization: Technical Committee Agricultural Food Products (ISO/TC 34), Sub Committee Oleaginous Seeds and Fruits (ISO/TC 34/SC 2), Sub Committee Milk and Milk Products (ISO/TC 34/SC 5), Working Group Animal Fats (WG 3) of Sub Committee Meat and Meat Products (ISO/TC 34/SC 6).
5. International Dairy Federation.
6. American Oil Chemists' Society.
7. Deutsche Gesellschaft für Fettwissenschaft.

spectra would be desirable. Therefore a series of pure monoacid triglycerides were extensively studied and vibrational analyses were carried out. The following chapters deal with the results of my studies and some applications to the detection of animal fats in other animal fats.

2 The polymorphism of triglycerides

2.1 Earlier investigations

One of the most interesting characteristics of triglycerides is their polymorphism. Heintz (1849) already reported two melting points for stearin. A solid sample melted at 51-52° C. After further heating it resolidified and melted again at 62-62½° C.

For some triglycerides, Duffy (1853) even found three melting points, e.g. for mutton stearine at 52.0°, 64.2° and 69.7° C, for beef stearine at 51.0°, 63.0° and 67.0° C. He noticed that the purer the fat, the more difficult it became to detect the intermediate point. He assumed that this melting behaviour was due to some form of isomerism. Duffy's excellent work has been either overlooked by later scientists, or else the intermediate form was thought to be due to impurities. So, for many years, only two melting points were reported for triglycerides, the phenomenon being called 'double melting'.

In 1915, however, Othmer reported three melting points for tristearin and trimyristin. In 1928 this was confirmed by Loskit, who added tripalmitin. In 1932, Weygand & Grüntzig claimed that even seven forms existed. However a careful study by Joglekar & Watson (1930) produced only two melting points for a number of very pure triglycerides.

At the end of the 1920's, Duffy's conclusions of eighty years before still gave the best explanation: there are three forms of monoacid triglycerides with different melting points, but with the intermediate melting point often difficult to detect.

2.2 X-ray analysis on powder diagrams

About 1930, X-ray analysis became available as new tool of analytical investigation (Malkin, 1931). Malkin and co-workers studied extensively the multiple melting of triglycerides, using thermal and X-ray analysis, and showed that polymorphism accounted for this phenomenon, i.e. different crystalline forms occur for a given compound. Polymorphism in general means the occurrence in either the solid or liquid phase of two or more physical distinguishable forms for the same substance.

Briefly, Malkin's method was to establish number and stability ranges of the various polymorphs by means of cooling and heating curves and, on the basis of this, to determine differences in structure by X-ray examination (Clarkson & Malkin, 1934; Malkin & Meara, 1939a, b; Carter & Malkin, 1939a, b). Malkin (review 1954) distinguished four solid forms. In order of increasing melting point and likewise increasing stability these are

- a 'vitreous' form, being not truly crystalline but possessing characteristics of a glass;
- an α form in which the chains are vertical and rotating;
- a β' form, possessing non-rotating tilted chains (Grüntzig, 1939; Clarkson & Malkin, 1948);
- a β form which is stable and in which the long chains are at an inclination to the glycerol groups.

Later on, Bailey et al. (1945), Filer et al. (1946) and particularly Lutton (1945) came to the conclusion that Malkin was partially wrong in his association of melting points with X-ray diffraction patterns.

With long-chain compounds, as triglycerides are, the observed spacings may be classified as 'long spacings' and 'short spacings'. The first refer to the length of the molecules, i.e. the distance between the planes formed by the methyl groups; the short spacings relate in some way to the cross-sectional arrangement or the width of the molecules. The long spacings are usually a linear function of the number of carbon atoms. In many cases tilting of long chain axes with respect to end group planes shortens the observed long crystal spacing. The short spacings, being linked up with the glycerol-head of the glyceride molecules, are practically independent of the chain length. The geometry of triglycerides and its possible variation from compound to compound cause major variations in crystal structure in the long-chain direction.

Contrary to Malkin, Lutton (1945, 1950; Lutton & Fehl, 1970) used the X-ray data of the short spacings as the primary basis for his nomenclature, as follows:

alpha	single strong line at about 4.1 Å
beta prime	usually two (occasionally more) strong lines at about 4.2 and 3.8 Å
beta	strong (usually strongest) line at about 4.6 Å.

It may be noted that initially Lutton (1950) consequently used the full name, e.g. beta prime rather than β' , but confusion nevertheless has occurred. Chapman (1957a) therefore has suggested the use of a suffix M for Malkin and L for Lutton. Hence a form of tristearin melting at 64-65° C could be referred to as α_M or β'_L . His proposal has not been followed by most other authors, however.

The controversy between Malkin and Lutton has led to considerable confusion in the literature. They based their nomenclature on different principles (Malkin: melting points, Lutton: X-ray data) and as is apparent from Table 2 they do not match, except for the form with the highest melting point.

Actually, both systems have their limitations (Larsson, 1965b; Chapman, 1965b).

The deadlock was broken by the introduction of infrared spectroscopy for studying polymorphism in glycerides.

In 1970, Lutton & Fehl have re-investigated the polymorphism of all saturated monoacid triglycerides from C_8 to C_{22} . The earlier results were in the main confirmed; minor variations in the short spacings were observed (Fig. 1). They reported, however, an exceptional phase for the stable form of C_9 and C_{11} triglycerides replacing

Table 2. Nomenclature for triglycerides according to Malkin and Lutton. X-ray and melting data for tristearin.

Author	Melting point (°C)	X-ray short species (Å)	Name	
Malkin	54.4	diffuse	4.15	vitreous
	65.0	4.15		α
	70.0	3.8 and 4.2		β'
	72.0	4.6		β
Lutton	59.9	4.15		alpha
	64	3.8 and 4.2		beta prime
	73.1	4.6		beta

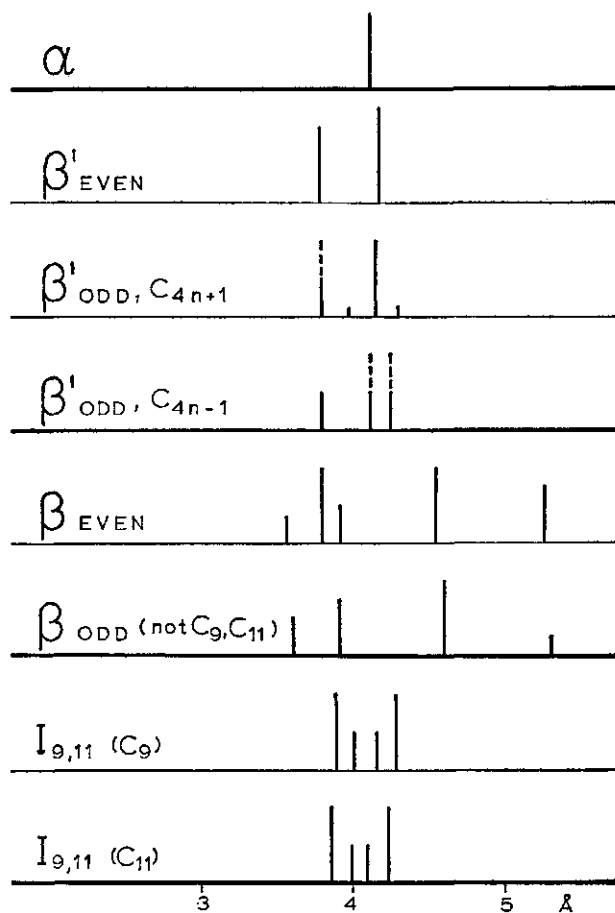


Figure 1. Short spacings of polymorphic forms of monoacid triglycerides C_8 - C_{20} (Lutton & Fehl, 1970).

Table 3. Melting points of monoacid triglycerides (Lutton & Fehl, 1970; Larsson, 1965b).

Triglyceride	α form	β' form	β form
C ₈ Tricaprylin	-51.0	-18.0	10.0
C ₉ Tripelargoin	-26.0	4.0	10.5 ^a
C ₁₀ Tricaprin	-10.5	17.0	32.0
C ₁₁ Triundecylin	2.5	27.0	31.0 ^a
		31.0 ^b	28.5 ^b
C ₁₂ Trilaurin	15.0	34.5	46.5
C ₁₃ Tritridecylin	24.5	41.5	44.5
C ₁₄ Trimyristin	33.0	46.0	58.0
C ₁₅ Tripentadecylin	39.0	51.0	55.0
C ₁₆ Tripalmitin	45.0	56.5	66.0
C ₁₇ Trimargarin	50.0	60.5	64.0
C ₁₈ Tristearin	54.7	64.0	73.3
C ₁₉ Trinonadecylin	59.0	65.5	71.0
C ₂₀ Triarachidin	62.0	69.0	78.0
C ₂₁ Triheneicosanoin	65.0	71.0	76.0
C ₂₂ Tribehenin	68.0	74.0	82.5

a. I_{9,11} forms, according to Lutton & Fehl.

b. Values reported by Larsson.

the β form, which they call (though inadequately) I_{9,11}. The short spacings of this form are said to be not of the β type but reminiscent of the β' form as is obvious from the figure (see further discussion in Section 3.2).

The melting points of the various forms were also re-examined (Table 3).

Knoop & Samhammer (1961) and Knoop et al. (1966) distinguished five β modifications, differing only in the long spacings, i.e. in the angle of tilting of the hydrocarbon chain. The following inclinations were found for tristearin

β_I	β_{II}	β_{III}	β_{IV}	β_V
90°	72°9'	59°12'	50°23.5'	42°50.5'

The usual β form is conceived as a mixture of these forms, as is apparant from the X-ray diagram (Fig. 2), the β_{III} form being dominant. Knoop & Samhammer's supposition that the β forms should be monoclinic or rhombic was not confirmed by other authors.

Gunstone (1964) tried to correlate the polymorphs of glycerides on their long spacings. He distinguished five groups with different angles of tilting, the five angles being different from those reported by Knoop et al.; they corresponded with the α_M , β'_M and β_M as follows;

Gunstone's group	V	U	T	S	R
angle of inclination	90°	68°	64°	57°	52°
Malkin's form	α_M	β'_M	β_M		

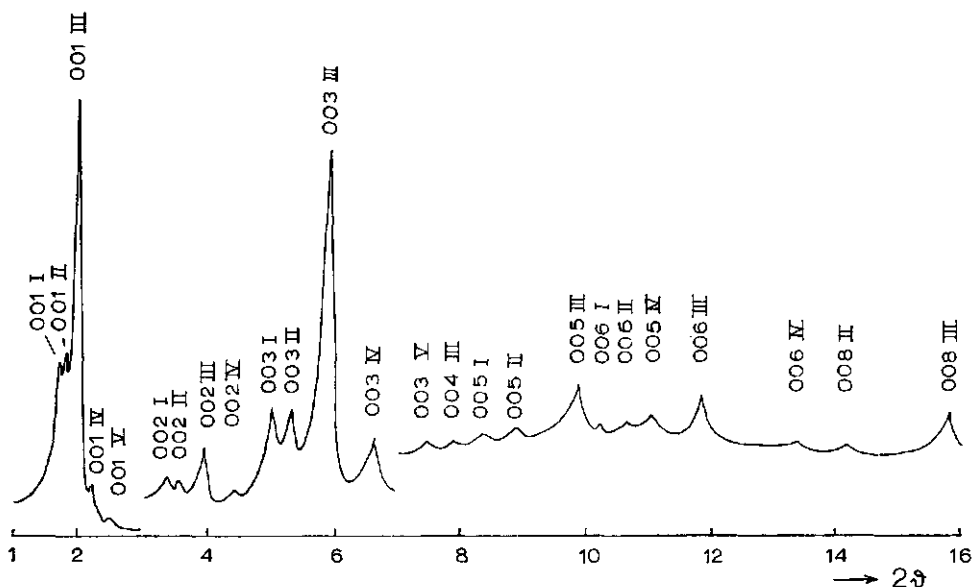


Figure 2. X-ray diagram of stearin, indicating the occurrence of five β forms (Knoop & Samhammer, 1961).

2.3 Single-crystal investigations

Within a crystal the smallest group of molecules whose repetition at regular intervals in three dimensions produces the lattice is called the 'unit cell'.

Certain crystals contain structural repetitions within the unit cell, which can be described by a much smaller 'subcell' (Vand, 1951). In triglycerides a subcell can be constructed describing the periodicity in the hydrocarbon chains. Some types of subcells for various packings of parallel hydrocarbon chains are illustrated in Fig. 3. The symbols used indicate the symmetry of the subcell and whether all zigzag planes are parallel (//) or every second plane is perpendicular (\perp) to the planes of the others. In the hexagonal packing the hydrocarbon chains are assumed to be rotating or in random orientation (Müller, 1932; Malkin, 1933; Chapman, 1965b).

Powder diagrams are inadequate for determining the dimensions of a unit cell or a subcell, and single crystals have to be examined.

For triglycerides their preparation is difficult, yet successful single-crystal investigations have been carried out on the β form of trilaurin (Vand & Bell, 1951; Larsson, 1963, 1965a) and of tricaprln (Jensen & Mabis, 1963, 1966).

The unit cell of this form was triclinic and contained two molecules. The subcell was also triclinic and contained two CH_2 groups. Their packing corresponds with Figure 3d. The angle between the chains and the a-b plane of the unit cell agreed with that predicted from the long spacings of powder diagrams.

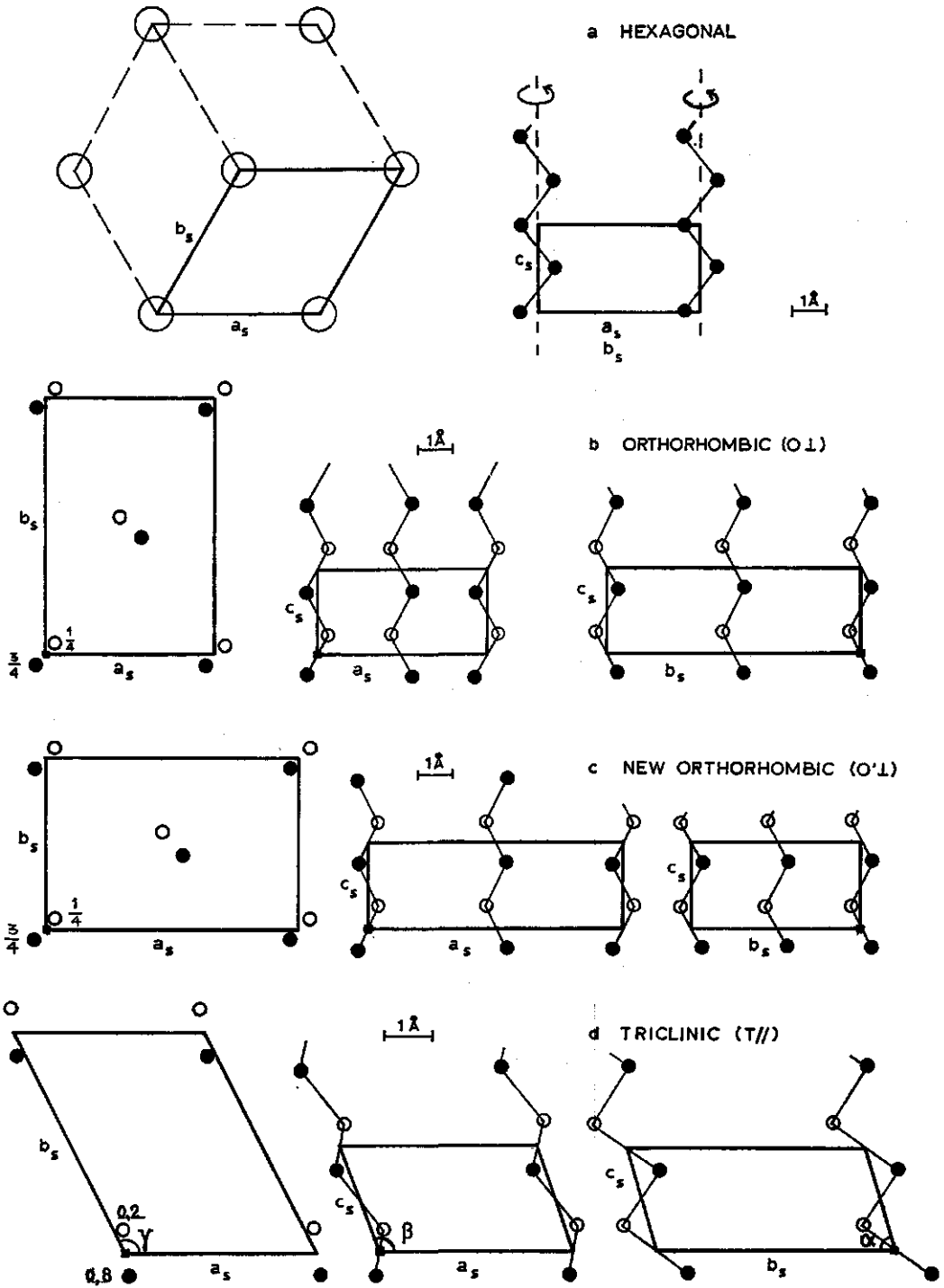


Figure 3. Some types of subcells (after Vand & Bell, 1951; Von Sydow, 1956; Abrahamsson, 1959a; Buchheim, 1970).

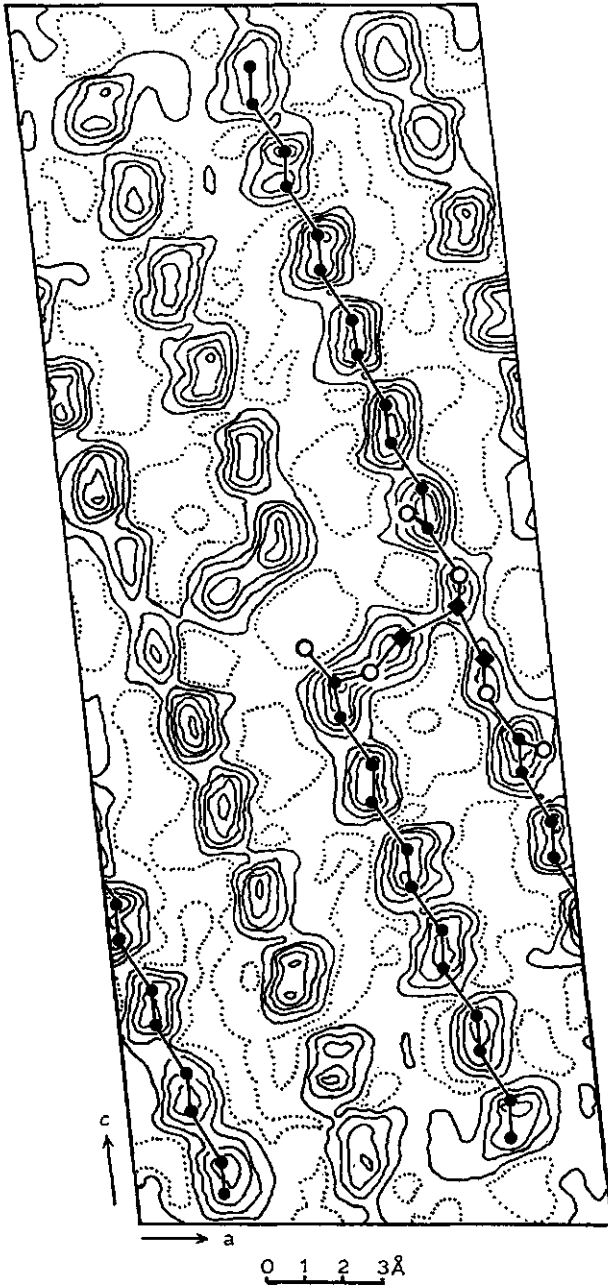


Figure 4. The arrangement of trilaurin in the crystal lattice (Chapman, 1962, after Vand).

- = glyceryl carbon
- = side-chain carbon
- = oxygen

From these examinations of single crystals it could be concluded that the triglyceride molecules pack in an asymmetrical tuning-fork configuration, Figure 4. The molecular arrangements along the b-axis and along the a-axis of the unit cell is shown in figures 5 and 6.

By the X-ray analysis of single triglyceride crystals only the stable β form has been studied successfully. In 1970, Buchheim calculated subcell- and unit-cell dimensions of other forms from electron-diffraction patterns. When using an electron beam instead of X-rays, much smaller single crystals are required, but the experimental difficulties are very much higher.

Buchheim observed an α form, two β' forms and two β forms of trilaurin (Table 4). One of the β' forms was identical with the former β' form having tilted chains, the other was a new form with vertical chains. The β forms corresponded with the β_{II} and β_{III} forms reported by Knoop et al. (1961, 1966).

Table 4. Polymorphs of trilaurin (Buchheim, 1970).

Form	Angle between hydrocarbon chain and base level	Unit cell	Orientation of hydrocarbon chains with respect to adjacent chains	Subcell
α	90°	hexagonal	random	hexagonal $a_s = b_s = 4.80 \text{ \AA}$ $c_s = 2.55 \text{ \AA}$ $\gamma_s = 120^\circ$
Vertical β'	90°	?	perpendicular	orthorhombic $a_s = 4.98 \text{ \AA}$ $b_s = 7.46 \text{ \AA}$ $c_s = 2.55 \text{ \AA}$
Tilted β'	62-63°	orthorhombic 8 molecules per unit cell $a = 22.93 \text{ \AA}$ $b = 5.67 \text{ \AA}$ $c = 65 \text{ \AA}$?	
β_{II}	73°	triclinic 2 molecules per unit cell $a = 11.60 \text{ \AA}$ $\alpha = 89^\circ$ $b = 5.30 \text{ \AA}$ $\beta = 85^\circ$ $c = 34.7 \text{ \AA}$ $\gamma = 96^\circ$	parallel	triclinic $a_s = 4.43 \text{ \AA}$ $\alpha_s = 76^\circ$ $b_s = 5.30 \text{ \AA}$ $\beta_s = 107^\circ$ $c_s = 2.56 \text{ \AA}$ $\gamma_s = 120^\circ$
β_{III}	61°	triclinic 2 molecules per unit cell $a = 12.28 \text{ \AA}$ $\alpha = 95.3^\circ$ $b = 5.48 \text{ \AA}$ $\beta = 95.8^\circ$ $c = 31.8 \text{ \AA}$ $\gamma = 100^\circ$	parallel	

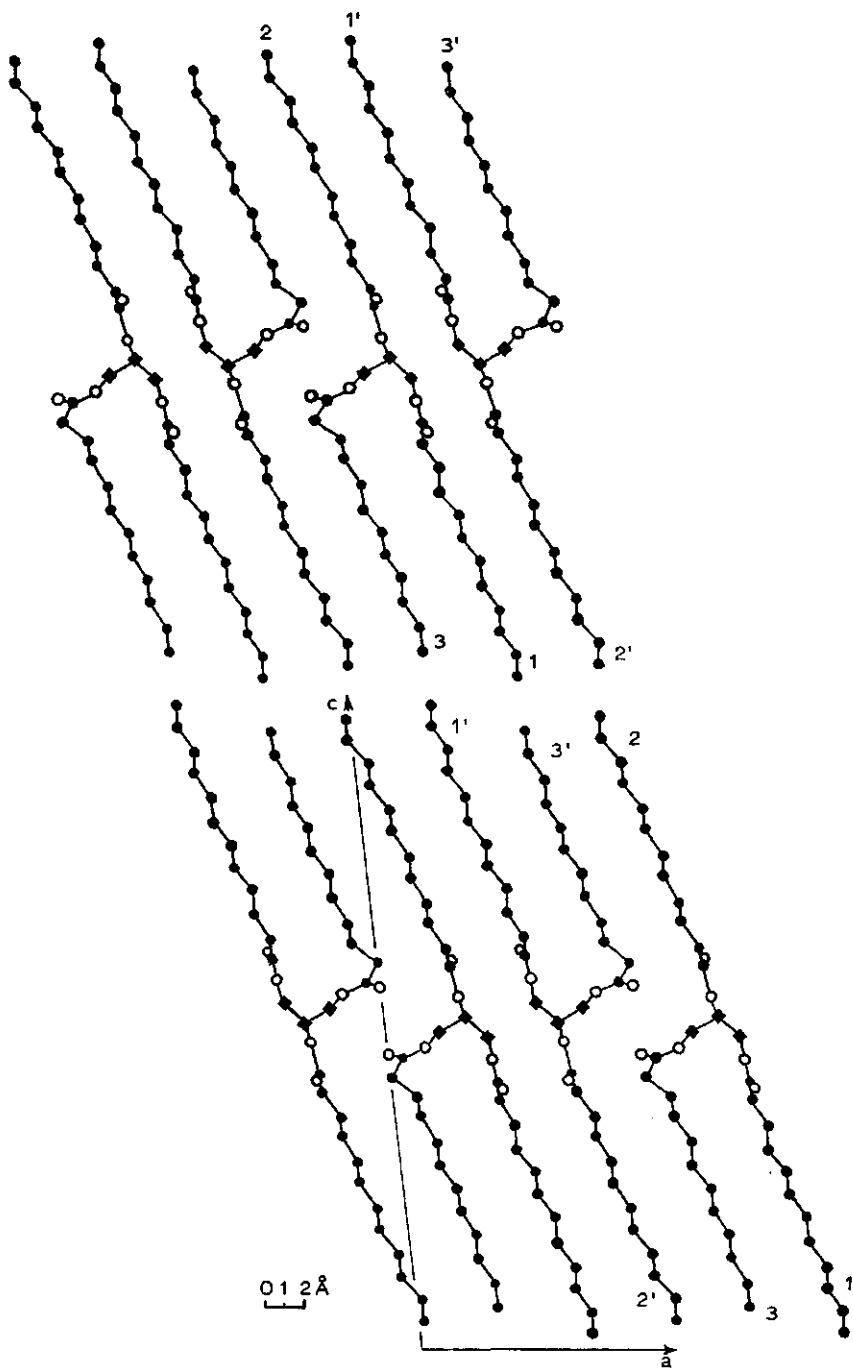


Figure 5. Molecular arrangement of trilaurin projected along the *b*-axis (Larsson, 1965a).

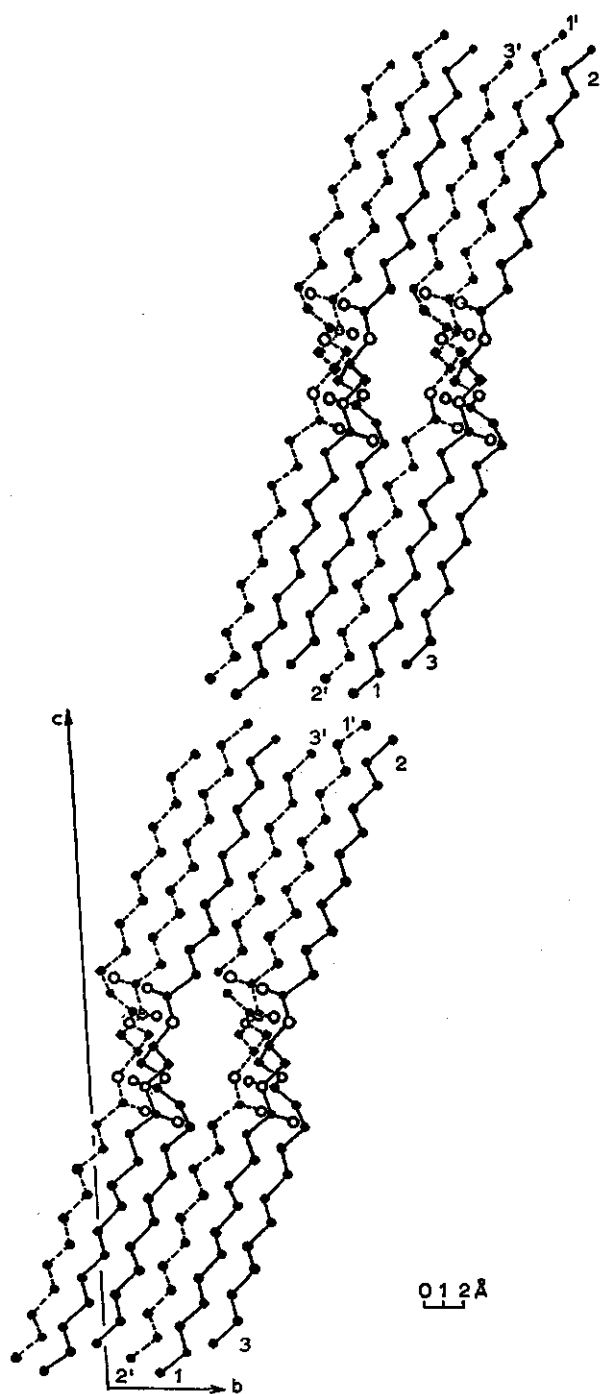


Figure 6. Molecular arrangement of trilaurin projected along the a -axis (Larsson, 1965a).

2.4 Infrared spectroscopy

The polymorphism of triglycerides and related compounds revealed by infrared spectroscopy has been extensively studied by Chapman (see his publications in the years 1956-65). In his study on triglycerides such as tristearin he obtained three kinds of spectra which may be compared with the three X-ray diffraction-patterns (Fig. 7).

The form obtained by quenching the melt from a high temperature to room temperature gave a spectrum not typical for a vitreous form. In the 1250 cm^{-1} region a regular series of bands occurred, giving definite evidence of crystallinity. As with spectra of α forms of other long-chain compounds, the CH_2 main rocking mode was a single band at 720 cm^{-1} . After melting and recrystallization the form transformed into the stable β form. The observations clearly showed that the lowest-melting form was not vitreous as suggested by Malkin, that its spectrum had much in common with that of the α forms of other long-chain compounds, that it was crystalline, and that Lutton had correctly considered it to be an α form. Moreover, this form exhibits strong birefringence (Quimby, 1950), which is also inconsistent with a vitreous form. The single band at 720 cm^{-1} is correlated with hexagonally-packed chains (Chapman, 1957b). Only one band was observed mainly because there was only one chain per primitive subcell and a large interchain-distance in this form.

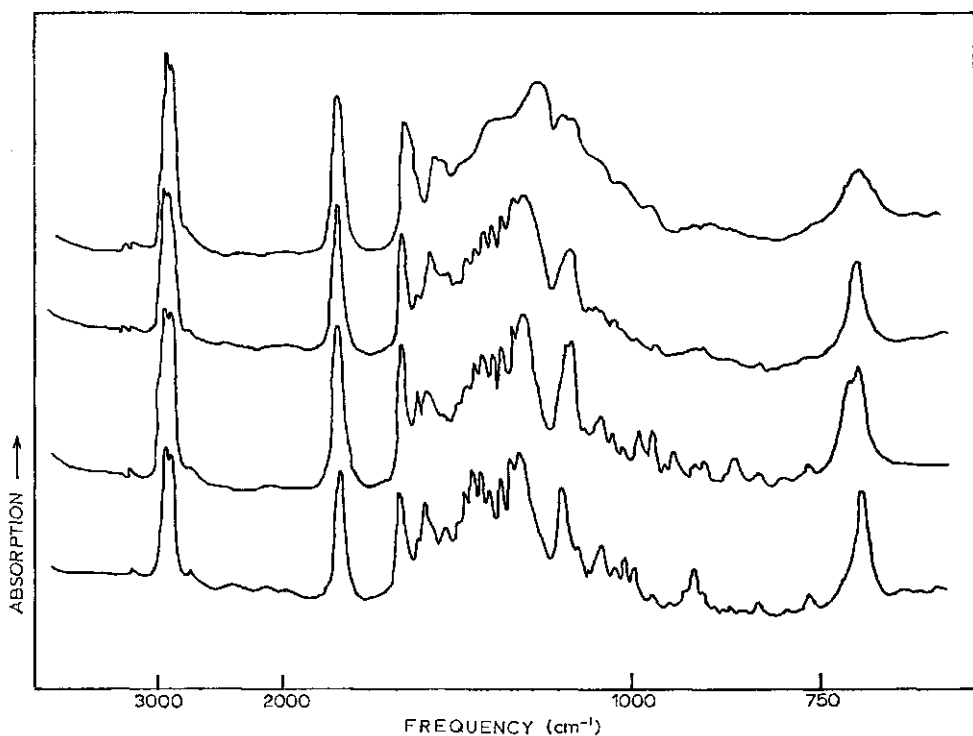


Figure 7. The polymorphic forms of tristearin (Chapman, 1956c).

An intermediate form crystallized when the melt was cooled to a temperature about two degrees above the melting point of the α form. The main CH_2 rocking mode in its spectrum was a doublet at 726 and 719 cm^{-1} indicating orthorhombic-packed ($\text{O}\perp$) chains and attributed to an interaction between neighbouring chains as there are two chains per subcell. As compared with the spectrum of the α form, the relative intensity of the bands in the 1250 cm^{-1} region had changed and new bands had appeared. This form of tristearin melted at 65° C and was then transformed into the β form. So it could not possibly be a hexagonally-packed or α form, and was correctly designated a β' form.

The stable β form was obtained by solvent crystallization. Its spectrum differed from that of the other forms in the relative intensities of the bands in the 1250 cm^{-1} region. There was also a strong band¹ at 890 cm^{-1} absent in the other spectra, and the main CH_2 rocking mode was single (at 717 cm^{-1}). This band was correlated with triclinic-packed (T/\parallel) chains and was single due to only one chain per subcell. Its shift was related to the change in the internal-potential-energy function of the molecule.

As Chapman (1962, 1965b) pointed out, if Malkin's interpretation of his X-ray data is rejected there is:

- a. consistency of pattern of infrared spectra of the triglycerides with those of other long-chain compounds,
- b. consistency of pattern of infrared spectra for various types of triglycerides,
- c. consistency of X-ray and infrared data.

The correlation between the packing of the hydrocarbon chains and the appearance of the infrared absorption in the 720 cm^{-1} region is also present in other compounds with long hydrocarbon chains, and has been confirmed by other authors too (Abrahamsson & Fischmeister 1959).

A sub- α form was reported by Jackson & Lutton (1950) and by Chapman (1960, 1962, 1965b) as a further form of triglycerides. When the temperature was lowered, the spectrum of the α form remained generally the same although the bands narrowed and sharpened, but between -50° to -70° C for tristearin the main CH_2 rocking mode in the 720 cm^{-1} region gradually and reversibly changed from a single band into a doublet. The doublet was reported to be similar to that observed in the spectrum of the intermediate β' form and the chains in the sub- α form were probably orthorhombically packed. Its short spacings were similar to those of the β' form (~ 3.7 and 4.2 Å). This sub- α form behaves according to the idea that with lower temperatures the chains rotate less rapidly and pack together more tightly.

By combining the infrared data of Chapman with the X-ray short-spacing data

1. In the triglycerides I investigated, this band was mostly observed between 900 and 895 cm^{-1} (band C in tables 10-25).

reported by Lutton, Larsson (1965b) has drawn up the following criteria for the nomenclature of glycerides in the solid state.

1. A form, crystallizing from the melt and giving only one strong short-spacing line at 4.15 Å is termed α . A form related to the α form by an enantiotropic transition is termed sub- α , irrespective of its short-spacing data.
2. A form showing two strong short-spacing lines at 3.8 and 4.2 Å or three strong lines near 4.27, 3.97 and 3.71 Å, and also exhibiting a doublet in the 720 cm^{-1} region of the infrared spectrum, is called β' .
3. A form not satisfying criteria 1 and 2 is called β .

2.5 Summary of Chapter 2

The polymorphism of triglycerides has been studied for more than a century. At present it is generally accepted that three crystallization forms exist (α , β' and β) which are distinguishable by their melting points, X-ray data and infrared spectra, as indicated in Table 5. The α form is the least stable; the α and β' forms are monotropic forms of the stable β form. Malkin's nomenclature is obsolete.

Some additional forms are reported.

A sub- α form, enantiotropic with the α form, arising when the α form is sufficiently chilled (Jackson & Lutton, 1950; Chapman, 1960, 1962, 1965b). Buchheim (1970) reports a 'vertical' β' form besides the usual tilted β' form. Knoop & Samhammer (1961) mention for the β modification five forms differing only in the angle of tilting (β_I to β_V), of which the β_{III} corresponds with the normal β form. Five (other) forms of different tilting are mentioned by Gunstone (1964).

Lutton & Fehl (1970) state that the stable form of C_9 and C_{11} is not the β form but another one, with a different X-ray pattern; it is termed $I_{9,11}$.

Table 5. Survey of polymorphic forms of triglycerides (summary).

	Melting point	X-ray short spacings	Infrared CH_2 main rocking	Hydro-carbon chain	Subcell
<i>Main forms</i>					
α	lowest	4.1 Å	720 cm^{-1}	vertical	hexagonal
β'	intermediate	4.2 and 3.8 Å	726 and 719 cm^{-1}	tilted	orthorhombic ($O \perp$)
β	highest	4.6 Å	717 cm^{-1} strong band at 890 cm^{-1}	tilted	triclinic ($T//$)
<i>Additional forms</i>					
sub- α		4.2 and 3.7 Å	726 and 719 cm^{-1}		orthorhombic?
$I_{9,11}$		~ 4.3 and ~ 3.9 Å			orthorhombic $\left\{ \begin{array}{l} O' \perp \text{stable?} \\ O \perp \text{stable?} \end{array} \right.$

3 Experimental procedures

3.1 Equipment

A Perkin Elmer infrared spectrophotometer, model 457, with a wave-number range of 4000 to 250 cm^{-1} was used in scanning the spectra.

The temperatures of the samples were controlled in an RIIC temperature chamber VLT-2 (Fig. 8) with a pressure vessel with magnetic valve and a home-made automatic temperature-controller (De Ruig, 1971). The temperature range was from -180 to $+250^\circ\text{C}$, with an accuracy of $\pm 5^\circ\text{C}$.

Under standard conditions the scanning speed was 400 $\text{cm}^{-1}/\text{min}$ over the range 4000-2000 cm^{-1} and 200 $\text{cm}^{-1}/\text{min}$ over the range 2000-250 cm^{-1} . For the spectra of the most interesting section (1500-400 cm^{-1}) the scanning speed was 50 $\text{cm}^{-1}/\text{min}$ with double scale expansion. The wave-number accuracy was below $\pm 4 \text{ cm}^{-1}$ from 4000-

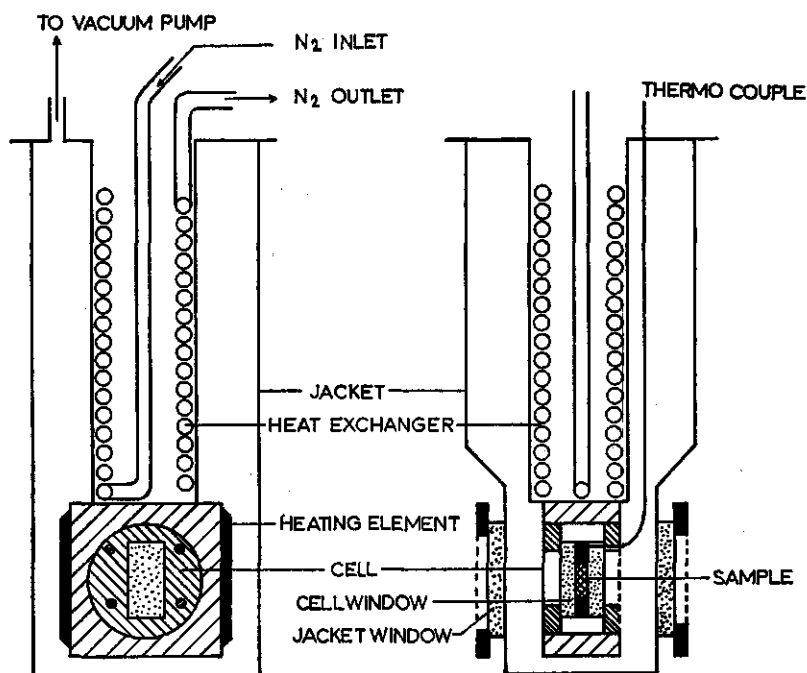


Figure 8. Variable temperature chamber with infrared cell.

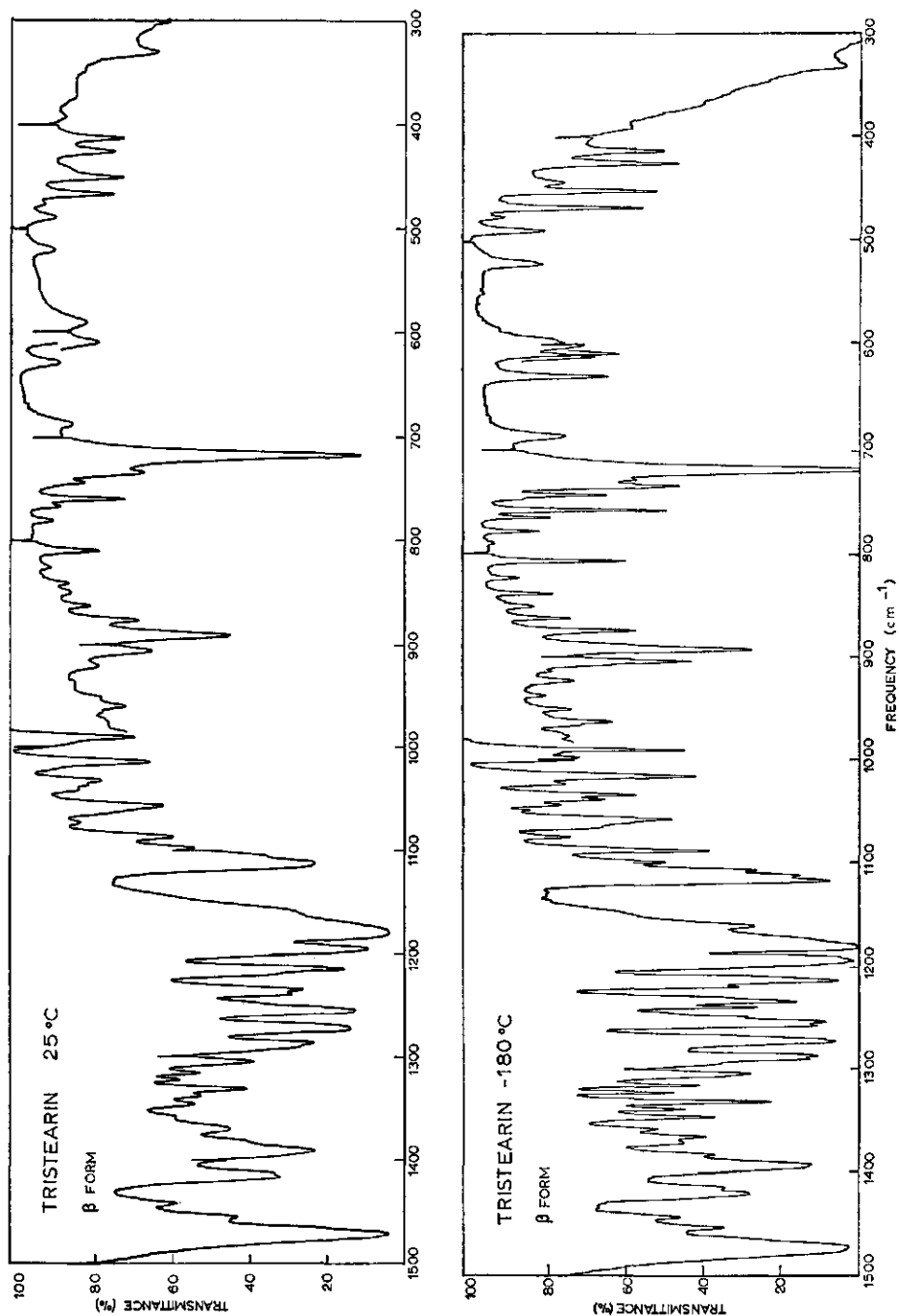


Figure 9a, b. Infrared spectrum at room temperature and at -180°C .

2000 cm^{-1} and below $\pm 2 \text{ cm}^{-1}$ between 2000 and 250 cm^{-1} . The resolution amounted to 2 cm^{-1} at 1000 cm^{-1} . At 600 cm^{-1} there is a grid change in the apparatus; around this frequency deviations of about 5 cm^{-1} do occur.

Marking pips indicate in the expanded spectra the wave numbers 1400, 1200, etc., with an accuracy of about $\pm 1 \text{ cm}^{-1}$.

The spectra of the solid states were scanned at -180°C . Such a low temperature sharpened absorption bands and gave a richer spectrum, as seen from Figure 9. At this temperature the α form is represented in the higher members of the homologous series by the enantiotropic sub- α form, apparent from the splitting-up of the 720 cm^{-1} band.

RIIC cells of the FH-01 type were used as demountable cells. To prevent fogging of the windows by moist condensation at low temperatures silver-chloride windows were chosen. Silver chloride cuts off frequencies below about 400 cm^{-1} . In some cases potassium-bromide pellets were used; they cut off the spectrum at about the same frequency. The cells were placed in the RIIC chamber which was provided with heated potassium-bromide windows and was evacuated before cooling.

3.2 Preparation of the samples

The various crystalline forms of the triglycerides can be obtained from the liquid phase or from the solvent.

For *crystallization from the liquid phase* a few drops of molten triglyceride were placed between two silver-chloride windows of an infrared cell; spacers of 0.025 or 0.05 mm thickness proved to be appropriate for obtaining good spectra. After mounting, the sample was quenched in liquid nitrogen. Under such conditions all triglycerides except the lowest terms crystallize into the α or sub- α form. The spectrum of this form was scanned at -180°C .

The transition of the α form into the β' form, and also of the β' form into the β form was achieved as follows. With the sample still in the infrared cell, its temperature was carefully raised a few degrees below the transition temperature, and left at this temperature for several hours or sometimes even days. Then, very slowly, the temperature was raised to just above the transition point. In this way the β' form and the β form were obtained successively from the same sample. Both spectra were examined again at -180°C . As the various forms of triglycerides are monotropic, the α form being the less stable and the β form the most stable, no reverse transition occurs when the β' and the β forms are cooled.

The melting points of the various forms are tabulated in Table 3 (Chapter 2).

The three forms were not obtained in all cases with this method. Some of the higher even triglycerides recrystallized directly from the α form into the β form. Still the β' form of C_{16} and C_{18} could be obtained by using a not highly-purified sample (approximately 95%, the rest being lower and higher triglycerides) and slow solidification at the melting point of the α form, followed by quick chilling. This is in accordance with Duffy (1853) who already found that from highly-purified tristearin the intermediate

form is hard to prepare. It has been proved for homologous β' forms, that the procedure mentioned above does not alter the infrared spectrum. The β' forms of C_{20} and C_{22} are not obtained so far.

By crystallization from a suitable solvent (acetone, diethyl ether, *n*-hexane) the most stable form was obtained. In general, thus, the β form was obtained. Some odd triglycerides, however, crystallized into the β' or a mixed $\beta' + \beta$ form.

The crystals were collected on a Büchner funnel, washed and dried at temperatures below the melting point. 10-15 mg of triglyceride was then ground with 700 mg potassium bromide in a mortar, and pressed into a pellet. After cooling to -180°C a spectrum was recorded.

The β form of C_9 is not obtained.

Besides the α and the β' form from C_{11} a third form was obtained with troubles by crystallization from acetone. Its infrared spectrum was similar to the spectra of β forms. In the X-ray diagram short spacings were found¹ at 3.03vs, 3.65s, 3.82s, 3.95vs, 4.18m, 4.37m, 4.57vs, 5.21m and 5.39m Å, also indicating the presence of a β form, perhaps mixed with β' . The form started to melt at 28.0°C ; at 28.8°C it recrystallized into the β' form, the latter melting between 29.6 and 30.4°C .

From these data I conclude that the present form is a metastable β form, while the β' form is the stable one for C_{11} . These results are in accordance with those of Larsson (1965b), cf. Table 3. No indication is found for the existence of the $I_{9,11}$ form as reported by Lutton & Fehl (1970).

3.3 Preparation and purification of the triglycerides

Most of the triglycerides studied were commercially available. The others were prepared from the corresponding acids by a method described by Clarkson & Malkin (1934) and Perron et al. (1969). According to this method 1.0 mole glycerol and 3.3 mole fatty acid are heated in 500 ml chloroform under a nitrogen atmosphere, with *p*-toluenesulfonic acid (2% w/w fatty acid) as a catalyst, at 140 to 180°C (depending on chain length) for 2 hours. Then the mixture is heated for 6 hours at 160 to 200°C under 25 mm pressure, dissolved in chloroform, filtered, and dried. Free fatty acids, mono-, di- and triglycerides are then separated by silica-gel column-chromatography.

Whenever required, the triglycerides were purified by multiple recrystallization from a diethyl-ether solution. The absence of mono- and diglycerides and free fatty acids was verified by thin-layer chromatography. The composition of the fatty-acid fraction was determined by gas-liquid-chromatographic analysis (GLC).

The monoacid triglycerides which were investigated are mentioned on the next page.

1. vs = very strong, s = strong, m = medium intensity.

Investigated triglycerides

triacetin, glycerol triethanoate, $C_3H_5(OOCC_2H_3)_3$
 tripropionin, glycerol tripropanoate, $C_3H_5(OOCC_2H_5)_3$
 tributyrin, glycerol tributanoate, $C_3H_5(OOCC_3H_7)_3$
 trivalerin, glycerol tripentanoate, $C_3H_5(OOCC_4H_9)_3$
 tricaproin, glycerol trihexanoate, $C_3H_5(OOCC_5H_{11})_3$
 triheptanoin, glycerol triheptanoate, $C_3H_5(OOCC_6H_{13})_3$
 tricaprylin, glycerol trioctanoate, $C_3H_5(OOCC_7H_{15})_3$
 tripelargoin, glycerol trinonanoate, $C_3H_5(OOCC_8H_{17})_3$
 tricaprin, glycerol tridecanoate, $C_3H_5(OOCC_9H_{19})_3$
 triundecylin, glycerol triundecanoate, $C_3H_5(OOCC_{10}H_{21})_3$
 trilaurin, glycerol tridodecanoate, $C_3H_5(OOCC_{11}H_{23})_3$
 tritridecylin, glycerol tritridecanoate, $C_3H_5(OOCC_{12}H_{25})_3$
 trimyristin, glycerol tritetradecanoate, $C_3H_5(OOCC_{13}H_{27})_3$
 tripentadecylin, glycerol tripentadecanoate, $C_3H_5(OOCC_{14}H_{29})_3$
 tripalmitin, glycerol trihexadecanoate, $C_3H_5(OOCC_{15}H_{31})_3$
 trimargarin, glycerol triheptadecanoate, $C_3H_5(OOCC_{16}H_{33})_3$
 tristearin, glycerol trioctadecanoate, $C_3H_5(OOCC_{17}H_{35})_3$
 trinonadecylin, glycerol trinonadecanoate, $C_3H_5(OOCC_{18}H_{37})_3$
 triarachidin, glycerol tritricosanoate, $C_3H_5(OOCC_{19}H_{39})_3$
 triheneicosanoin, glycerol triheneicosanoate, $C_3H_5(OOCC_{20}H_{41})_3$
 tribehenin, glycerol tridocosanoate, $C_3H_5(OOCC_{21}H_{43})_3$

Source

Unilever-Emery, Gouda, GLC: 99.9% C_2
 synthesized from propanoic acid, GLC: 99.0% C_3
 Fluka, purum grade, GLC: 99.8% C_4
 synthesized from valeric acid, GLC: 99.9% C_5
 Fluka, technical grade, GLC: 99.4% C_6
 synthesized from enanthic acid, GLC: 99.8% C_7
 Fluka, technical grade, recrystallized, GLC: 94.6% C_8
 synthesized from pelargonic acid, GLC: 94.9% C_9
 Fluka, technical grade, recrystallized, GLC: 91.4% C_{10}
 synthesized from undecanoic acid, GLC: 98.8% C_{11}
 Fluka, purum grade, recrystallized, GLC: 99.2% C_{12}
 synthesized from tridecanoic acid, GLC: 98.6% C_{13}
 Fluka, purum grade, recrystallized, GLC: 96.9% C_{14}
 synthesized from pentadecanoic acid, GLC: > 99.8% C_{15}
 Fluka, purum grade, recrystallized, GLC: 99.7% and (for β') 96.5% C_{16}
 synthesized from heptadecanoic acid, GLC: 99.3% C_{17}
 Fluka, purum grade, recrystallized, GLC: 98.1% and (for β') 95.0% C_{18}
 synthesized from nonadecanoic acid, GLC: 99.8% C_{19}
 synthesized from arachidic acid, GLC: 99.4% C_{20}
 synthesized from heneicosanoic acid, GLC: 97.4% C_{21}
 synthesized from behenic acid, GLC: 98.9% C_{22}

3.4 Preparation of deuterated triglycerides

Besides normal triglycerides three deuterated triglycerides were synthesized, i.e.:
glycerol-tri-(perdeutero-laurate), $C_3H_5[O-CO-(CD_2)_{10}-CD_3]_3$ I
(perdeutero-glycerol)-trilaurate, $C_3D_5[O-CO-(CH_2)_{10}-CH_3]_3$ II
glycerol-tri-(α -dideutero-laurate), $C_3H_5[O-CO-CD_2-(CH_2)_9CH_3]_3$ III

A method described by Nguyễn Đình-Nguyên & Stenhagen (1967) was used for the preparation of perdeutero-lauric acid (IV) and of perdeutero-glycerol (V). By this method, hydrogen atoms are exchanged by deuterium with aid of a metal catalyst (Pt), an alkaline catalyst (NaOD) and a promotor (D_2O_2).

Perdeutero-lauric acid The metal catalyst was prepared by stirring 2 g PtO_2 and 15 ml D_2O (99.75%) with D_2 gas for 30 h at $40^\circ C$, to complete reduction of PtO_2 .

For preparing the alkaline catalyst and promotor 1.4 g Na_2O_2 was slowly added to 90 g D_2O with cooling, to give a solution containing theoretically 1.5 g NaOD and 0.6 g D_2O_2 .

For preparation of perdeutero-lauric acid (IV), the metal and alkaline catalysts and promotor were flushed with D_2O (total amount 30 ml) into an autoclave and 3.52 g lauric acid (99.9%) was added. The reaction mixture was heated at $240^\circ C$ for 28 h in 1.5 atm D_2 , and continuously stirred. After cooling of the mixture, H_2O and D_2O were evaporated *in vacuo* at $60-80^\circ C$. The residue was flushed back into the autoclave with a total of 130 ml D_2O and the same treatment was repeated.

The deuterated water was evaporated and diluted hydrochloric acid was added to convert the perdeutero-laurate into the acid. The acid was extracted with diethyl ether, washed with distilled water and dried. The yield was 2.63 g (IV) or 75%.

The degree of exchange was checked by nuclear magnetic resonance (nmr) and mass spectrometry measurements.

By nmr proved 89% D to be exchanged (with respect to H of COOH), viz. 100% α CD_2 , 87% $(CD_2)_9$, 90% CD_3 .

The mass spectrum gave 90% D (42% D_{23} , 31% D_{22} , 13% D_{21} , 4% D_{20} , lower each < 1%).

Perdeutero-glycerol This compound was prepared in a similar way using 1 g PtO_2 , 0.69 g Na_2O_2 and 1.62 g glycerol. The glycerol was treated two times in the autoclave with 60 ml D_2O at $180^\circ C$ for 28 h in a deuterium atmosphere.

The mixture was flushed out of the autoclave with 10 ml H_2O , neutralized by ion exchange with 7.5 g Dowex 50Wx8, 200-400 mesh, dried on a steam bath under vacuum (20-50 mm). It yielded 0.292 g or 18%.

All hydrogens were exchanged by deuterium (nmr: 100%).

Dideutero-lauric acid 5 g lauric acid (99.9% C_{12}) was treated in an autoclave with deuterium gas (70 atm) for 24 h at $240^\circ C$, with the presence of Raney nickel.

The mass spectrum showed > 90% dideutero-lauric acid; according to the nmr

spectrum, the α protons were exchanged by deuterium.

Preparation of the triglycerides From the deuterated compounds, the triglycerides, I, II and III were prepared in the usual way, as described in Section 3.3.

4 The interpretation of infrared spectra

4.1 Vibration modes and characteristic bands

As, for lack of exact definitions, in infrared spectroscopy the terminology and the symbols for the normal vibrations of the atoms in a molecule is not uniform, Table 6 gives a summary of the terms used in this publication.

Almost independent of the total composition of the molecule, certain groups of atoms cause characteristic absorption bands in the spectrum. Such bands are found e.g. for ν C-H in the 2900 cm^{-1} region, for δ C-H at about 1400 cm^{-1} , for ν C-O between 1250 and 1060 cm^{-1} , and for ν C=O at 1750 - 1700 cm^{-1} . They vary slightly, dependent on other groups in the molecule, for ethers compared with esters, for methyl compared with methylene, etc., as well as for various compounds of the same series of compounds. This means that infrared spectra can be very useful in deducing the composition of an unknown compound.

For a large number of absorption bands in the infrared spectra the origin is as yet unknown, especially between 1350 and 900 cm^{-1} . The band collection as a whole in this region is specific for a certain compound. Therefore this region is generally referred to as the 'fingerprint region'.

Some vibrations modes give rise to a single band, e.g. the carbonyl stretching mode. Other vibration modes cause a number of related bands. I define:

Band series: the single bands of one type of vibration in a series of compounds (e.g. the carbonyl-stretching band series in fatty-acid esters from C_2 to C_{18}).

Band progression: the absorption bands which belong to one type of vibrations in one compound (the methylene-wagging band-progression in methyl laurate).

Band distribution: the absorption bands of one type of vibrations in a series of compounds (the methylene-wagging distribution in fatty-acid esters).

4.2 The infrared spectra of triglycerides

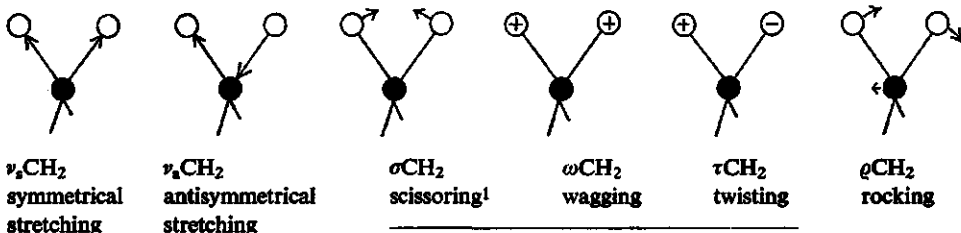
The infrared spectra from 4000 - 400 cm^{-1} of tristearin in the α form and in the β form are shown as examples of triglyceride spectra (Figure 10).

In the region 4000 - 1500 cm^{-1} only small variations are observed throughout the homologous series of triglycerides. Remarkable variations do occur in the region 1500 - 400 cm^{-1} ; for different compounds of the series, as well as for different phases of the same compound. Therefore in this study only the latter region will be considered.

Until now no concerted effort has been made to assign the multitude of absorption

Table 6. Nomenclature of normal vibrations.

a. Normal vibrations of the methylene group

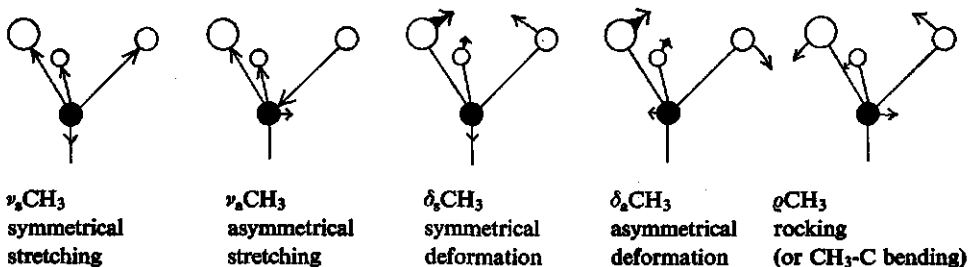


deformation vibrations

stretching vibrations

bending vibrations

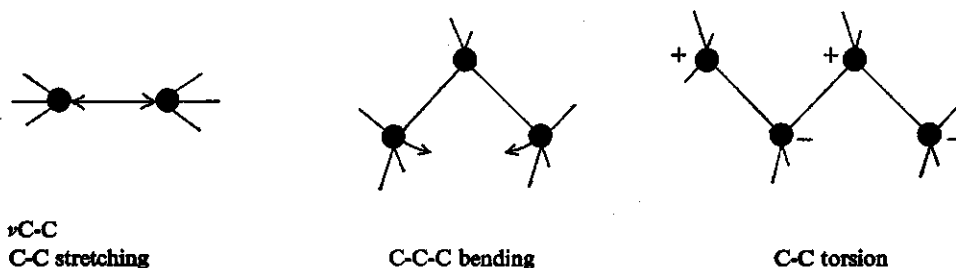
b. Normal vibrations of the methyl group



stretching vibrations

bending vibrations

c. Normal skeletal vibrations



d. Normal vibrations of other groups of atoms

Similar symbols; e.g. $\nu\text{C=O}$: carbonyl stretching vibration
 $\nu\text{C-O}$: C-O stretching vibration

1. In other publications also termed bending.

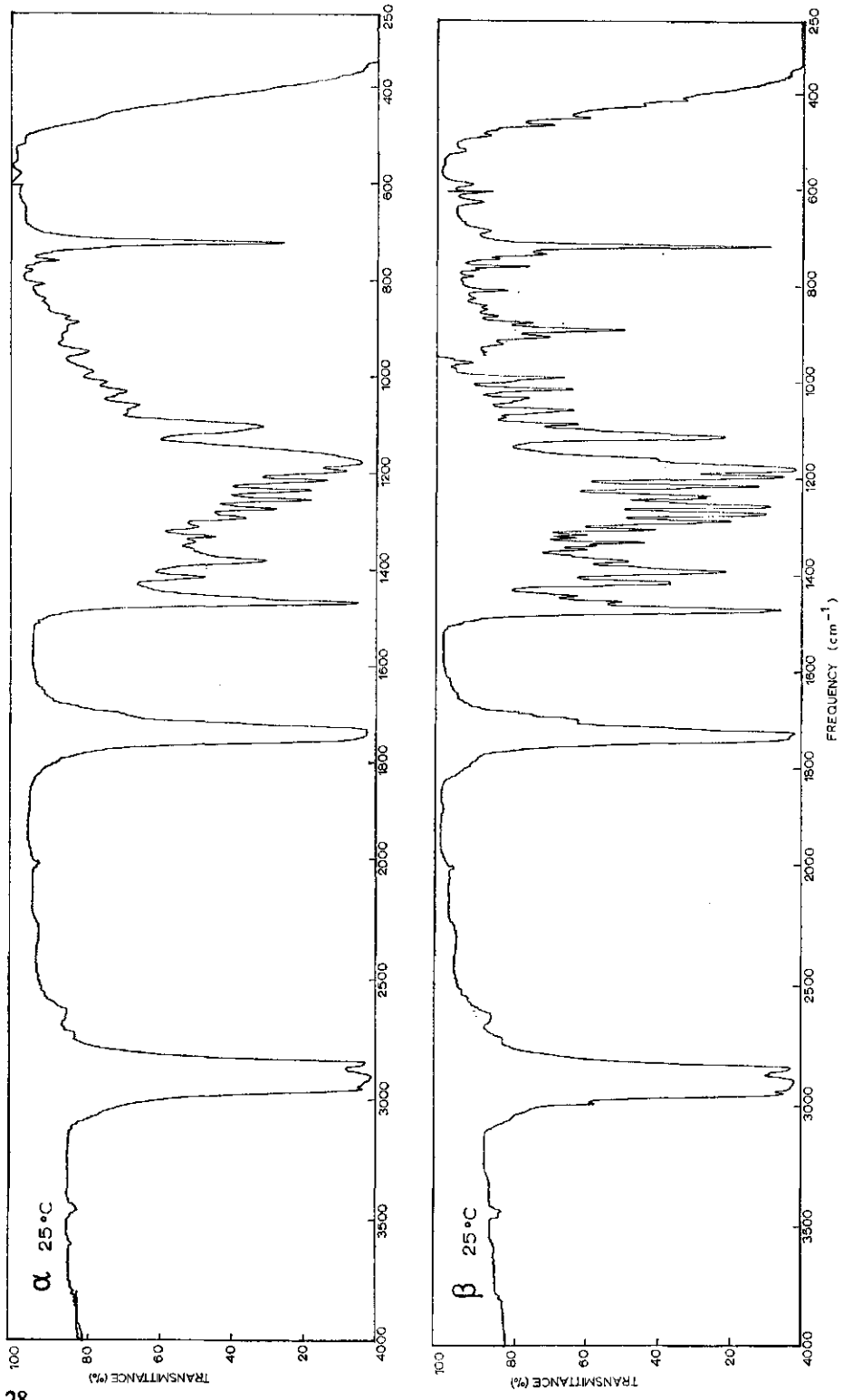


Figure 10a, b. Infrared spectra of tristearin.

bands in the fingerprint region. I will attempt to interpret these bands in Chapter 5. Vibrational analyses by other authors on other long chain compounds, particularly *n*-paraffins will be reviewed in Sections 4.4-4.6. Molecular vibrations in general will be considered in Section 4.3, and Section 4.7 will apply this information to a theoretical treatment of band collections in triglycerides.

4.3 The vibrations within a molecule

An *n*-atomic molecule has $3n$ degrees of freedom, including three translations and three or two (for linear molecules) rotations of the molecule as a whole. To characterize the remaining $3n - 6$ or $3n - 5$ internal vibrations it is convenient to introduce an equal number of independent internal *normal vibrations*. The number of energy bands actually observed may be considerably lower, some reasons being:

- bands are beyond the range of the measured spectrum,
- bands are too weak,
- bands are forbidden, because only vibrations accompanied by a change in dipole moment are active in the infrared, so that symmetric vibrations are not observed. (These bands can be active in the Raman spectra.)

The vibrations of two adjacent atoms in a molecule can to a first approximation be described by Hooke's law for the simple harmonic oscillator, so that the vibration frequency is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{\mu}} \quad (1)$$

with

ν = the frequency of the vibration

f = the force constant of the bond for this vibration

μ = the reduced mass of the vibrating system,

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

where m_1 and m_2 are the masses of the vibrating atoms.

Unbranched, long-chain molecules with periodic structures can be considered as series of point masses, connected by chemical bonds with certain stretching- and bending-force constants. For the mathematical calculation of the molecular vibrations in such chains the coupled-oscillator model can be used (Born & Von Kármán, 1912; Bartholomé & Teller, 1932; Kirkwood, 1939; Pitzer, 1940; Zbinden, 1964).

Suppose we have a row of *n* point masses *m* connected by springs with a stretching-force constant *f* and with interaction only between two neighbouring masses. For each vibration mode, *n* normal vibrations are found, with frequencies ν_k :

$$v_k = 2 v_o \sin \frac{\pi d}{\lambda_k} \quad (2)$$

where

$$k = 1, 2, \dots, n$$

d = distance between two adjacent point masses

$$v_o = \text{eigenfrequency of one point mass} = \frac{1}{2\pi} \sqrt{\frac{f}{m}}$$

λ = wave length

λ_k is given by (Zbinden, 1964)

$$\lambda_k = \frac{2n}{k-1} d \text{ (free ends) or } \lambda_k = \frac{2(n+1)}{k} d \text{ (fixed ends)} \quad (3a, b)$$

(see Fig. 11 for the fixed boundary case).

The phase shift φ_k between two adjacent point masses is given by the Born-Von Kármán (1912) periodicity condition

$$\varphi_k = \frac{2\pi d}{\lambda_k} \quad (4)$$

Substituting (3a, b) in (4) gives

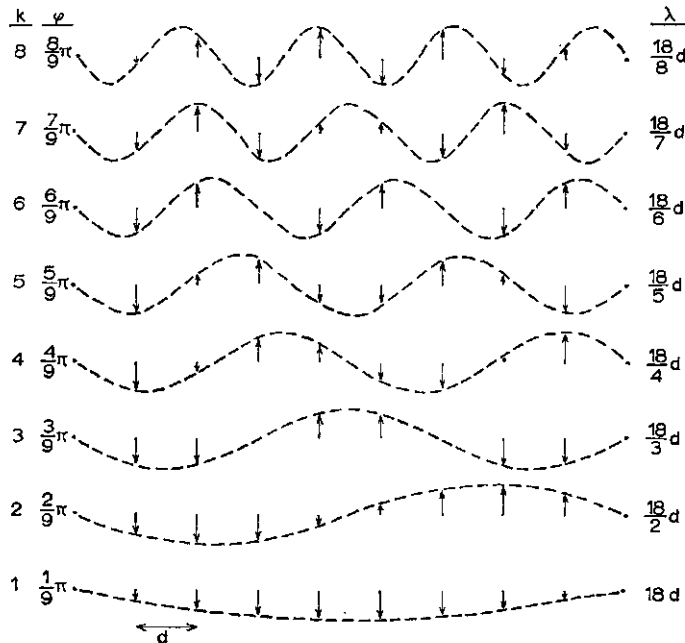


Figure 11. Vibrations of a linear chain of eight point masses with fixed ends (Zbinden, 1964).

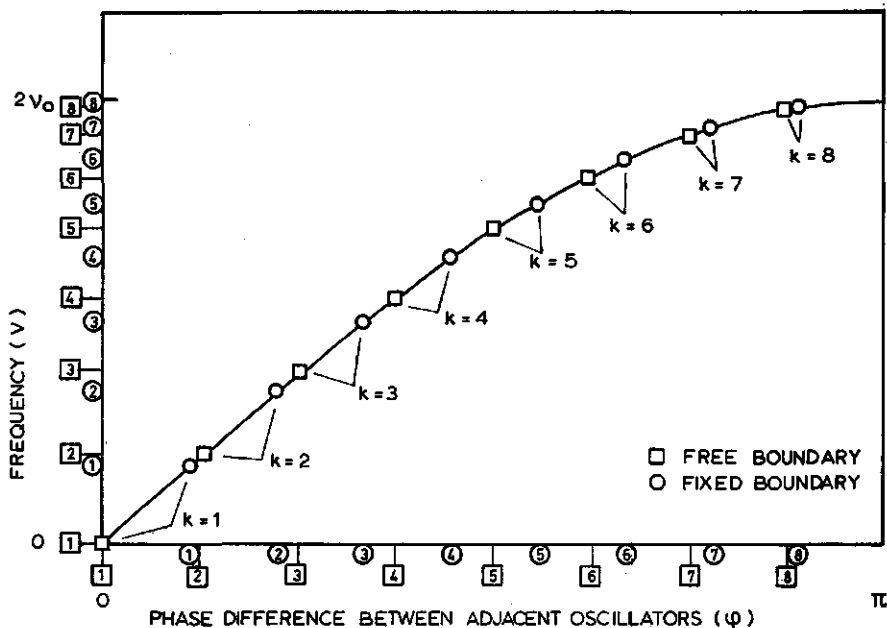


Figure 12. Frequency branches for the vibrations in a chain of eight point masses with fixed and free boundaries (Zbinden, 1964).

$$\varphi_k = \frac{\pi(k-1)}{n} \text{ (free ends) or } \varphi_k = \frac{\pi k}{n+1} \text{ (fixed ends)} \quad (5a, b)$$

where $k = 1, 2, \dots, n$.

Substituting (4) in (2) gives

$$v_k = 2 v_0 \sin \frac{\varphi_k}{2} \quad (6)$$

which indicates that the frequency is a function of the variable φ only.

Figure 12 gives the frequency-phase curve for eight point masses for the fixed and the free boundary model. These models represent extreme cases: actually the vibration modes in a molecule will be intermediate.

4.4 Vibrational analyses of *n*-paraffins

X-ray and infrared analyses have shown that hydrocarbons in the crystalline state assume the planar zigzag form (Müller, 1928; Krimm et al., 1967), so that the coupled-oscillator model can be applied for calculations of their molecular vibrations.

Vibrational analyses of *n*-paraffins and related compounds have been carried out by a large number of authors, a.o. Kellner, 1945; Axford & Rank, 1949, 1950; Brown & Sheppard, 1950, 1954a, b, 1955; Brown et al. 1950, 1954a, b; Barrow, 1951; Primas

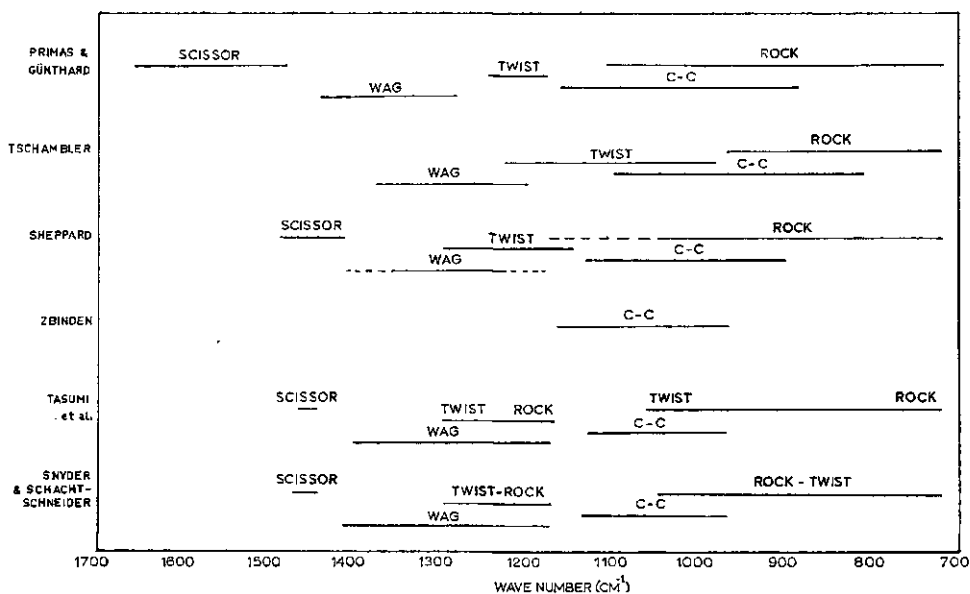


Figure 13. Frequency ranges for methylene and skeletal vibrations of normal hydrocarbon chains.

& Günthard, 1953a, b; Tschamler, 1954; Liang et al., 1956; Krimm et al., 1956; Sheppard, 1959; Nielson & Holland, 1960, 1961; Nielson & Hathaway, 1963; Tasumi & Shimanouchi, 1962; Tasumi et al., 1962; Snyder, 1960, 1961; Snyder & Schachtschneider, 1962, 1963; Schachtschneider & Snyder, 1963; Zbinden, 1964.

These experimental and theoretical studies agree in that the distributions of frequencies for the same type of vibrations are confined to relatively well-defined regions. Estimates of the location of these regions by various reported authors are given in Figure 13. There are some disagreements, while there are interactions of unknown magnitude, and also while perturbations from the methyl or other end groups are not taken into account.

As the calculations of Snyder and Schachtschneider are the most extensive and detailed, in the next sections I will use data especially from these authors.

4.5 Band distributions in *n*-paraffins

In polymethylene chains the distributions are due to methylene and skeletal vibrations.

There are six fundamental methylene vibrations: antisymmetrical stretching, symmetrical stretching, scissoring, wagging, twisting and rocking (Table 6). The carbon chain itself has three fundamental modes: C-C stretching, C-C-C angle bending and torsional vibrations about internal C-C bonds. This gives rise to nine separate distributions of frequencies. Figure 14 shows the frequency-phase diagrams for these

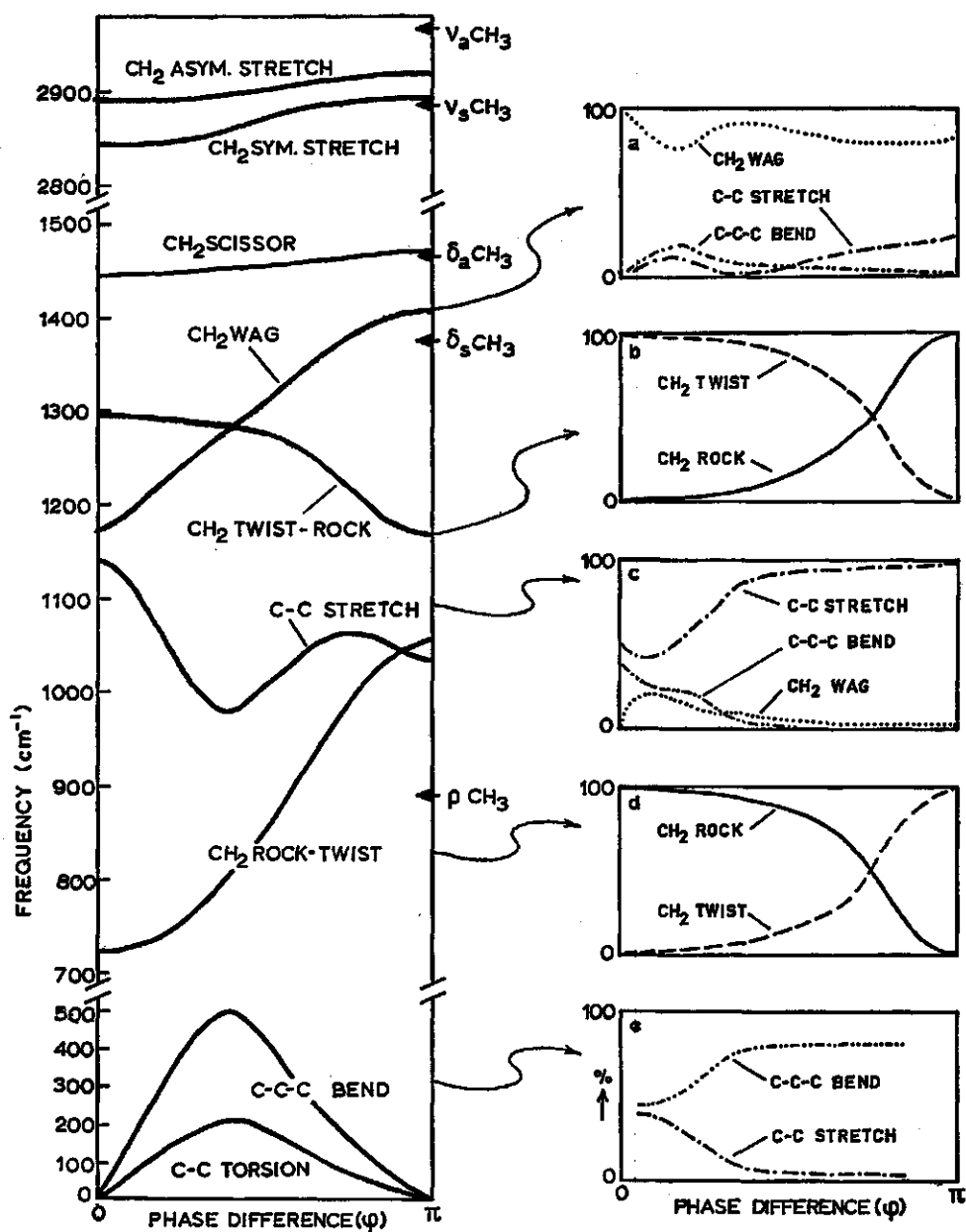


Figure 14. Frequency-phase diagrams of fundamental methylene and skeletal vibrations.

Contribution of fundamental vibration modes to the apparent

- methylene wagging (fig. 14a),
- methylene twisting-rocking (fig. 14b),
- skeletal stretching (fig. 14c),
- methylene rocking-twisting (fig. 14d) and
- skeletal bending (fig. 14e) modes.

distributions, as theoretically calculated and experimentally verified as far as possible by Tasumi et al. (1962).

There are two limiting modes to each progression, viz. the in-phase mode $\varphi = 0$ and the out-of-phase mode $\varphi = \pi$; which is which depends on how the symmetry coordinates are defined. The nomenclature adopted by Schachtschneider and Snyder sometimes is the reverse of that used by Tasumi.

The apparent distributions in Figure 14 are in general not true fundamental modes, but a combination of fundamental modes. The contributions of the fundamental modes to the apparent modes as calculated by Tasumi et al. are illustrated in Figure 14 a-e for the methylene wagging, methylene twisting-rocking, skeletal stretching, methylene rocking-twisting and skeletal bending modes respectively. The skeletal stretching and bending modes contribute to the methylene-wagging distribution (Figure 14a), etc.

Schachtschneider and Snyder (1963) also included coupling with methyl vibration modes in their calculations. The methyl vibration frequencies reported by these authors are indicated in Figure 14. Their conclusions (Table 7) agree in the main those of Tasumi et al.

Methylene twisting and rocking vibrations appeared in two regions, one between ~ 1295 and ~ 1170 cm^{-1} and the other between ~ 1060 and ~ 720 cm^{-1} . Earlier investigators had supposed that these regions contained twisting modes and rocking modes, respectively (Figure 13). The terms 'twisting-rocking' and 'rocking-twisting'

Table 7. Classification of normal modes according to the character of their motion (Schachtschneider & Snyder, 1963)

CH ₃ asymmetric C-H stretching: almost pure $\nu_a\text{CH}_3$
CH ₃ symmetric C-H stretching: almost pure $\nu_s\text{CH}_3$
CH ₂ antisymmetric C-H stretching: almost pure $\nu_a\text{CH}_2$
CH ₂ symmetric C-H stretching: almost pure $\nu_s\text{CH}_2$
CH ₃ asymmetric deformation: $1.6 \delta_a \text{CH}_3 + 0.4 \rho\text{CH}_3$
CH ₂ scissoring: σCH_2 , strongly coupled with $\delta_a\text{CH}_3$, coupling strongest near $\varphi = \pi$ and least near $\varphi = 0$
CH ₃ symmetric deformation: almost pure $\delta_s\text{CH}_3$, except when the wagging mode is near; then strong coupling with ωCH_2 occurs
CH ₂ wagging: mostly ωCH_2 with some νCH_2 and $\delta_a\text{CH}_3$
CH ₂ twisting-rocking: pure twist at $\varphi = 0$, pure rock at $\varphi = \pi$; from $\varphi = 0$ to $\varphi = \pi$ ratio rock/twist varies from 0 to ∞
C-C stretching: mostly $\nu\text{C-C}$ with strong coupling with ρCH_3 and C-C-C bending near $\varphi = 0$
CH ₃ terminal rocking: for long chains ($\text{CH}_2 > \sim 10$): mainly ρCH_3 , with $\nu\text{C-C}$, ωCH_2 and C-C-C bending
CH ₂ rocking-twisting: pure rock at $\varphi = 0$, pure twist at $\varphi = \pi$; from $\varphi = 0$ to $\varphi = \pi$ ratio twist/rock varies from 0 to ∞
C-C-C bending: almost pure C-C-C bending except near $\varphi = 0$ where coupling with $\nu\text{C-C}$ occurs
C-C torsion: CH ₂ -CH ₂ torsion with contribution of CH ₃ -CH ₂ torsion, greatest at highest frequencies

for these distributions were proposed by Snyder and Schachtschneider. Although the 720 cm^{-1} limit corresponding to $\varphi = 0$ is indeed an in-phase methylene-rocking mode, the 1060 cm^{-1} is an out-of-phase twisting mode. Similarly, although the 1295 cm^{-1} limit is an in-phase twisting mode, the 1170 cm^{-1} limit is an out-of-phase rocking mode.

The C-C stretching distribution had a minimum in its frequency-phase curve. This implied an overlap in the successive absorption bands due to this vibration mode, which hindered the assignments. Pitzer (1940) already has deduced that a coupling of the C-C stretching mode with the C-C-C bending mode gives a curve with a minimum.

Snyder and Schachtschneider have pointed out that for shorter chains, particularly for those modes to which end groups contributed, φ and consequently k lose their physical significance.

4.6 Vibrational analysis of fatty-acid compounds

The infrared spectra of fatty acids and their salts and esters have been studied by various authors (review: Chapman, 1965b). In this section special attention will be paid to band progressions in these compounds.

Jones and Sinclair described a distribution of uniformly spaced bands in solid fatty acids and methyl esters from C_{12} to C_{21} between 1350 and 1180 cm^{-1} , increasing in number with the chain length (Jones et al., 1952; Sinclair et al., 1952a, b). The band progression was diminished in intensity or destroyed by introduction of unsaturated linkages. In *cis* compounds an irregular pattern was obtained. The spectrum of the *trans*-unsaturated elaidic acid closely resembled that of one of the saturated acids of short chain length (C_9 and not e.g. C_{12} as the authors mention), suggesting that the two sections of the chain on each side of the double bond behave as more or less independent units. These observations substantiated the view that a linear zigzag chain in the crystal is required for a well defined progression.

Corish & Chapman (1957) found similar bands in the spectra of lower homologues (C_2 to C_{12}), although the regularity seemed to decrease with decreasing chain length.

Von Sydow (1955) pointed out that the positions of the band progression peaks were not merely related to the chain length but also dependent on crystal forms.

By empirically defining the band progression region as 1350 - 1180 cm^{-1} the following relationship is reported for straight chain fatty acids by Meiklejohn et al. (1957):

Number of carbon atoms in the chain: n

$$n \text{ even} \quad \text{Number of bands} = \frac{n}{2}$$

$$n \text{ odd} \quad \text{Number of bands} = \frac{n+1}{2}$$

This 'rule of two' relationship is valid for solid acids and soaps. A compound with an odd number of carbons may be distinguished from the next higher even

numbered acid which has the same number of progression bands by a shift in wave length of the entire progression.

More of the progression bands for a soap can be seen than for the corresponding acid, due to the removal of the interfering C-O stretching band at 1307 cm^{-1} .

Using the 'rule of two', observed by Meiklejohn et al., Susi (1959) determined the position of the double bond in *trans*-6- through 11-octadecenoic acids. The number of bands was related to the total length of the chain segment next to the carbonyl group. Contrary to saturated acids, no distinct carboxyl band was found in the band-progression region. Some weak bands occurring between the main progression bands,

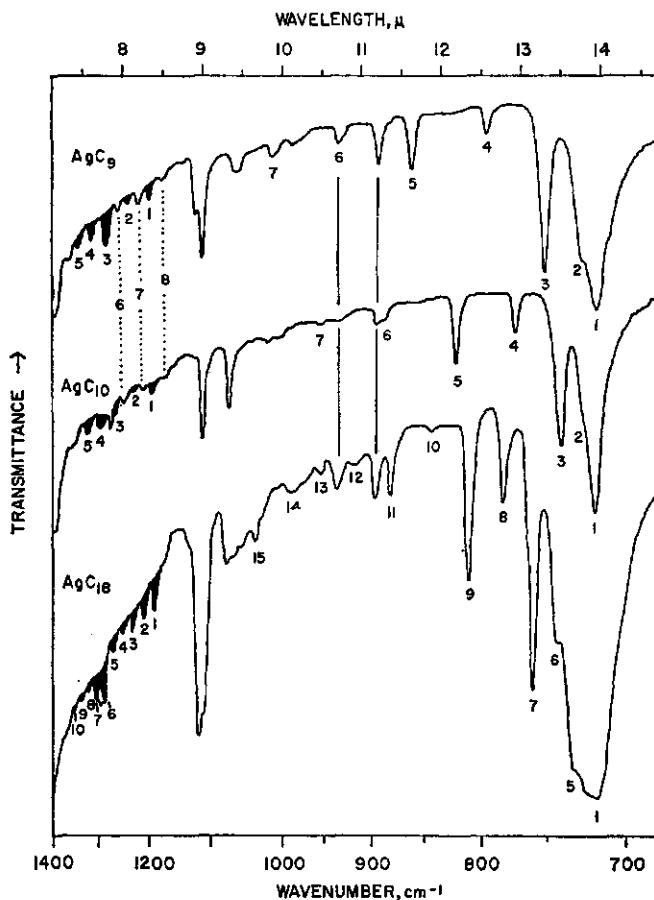


Figure 15. Infrared spectra of the silver salts of saturated C_9 , C_{10} and C_{18} fatty acids (Kirby et al., 1965).

Peaks assigned to methylene vibrations are numbered;

- black peaks = wagging
- peaks joined by dotted lines = twisting-rocking
- the remainder = rocking-twisting

Peaks joined by solid lines are assigned to end group vibrations.

and partially overlapping with them, might be caused by the terminal chain segments (from the double bond to the methyl group). These segments behave much like unsubstituted *n*-paraffins, which show progression bands of considerably lower intensity and less regular spacings than the corresponding fatty acids.

Kirby et al. (1965) studied the methylene wagging, twisting and rocking vibrations in salts of saturated and unsaturated fatty acids. Some spectra are shown in Figure 15.

In the region 1070-710 cm^{-1} the increase of the number of peaks with chain length in saturated salts corresponded closely to hydrocarbon behaviour, as reported by Snyder & Schachtschneider (1963). Forbidden peaks in the hydrocarbons were the weaker ones in the salt spectra. Salts with various cations gave practically identical curves.

In *cis*-unsaturated salts there were relatively fewer peaks. The *trans*-unsaturated elaidate salts spectra, however, were more similar to the corresponding saturated salts. Therefore the methylenes in the carboxylate segment produce the peaks in the *cis*-compounds, but the *trans*-compounds give the vibration of the entire length of chain. Apparently the *cis*-double bond disrupts the vibration of the fatty radical as a unit, but the slight distortion of the chain by a *trans*-double bond does not prevent coupling of the rocking-twisting modes of the segments at opposite sides of this double bond.

The region 1380-1170 cm^{-1} was more confusing due to overlapping of the methylene wagging and methylene twisting-rocking vibration peaks. The total number of peaks and the relative intensities depended on the cation. Certain peak positions shifted very little with different cations. These were assigned to methylene wagging vibrations. Other peaks were seen only with some cations, particularly in silver and barium salts;

Table 8. Number of methylene groups in the chain of unsaturated compounds (Kirby et al., 1965).

Compound	Formula	Chain length as concluded from	
		methylene wagging 1380-1170 cm^{-1}	methylene rocking-twisting 1070-710 cm^{-1}
<i>Cis</i> -configuration			
petroselenate	$\text{CH}_3(\text{CH}_2)_{10}\text{CH} = \text{CH}(\text{CH}_2)_4\text{COO}^-$	4	4
palmitoleate	$\text{CH}_3(\text{CH}_2)_5\text{CH} = \text{CH}(\text{CH}_2)_7\text{COO}^-$	7	7
oleate	$\text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_7\text{COO}^-$	7	7
11-eicosanoate	$\text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_9\text{COO}^-$	9	9
erucate	$\text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_{11}\text{COO}^-$	11	11
	Conclusion:	carboxylate segment only	carboxylate segment only
<i>Trans</i> -configuration			
elaidate	$\text{CH}_3(\text{CH}_2)_7\text{CH} = \text{CH}(\text{CH}_2)_7\text{COO}^-$	7	16
	Conclusion:	carboxylate segment only	total chain

these peaks were assigned to methylene twisting-rocking vibrations.

Unsaturated salts had fewer peaks in this region than saturated salts of the same chain length. The number and position of the peaks was related to the length of the carboxylate segment. This holds for *cis* as well as for *trans*-unsaturated salts in this region. Here in all respects elaidate spectra agreed with those of oleate salts.

Apparent chain lengths in unsaturated compounds concluded from comparison with saturated compound data are summarized in Table 8.

4.7 Theoretical considerations about distributions in triglycerides

In the preceding sections the coupled-oscillator model has been shown to work fairly well for a linear methylene zigzag chain. Thus a chain of n methylene groups will have n vibrations for each of the six fundamental methylene vibration modes (Section 4.3 and 4.5). For the skeletal vibrations there will be $n - 1$ C-C stretching vibrations, $n - 2$ C-C-C bending vibrations and $n - 3$ C-C torsion vibrations.

I applied the model to the triglycerides under investigation, with the aim of calculating the number of bands for a given compound. This treatment appears to involve some practical and theoretical difficulties.

In practice it appears that the actual number of bands found in the spectra does not agree with that predicted for the following reasons (cf. Chapter 5; see also Figure 14).

The absorption regions of the *methylene antisymmetric* and *symmetric stretching* distributions are too small for separate bands to be identified.

The *methylene wagging* distribution is above 1385 cm^{-1} masked by the strong methyl symmetric deformation band.

The *methylene twisting-rocking* bands are very weak compared to the methylene wagging modes, which absorb in the same region.

At the high frequency end, the intensities of the *rocking-twisting* bands are also weak, and moreover there is an overlap with the *C-C stretching* modes. Identification of the latter is further hampered by the minimum in its frequency-phase curve (Figure 14).

The other *skeletal bending* and *torsion* vibrations fall totally or almost totally outside the examined region.

Besides these practical difficulties there are also some theoretical problems.

The model contains the simplifications of discounting the intramolecular and intermolecular effects which actually do occur.

For a polymethylene chain having n carbon atoms, mostly a phase difference

$$\varphi_k = \frac{\pi(k-1)}{n} \quad (5a)$$

where $k = 1, 2, \dots, n$

is accepted (Section 4.3), but there are several variations between authors as cited in Section 4.4.

The phase difference of the normal coordinates of a finite chain is difficult to find when appreciable coupling between two symmetry coordinates occurs (Tasumi et al., 1962; Pitzer, 1940). The phase differences of the resultant normal coordinates will then not agree with that from formula (5a), and cannot be defined in this way. In practice, however, workable results are obtained, even when coupling occurs.

Special problems are the border conditions and the choice of chain length which has to be considered in a given compound. As to the border conditions, Zbinden (1964) has pointed out, that the fixed-end model seems more realistic for the methylene rocking-twisting distribution in hydrocarbons than the free-end model. This justifies the use of formula (5a) in that case.

As far as the choice of chain length, the question is whether the end groups have to be taken into account, especially when this concerns a methyl group.

For the skeletal vibrations generally it is assumed that this is so (Brown, Sheppard & Simpson, 1954a; Sheppard, 1959; Schachtschneider & Snyder, 1963); it is a plausible assumption. An n -paraffin with n methylene groups will then have $n + 1$ C-C stretching vibrations, n C-C-C angle bending vibrations, $n - 1$ C-C torsion vibrations.

For the calculation of the number of vibrations in C-H distributions, however, most authors discount the CH₃ groups (Brown, Sheppard & Simpson, 1954a; Sheppard, 1959; Tasumi et al., 1962; Schachtschneider & Snyder, 1963; Kirby et al., 1965). Brown & Sheppard (1955) compare decamethylene halides with n -dodecane 'which has the same number of CH₂ groups'.

However, comparison of the methylene wagging distribution of n -alkyl bromides (Brown & Sheppard, 1954a) with those of n -paraffins (Snyder & Schachtschneider, 1963) suggests that the total number of carbons, including the CH₃ groups is the significant figure.

Results obtained by Meiklejohn et al. (1957) on saturated long-chain fatty acids, and by Susi (1959) on octadecanoic acids also indicate that the number of bands is closely related to the total length of the chain or chain segment rather than the number of methylene units. The same conclusion is suggested by data of Corish & Chapman (1957).

Snyder & Schachtschneider (1963) point out that in cases where strong interaction does occur between the methylene chain and the methyl group vibrations, an extra mode $k = 0$ or $k = n + 1$ seems to occur. They report the mode $k = n + 1$ for some of the rocking-twisting and twisting-rocking distributions.

As in triglycerides two different end groups are present in the hydrocarbon chain segments, namely one methyl and one carbonyl group, the border conditions will differ from those of n -paraffins. Intra- and intermolecular effects can be expected. Nevertheless I succeeded in assigning distributions in triglycerides with help of n -paraffins data. I found a remarkable agreement between the progressions of the methylene rocking-twisting and the methylene-wagging modes in triglycerides [CH₃-(CH₂) _{$n-2$} -COO]₃C₃H₅ and paraffins CH₃-(CH₂) _{$n-3$} -CH₃ respectively; that means, a C _{n} triglyceride has to be compared with a C _{$n-1$} n -paraffin.

Table 9. Compounds showing corresponding band progressions for methylene vibrations.

Compound	Formula
C _{n-1} paraffin	CH ₃ -(CH ₂) _{n-3} -CH ₃
C _{n-1} alkyl bromide	CH ₃ -(CH ₂) _{n-2} -Br
C _n fatty-acid salt	CH ₃ -(CH ₂) _{n-2} -COONa
C _n triglyceride	[CH ₃ -(CH ₂) _{n-2} -COO] ₃ C ₃ H ₅

In the case of the C-C stretching mode the situation is less clear, but it seems that the best agreement is obtained when the same rule is assumed to be valid.

For fatty-acid salts from acetates to behenates, Kirby et al. (1965) account for the methylene groups only. I have evaluated the reported methylene distributions with respect to those of the *n*-paraffins as given by Snyder & Schachtschneider and of the triglycerides, and could conclude that a C_n fatty acid salt, a C_n triglyceride and a C_{n-1} paraffin correspond to each others.

If it is assumed that the methyl groups do not participate in the methylene vibration, the same chain length can be constructed in the considered compounds (Table 9) when the α-CH₂ having a particular position is also excluded in the substituted hydrocarbons. The length of the vibrating hydrocarbon chain, and in consequence also the number of bands then will be *n* - 3.

If, on the other hand, the α-CH₂ is counted with the other methylenes, also the methyl groups have to be included to obtain the same chain lengths and the chain length and the number of bands will be *n* - 1.

As the total number of bands cannot be determined from the spectra, these suppositions cannot be verified directly from the spectroscopic results. The latter proposition is indirectly confirmed, however, from the examination of an α-dideuterated triglyceride, Section 5.5.3. This showed that in triglycerides all methylene groups take part in the methylene vibrations, including the α-CH₂. So I conclude that probably methyl end groups take part to methylene vibrations of long-chain hydrocarbons and related compounds.

5 The infrared spectra of the triglycerides

5.1 Presentation of the spectra of triglycerides C_2 - C_{22}

The infrared spectra from 1500 to 400 cm^{-1} of triglycerides from triacetin (C_2) to tribehenin (C_{22}) were recorded using the technique described in Chapter 3 (Figs. 16-36).

The minimum scanning temperature, about -180°C , was limited by the temperature of the cooling medium: liquid nitrogen. At this temperature spectra of the polymorphic crystalline states were obtained from trienantoin (C_7) up (Figs. 21a, b, c, 36a, b, c). For the series triacetin (C_2) to tricaproin (C_6) no solid state spectra could be obtained. In these cases the spectra at -180°C are shown, although not of a crystalline state (Figs. 16a-20a).

The spectra of the liquid form (Figs. 16d-36d) were examined either at room temperature or, for the higher members, at elevated temperature, above the melting point. On these spectra the scanning temperatures are indicated.

In all spectra the wave numbers 1400, 1300, etc. are indicated by a marker pip. Sometimes two weak bands at about 660 cm^{-1} are present due to absorption of water vapour.

The band positions in the polymorphic forms are collected in tables 10-25.

Most of the very weak and weak bands are considered to originate from so far unknown higher-order interactions and are ignored. I could assign the majority of the observed medium and strong bands to definite vibration modes. These assignments, which are based on the spectra in figures 21-36 and on other spectra, not shown here, are listed in tables 10-25. Various series of bands will be considered in detail in the following sections.

(Text continued on page 116.)

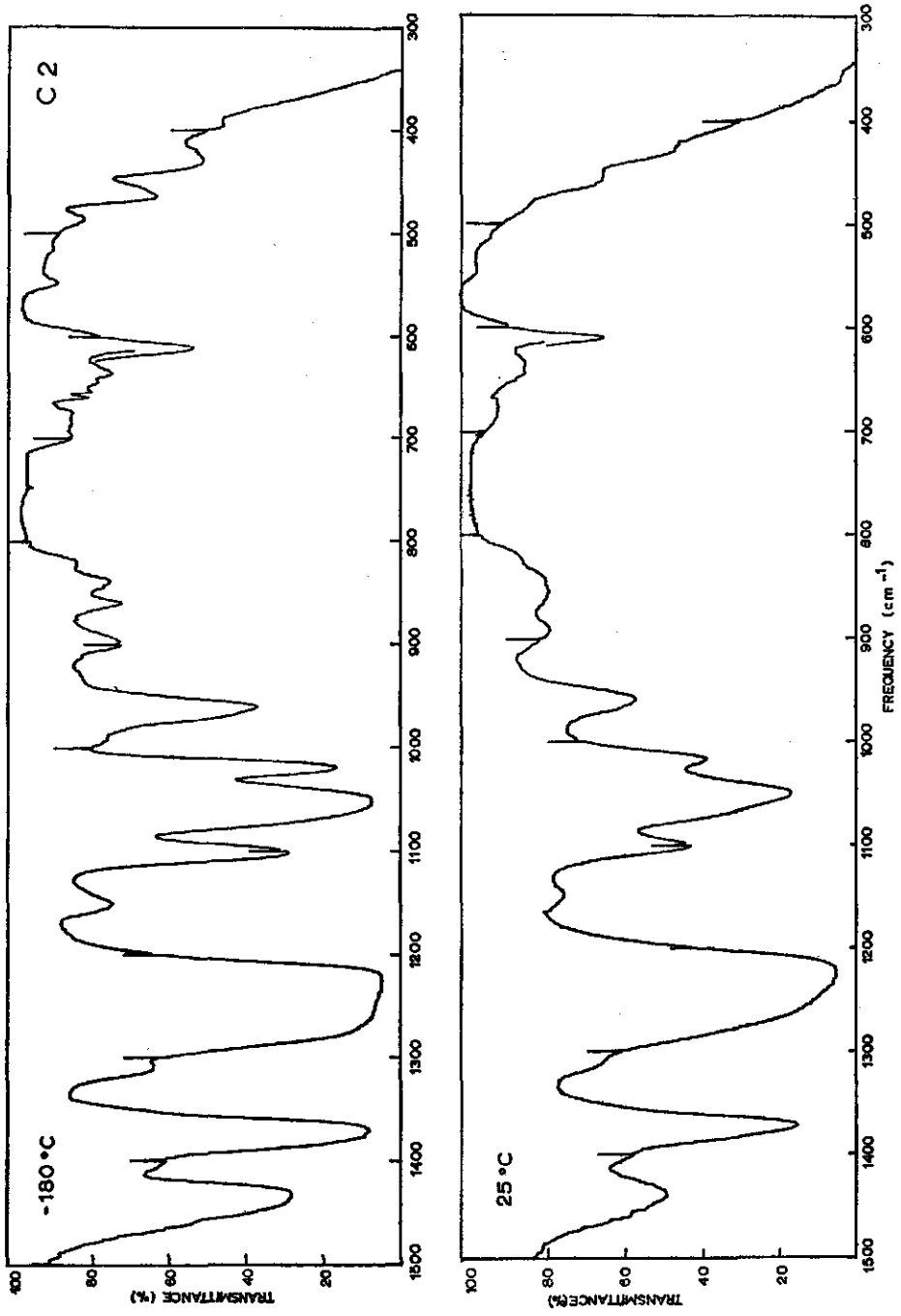


Figure 16a, d. Infrared spectra of triacetin.

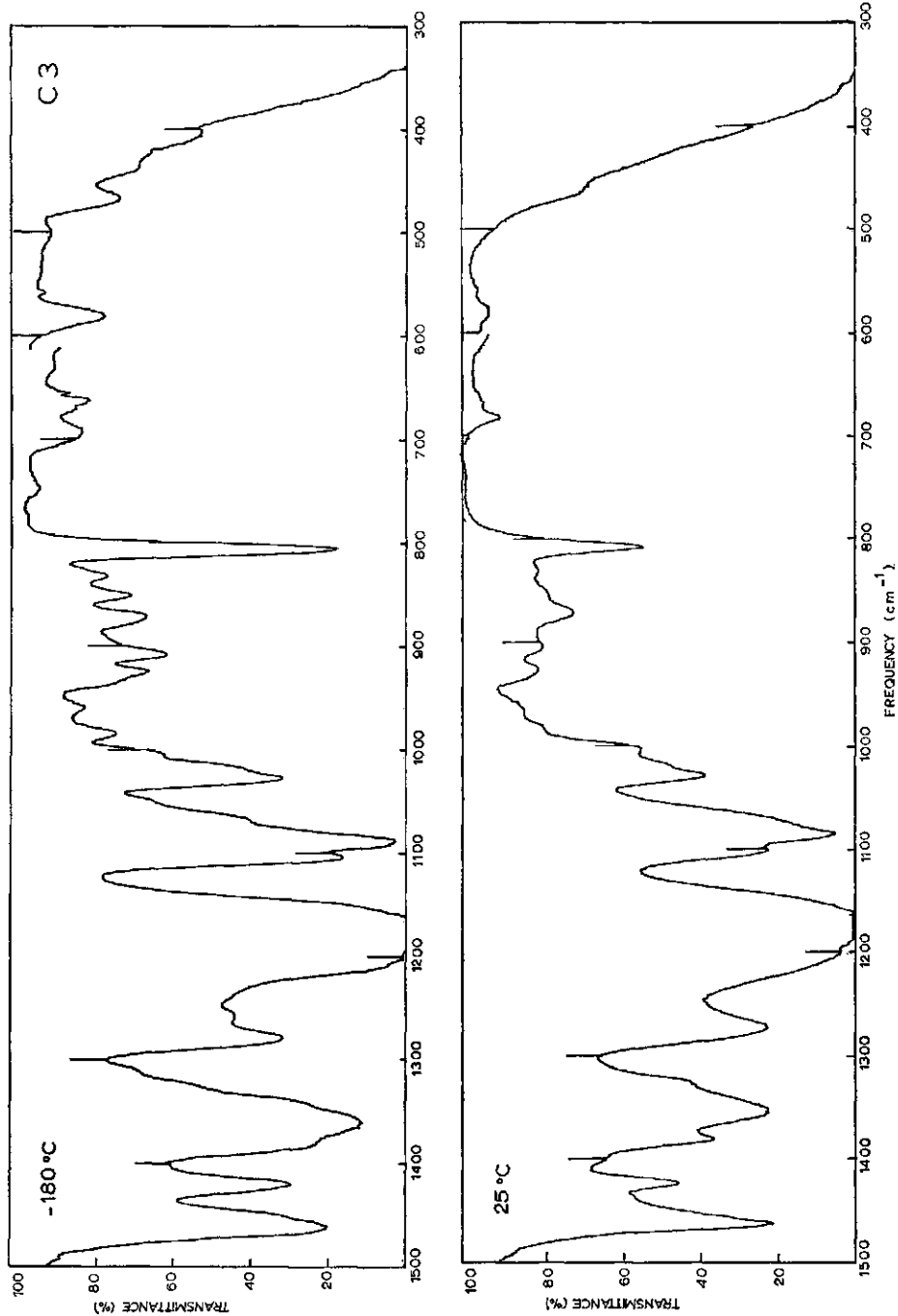


Figure 17a, d. Infrared spectra of tripropionin.

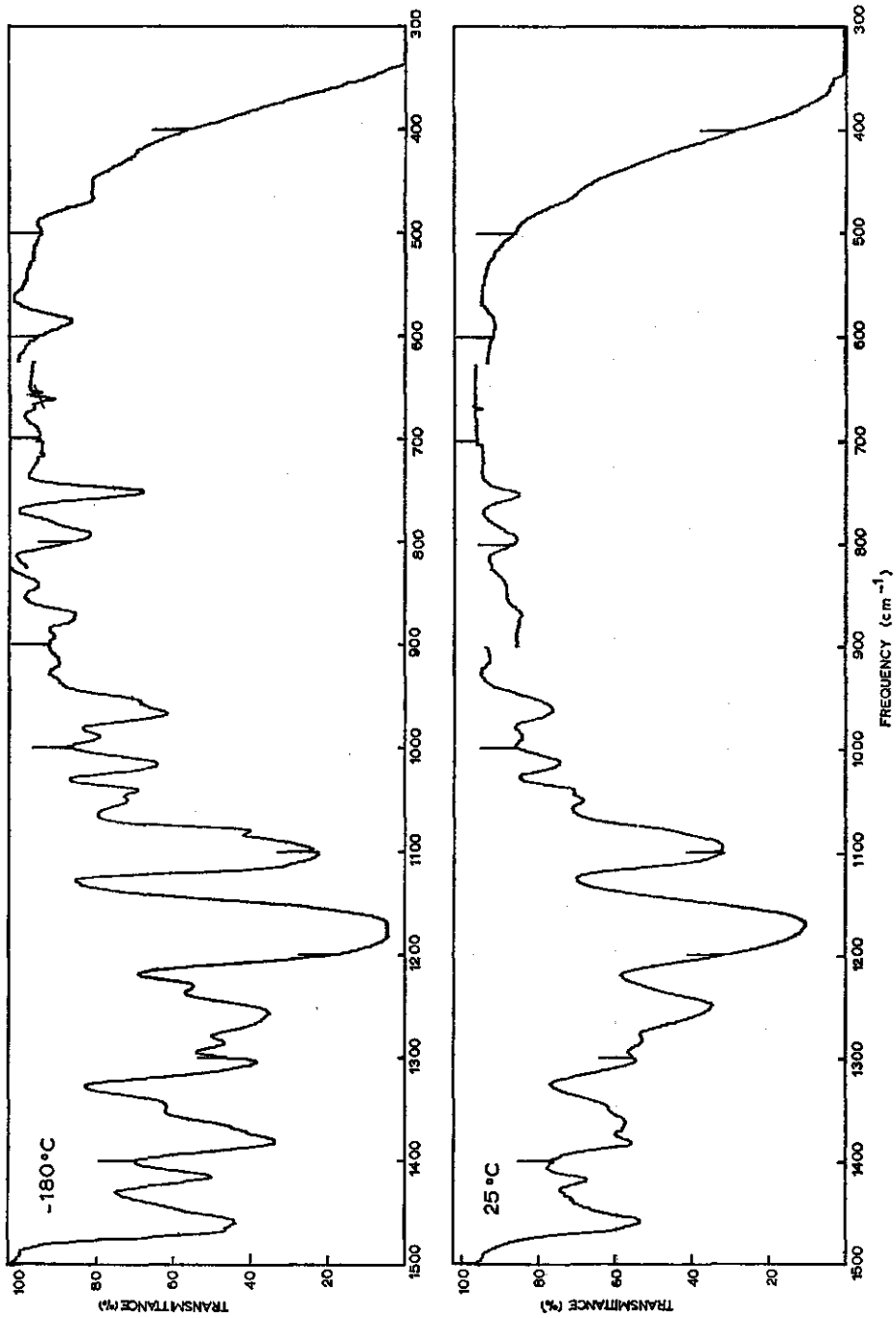


Figure 18a, d. Infrared spectra of tributyrin.

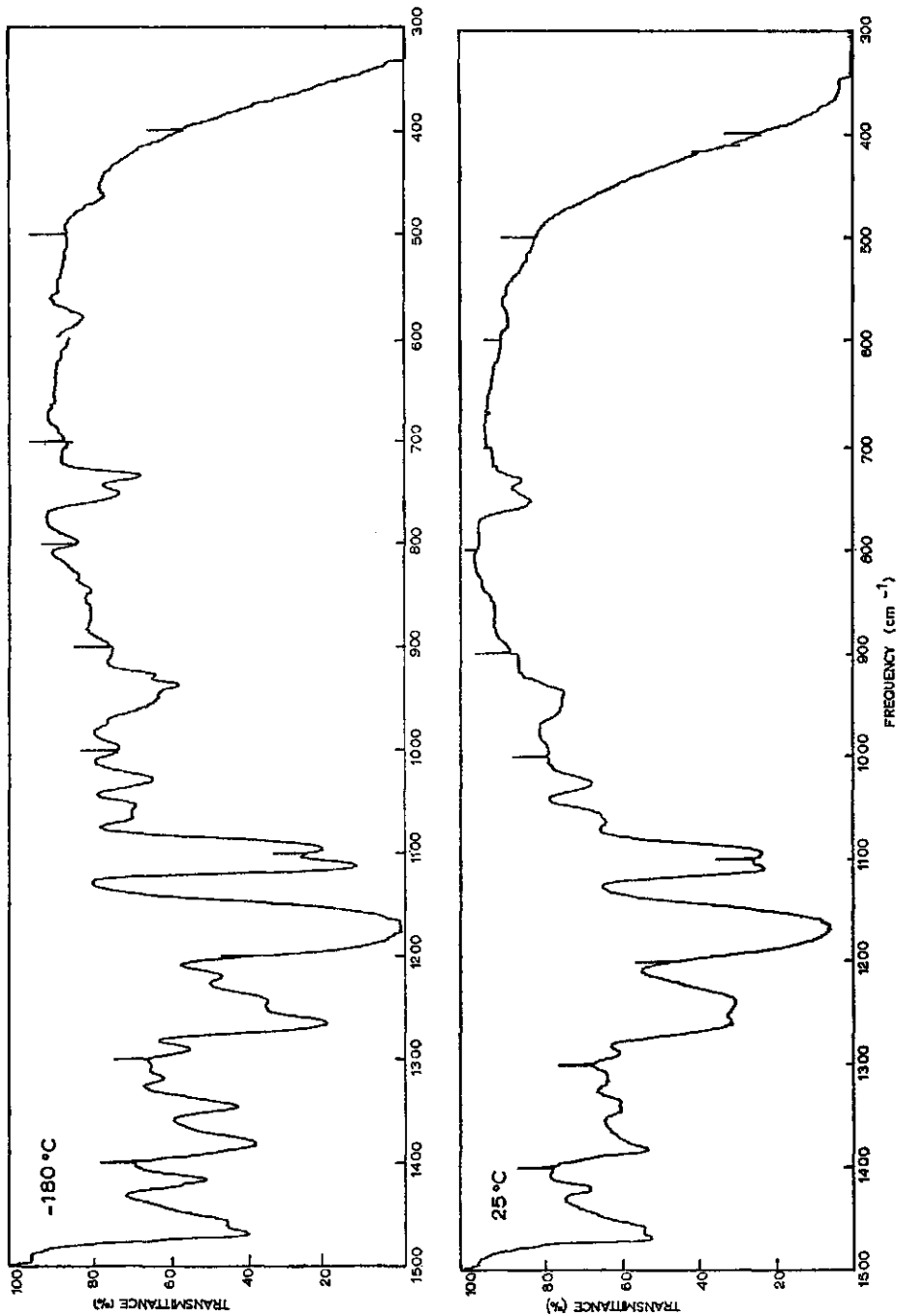


Figure 19a, d. Infrared spectra of trivalerin.

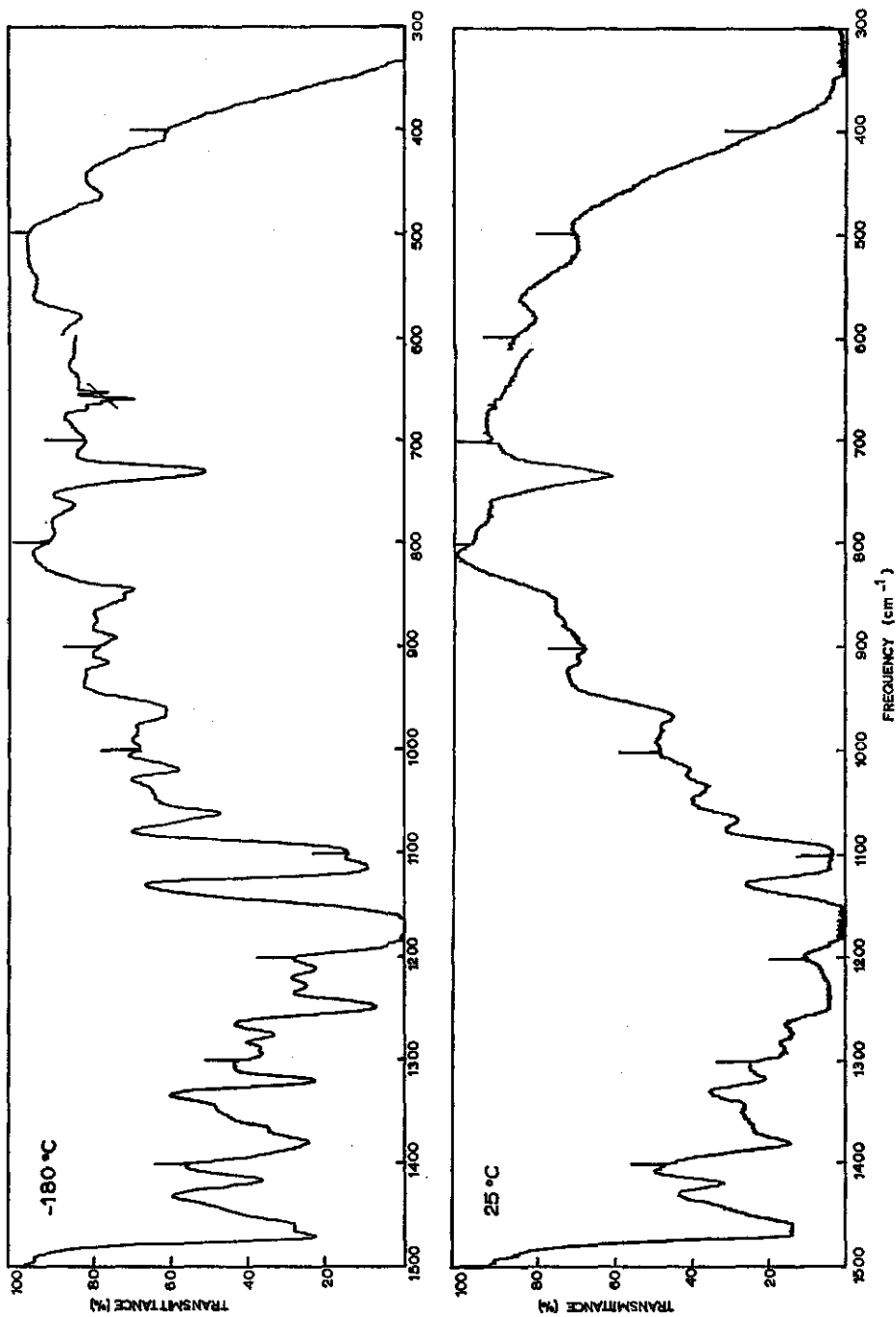
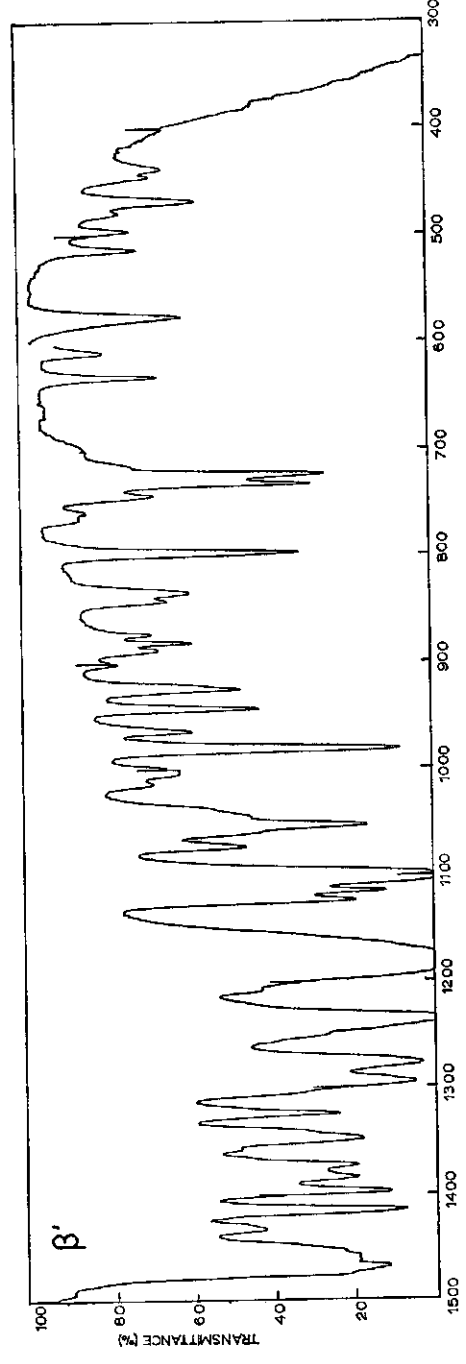
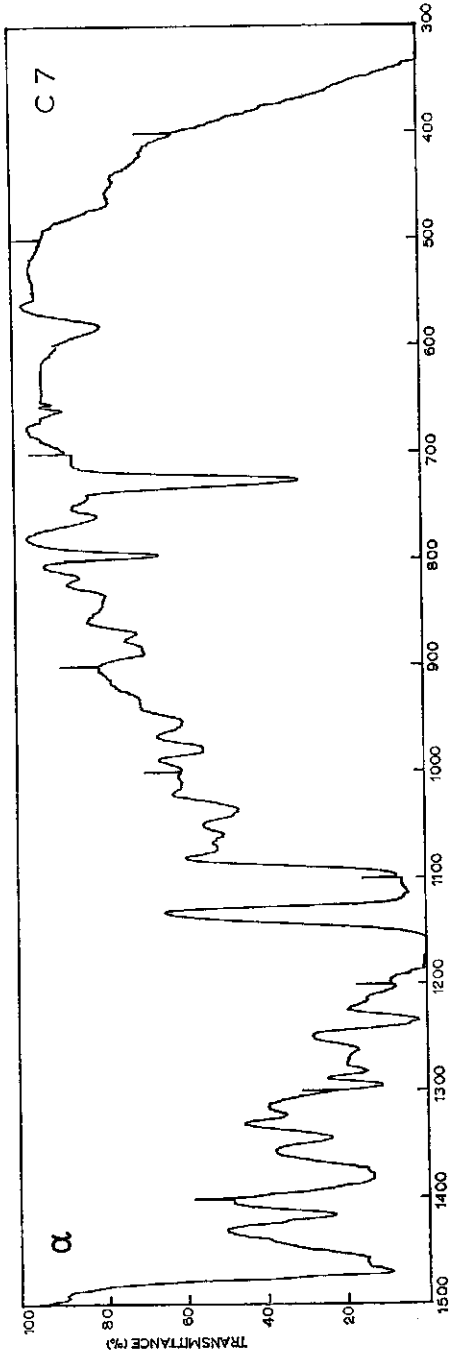


Figure 20a, d. Infrared spectra of tricaproin.



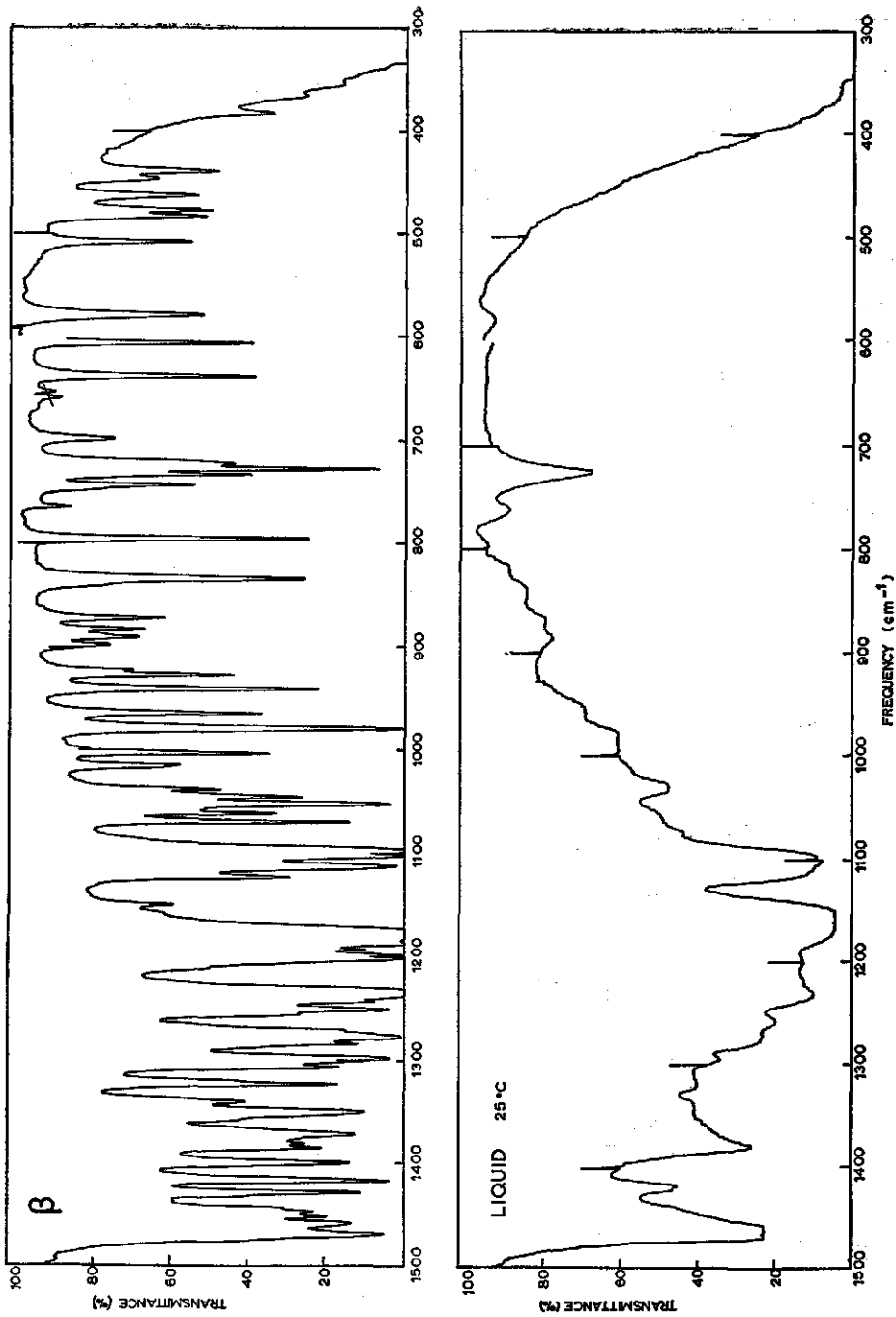
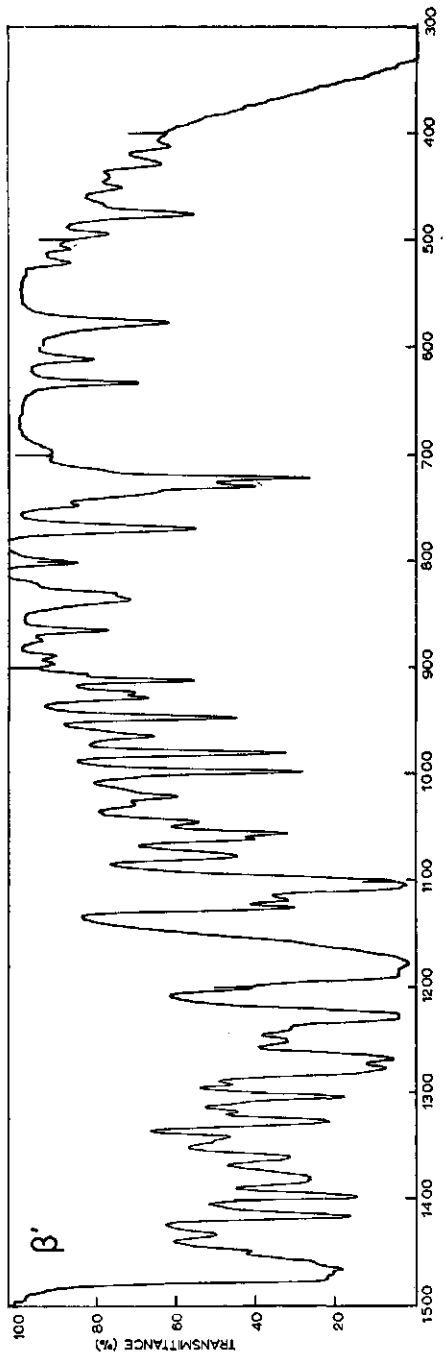
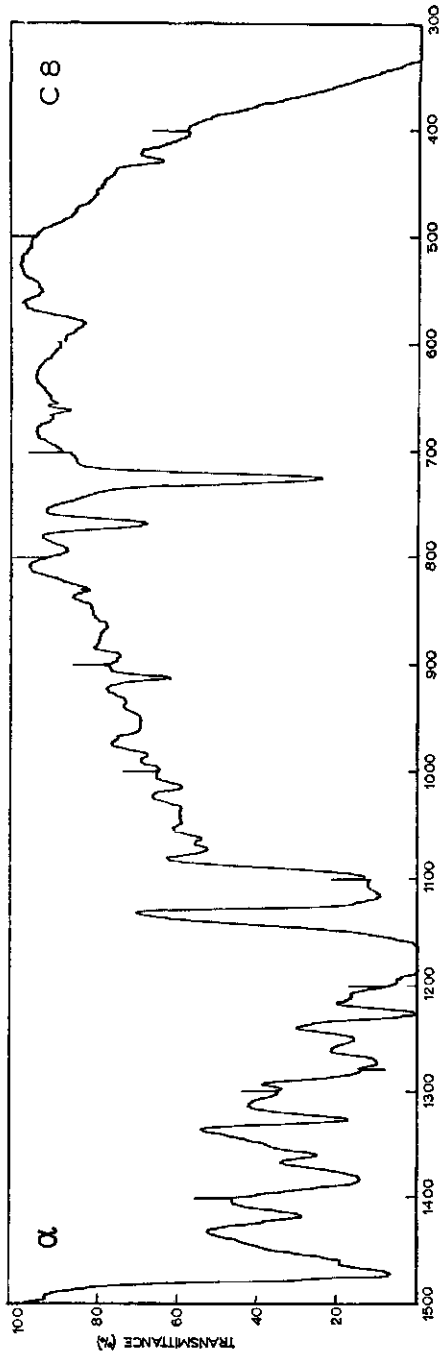


Figure 21a, b, c, d. Infrared spectra of trienanthoin.



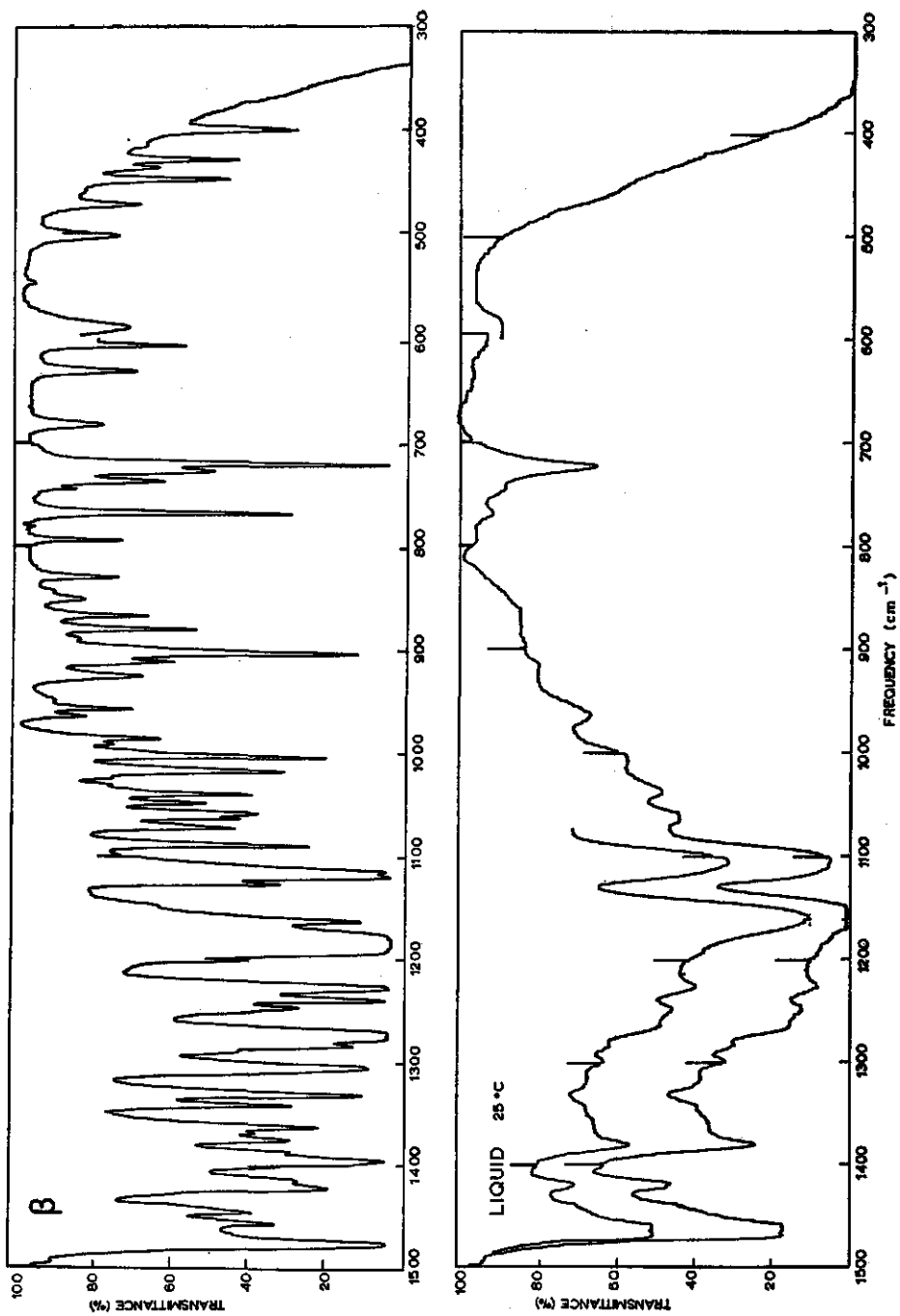
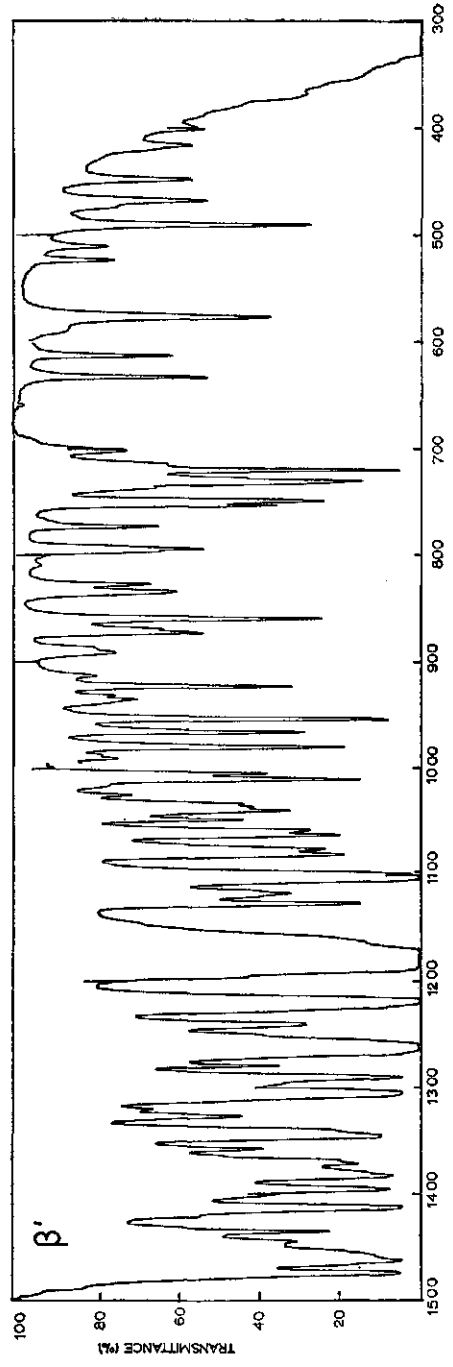
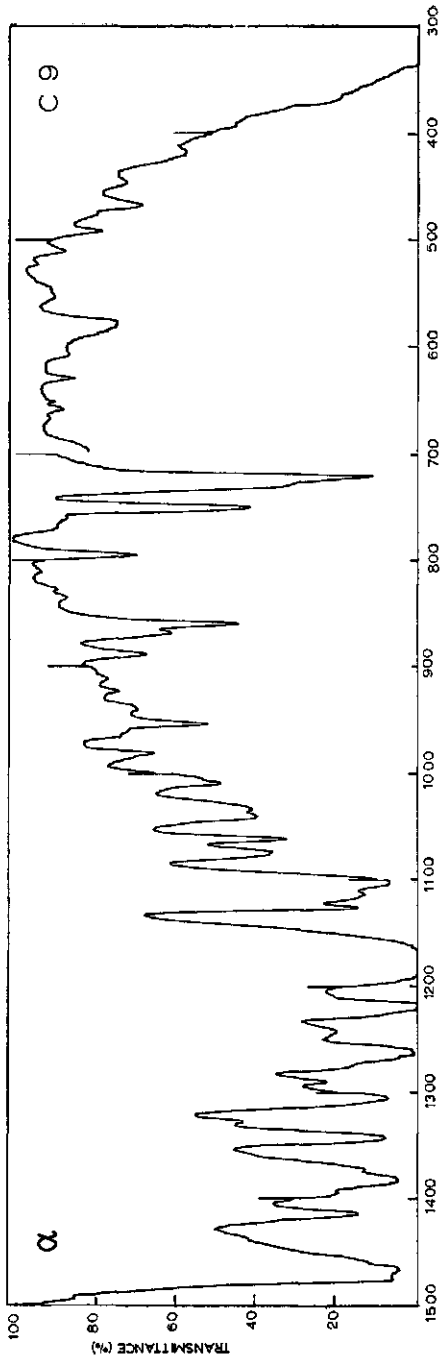


Figure 22a, b, c, d. Infrared spectra of tricaprilyn.



β form omitted

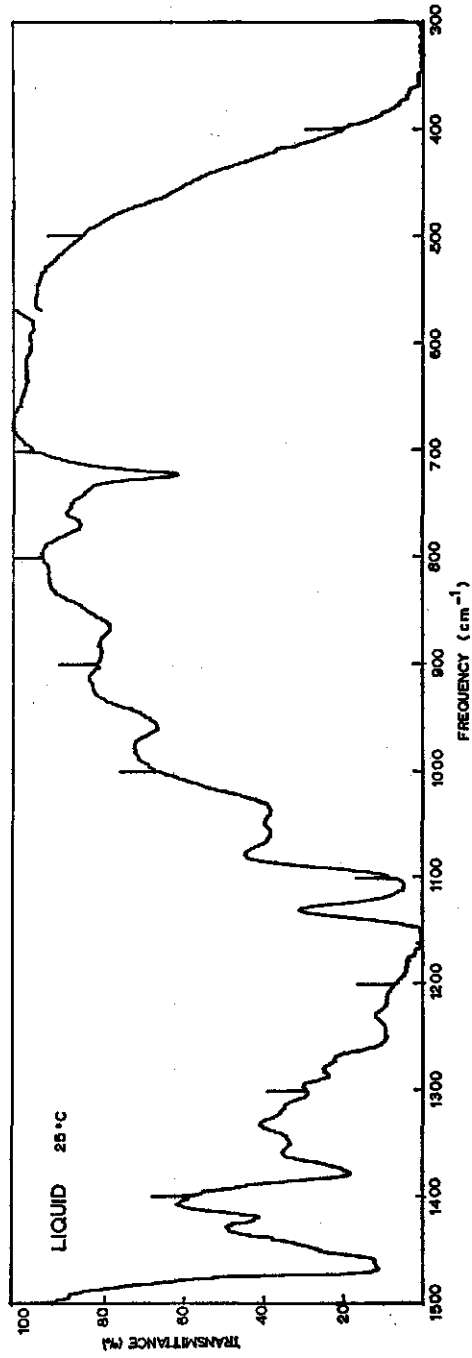
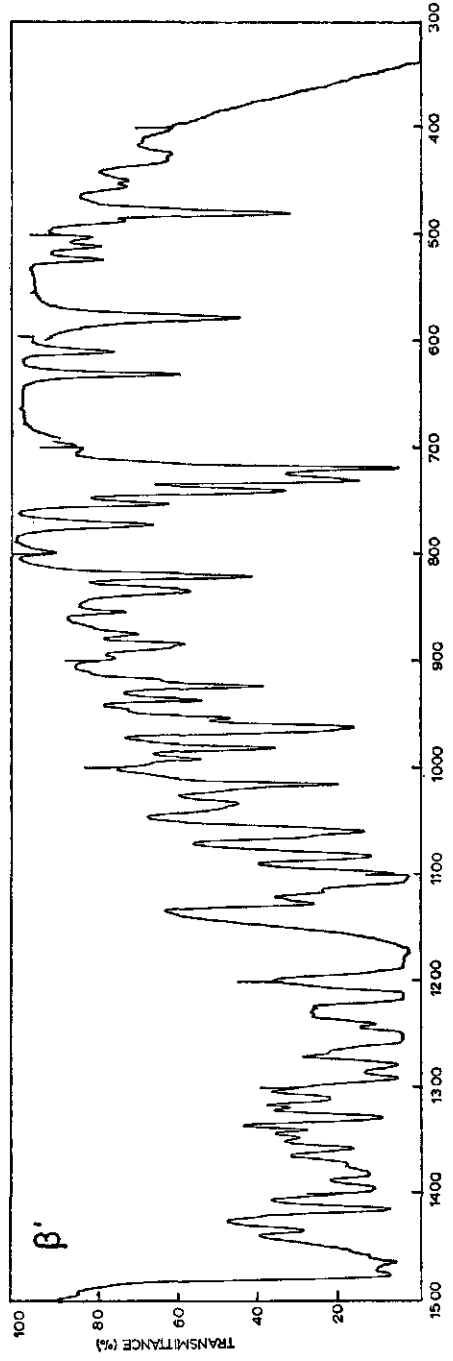
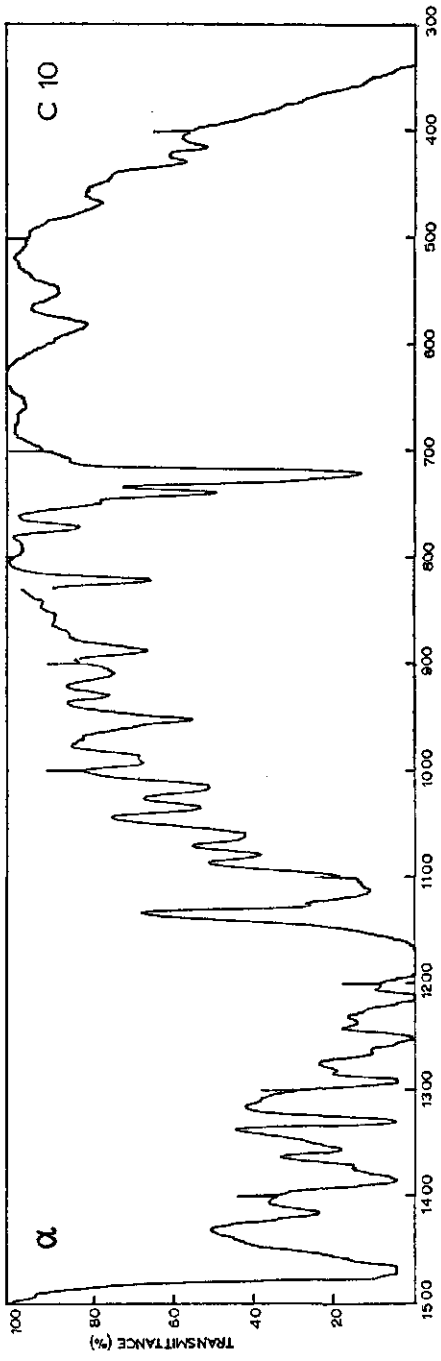


Figure 23a, b, d. Infrared spectra of tripelargoin.



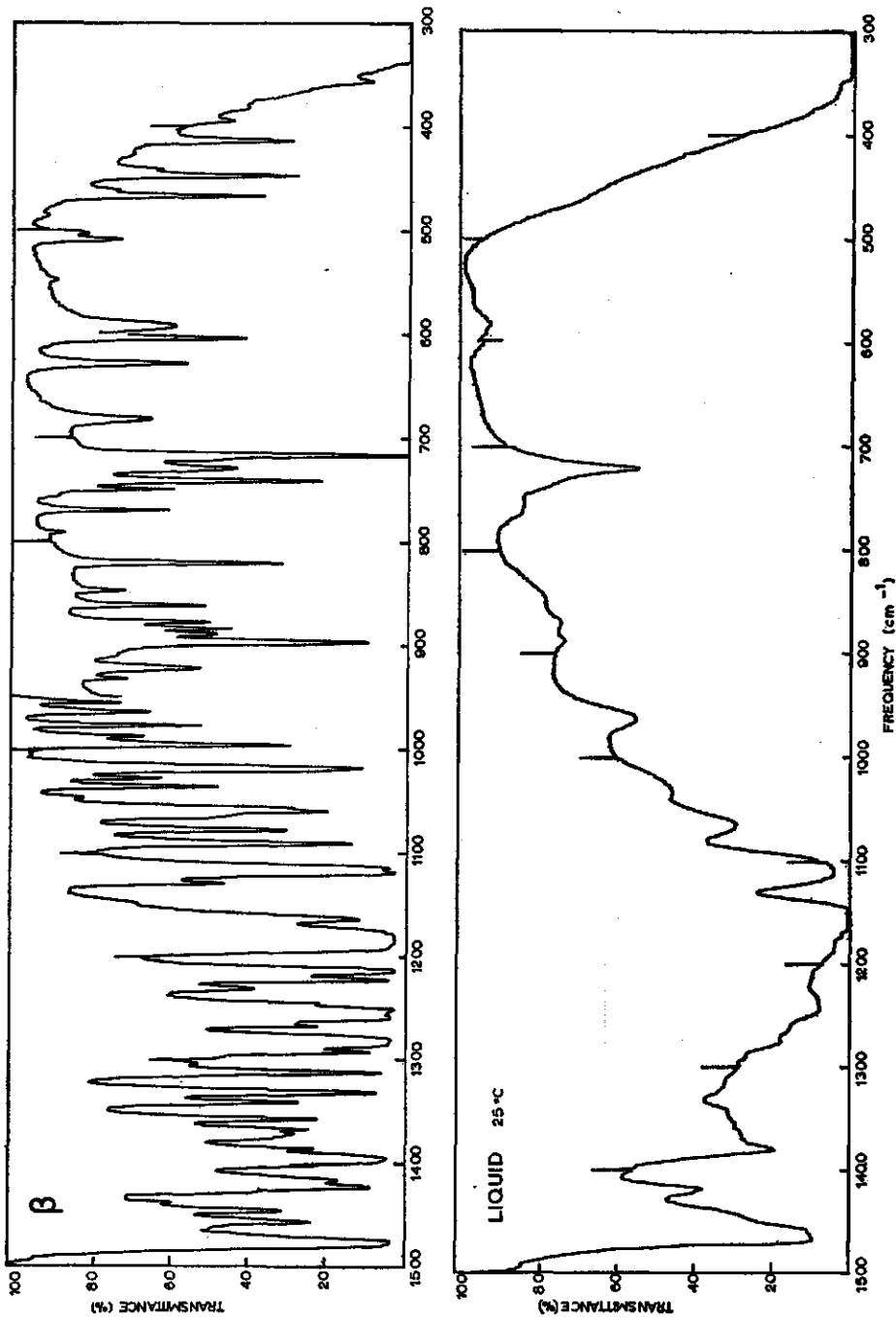
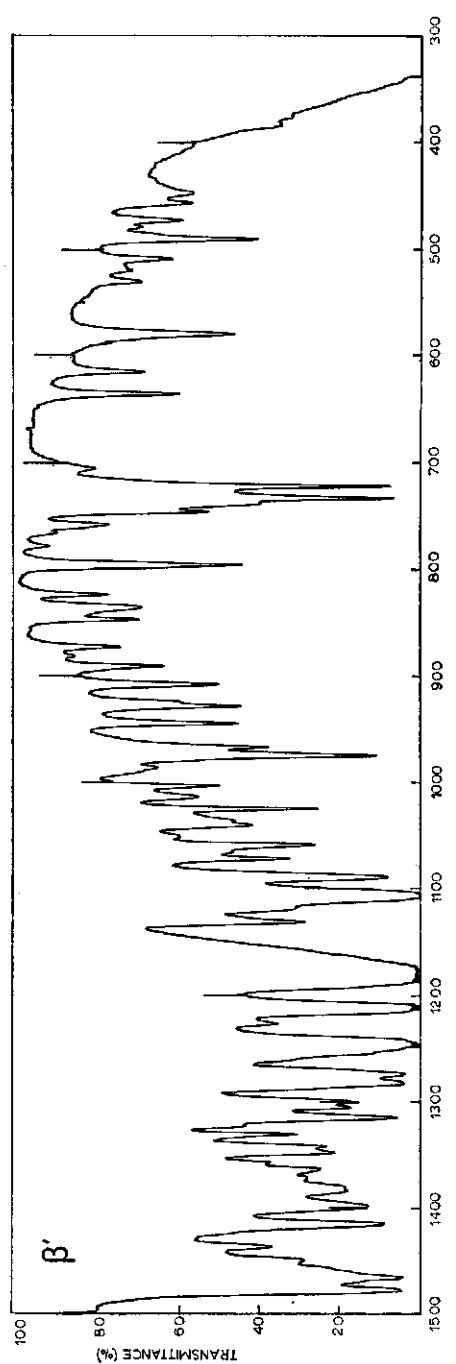
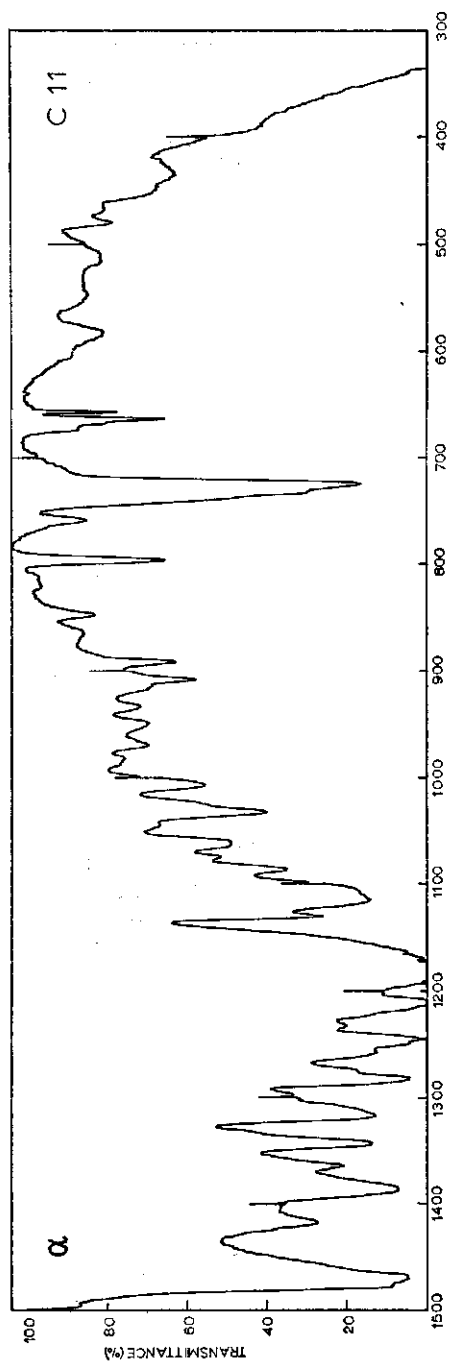


Figure 2Aa, b, c, d. Infrared spectra of tricaptin.



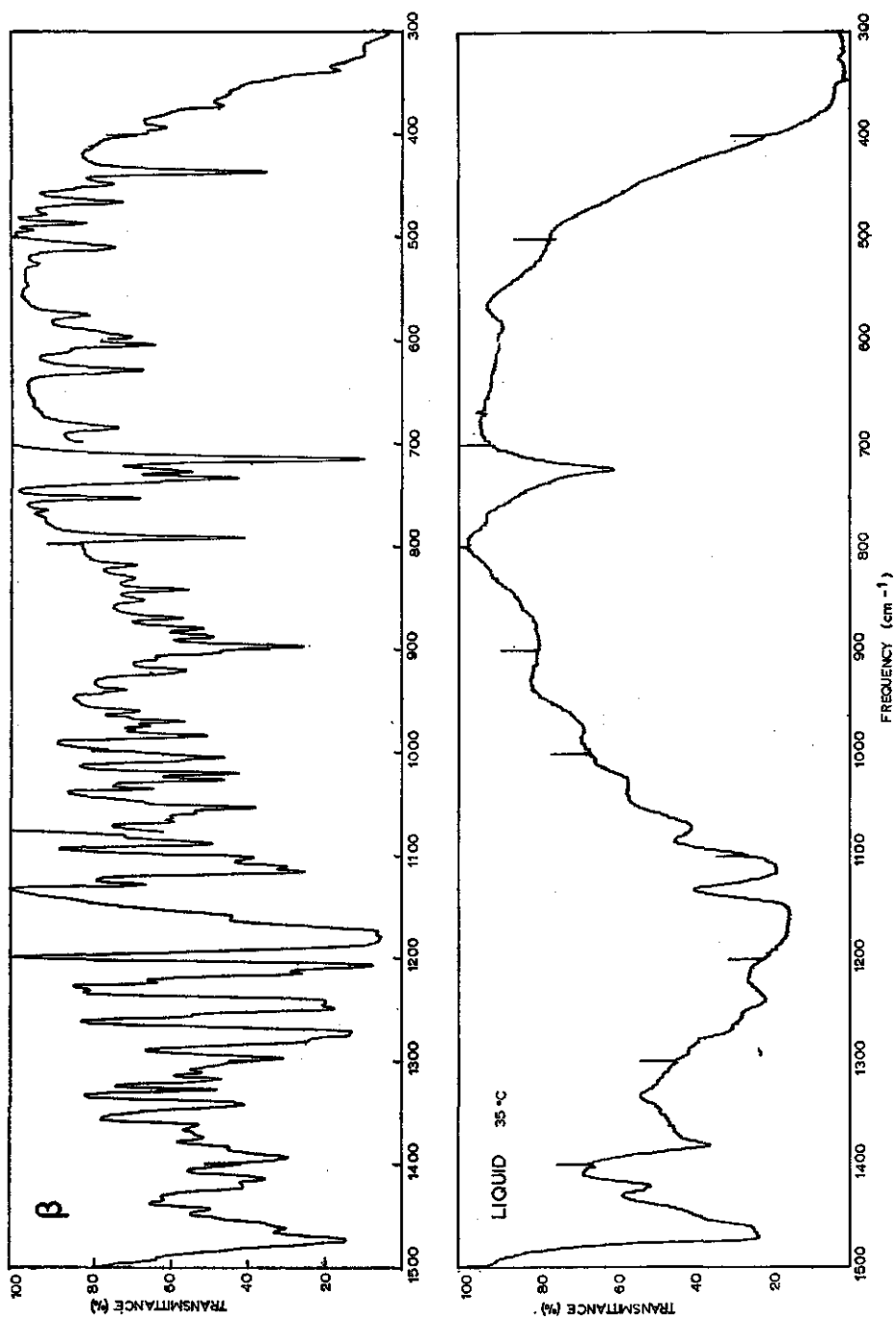
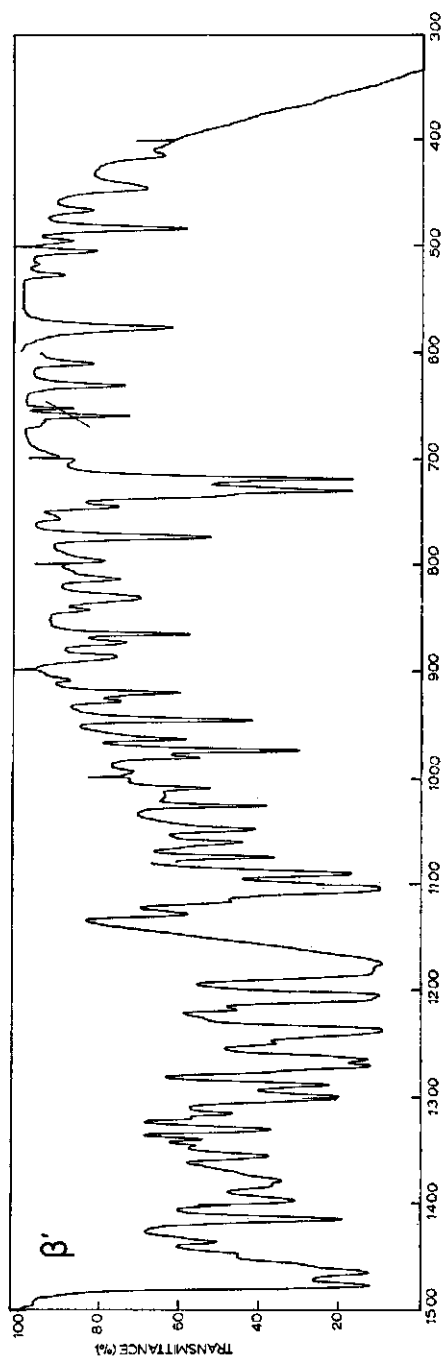
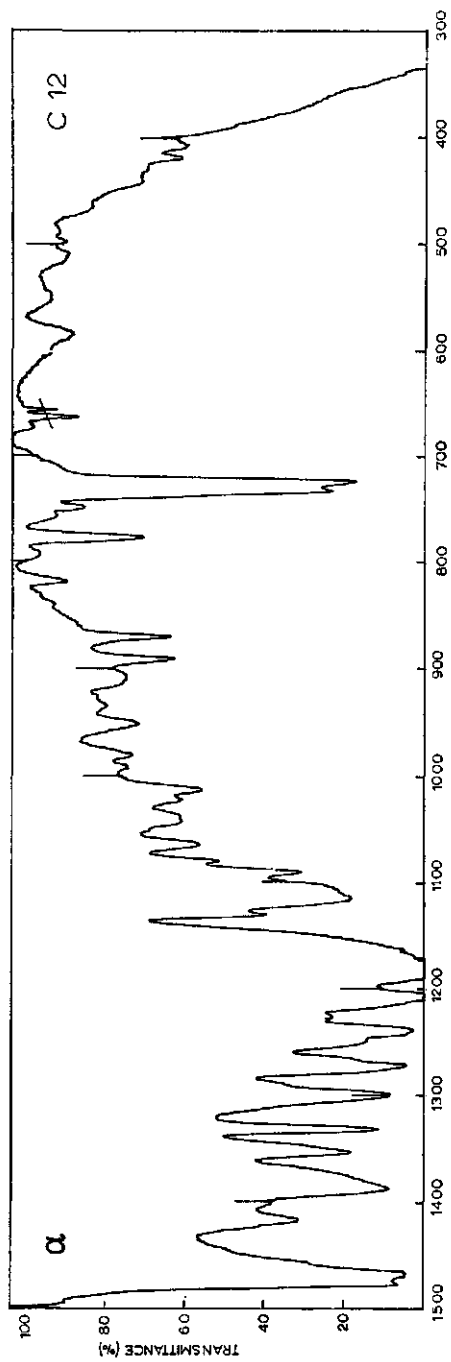


Figure 25a, b, c, d. Infrared spectra of triundecylin.



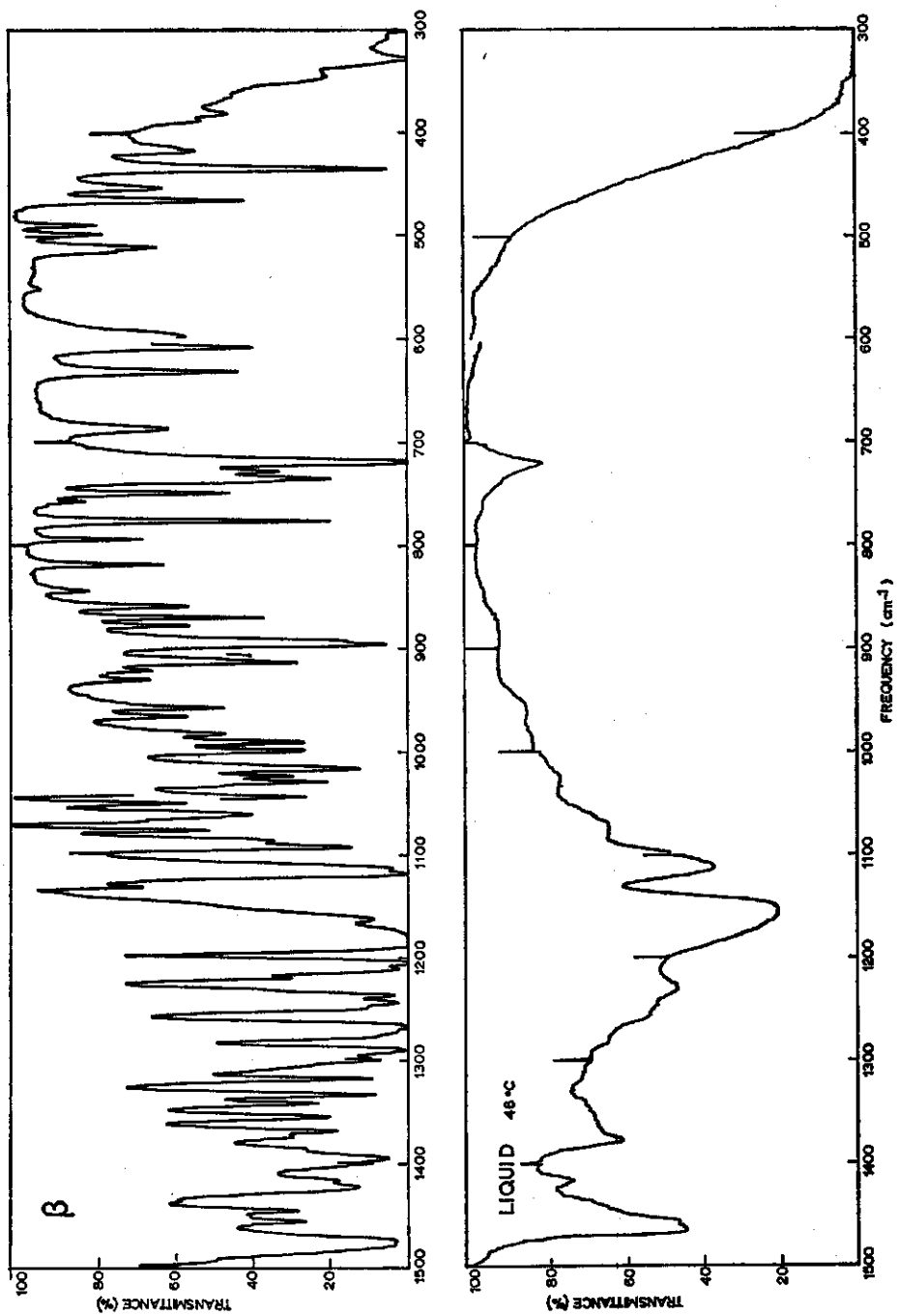
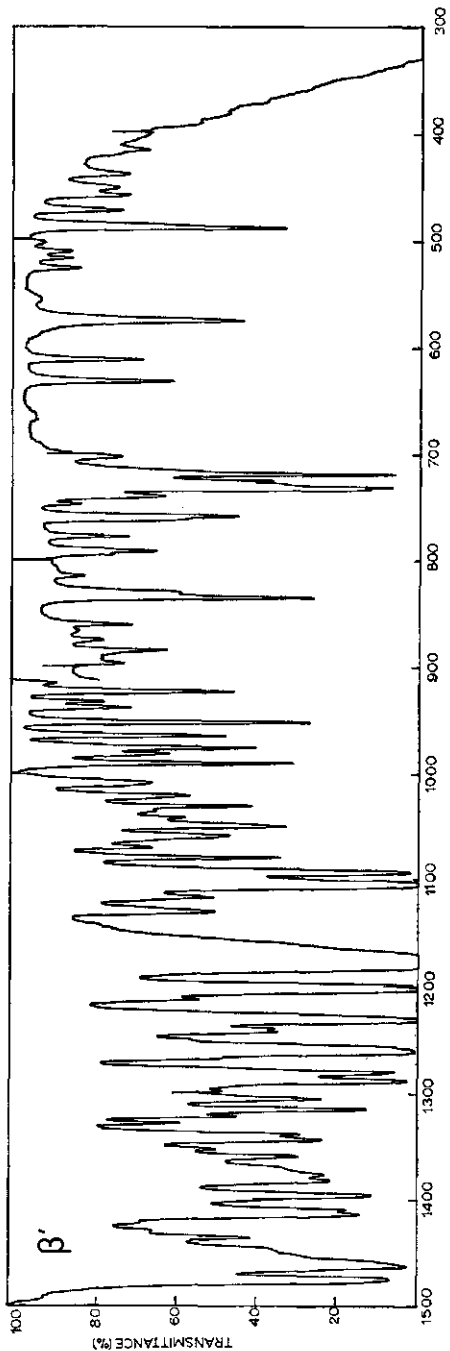
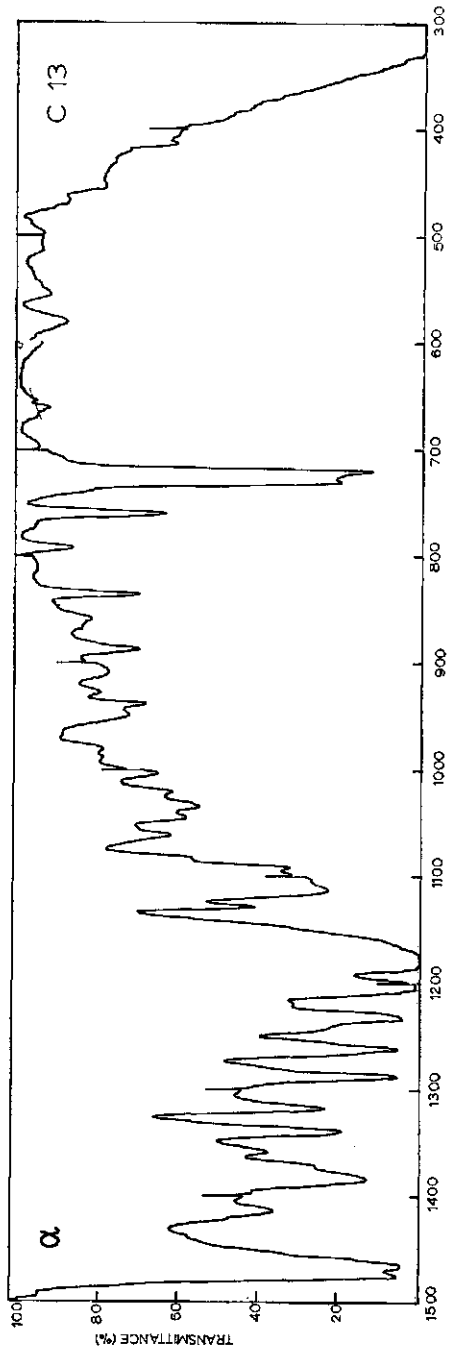


Figure 26a, b, c, d. Infrared spectra of trilaurin.



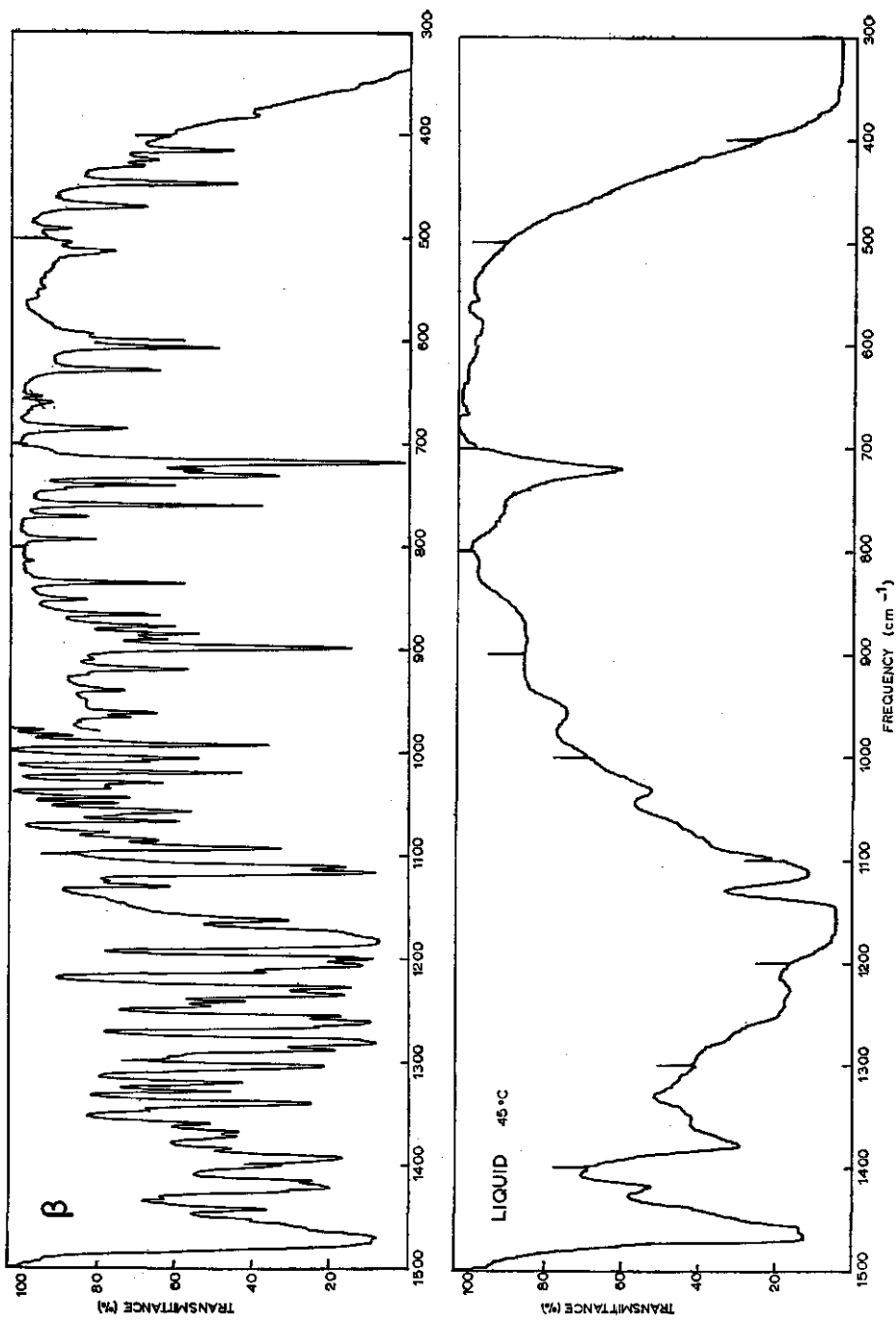
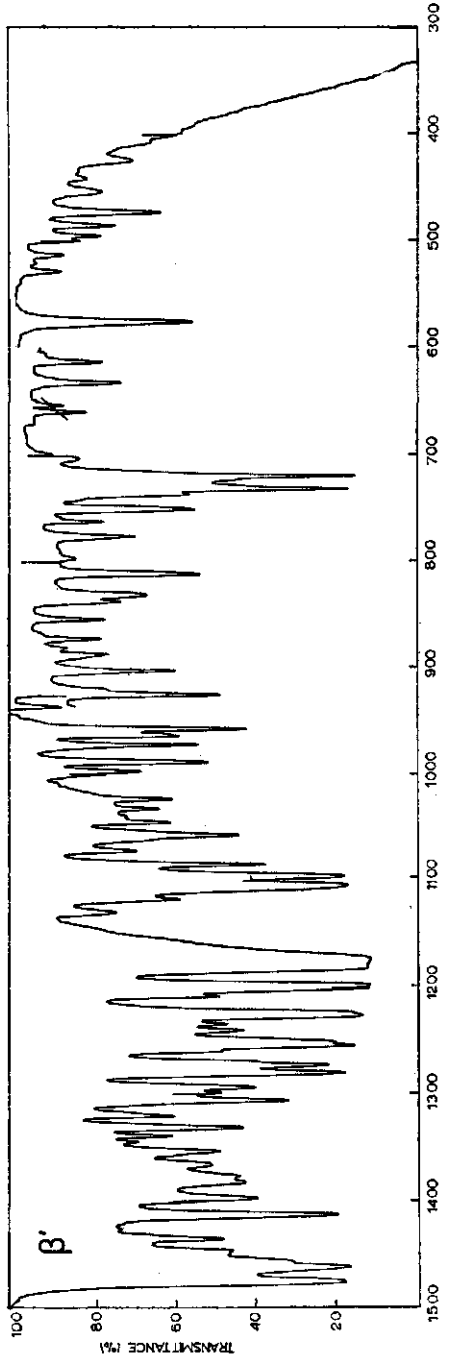
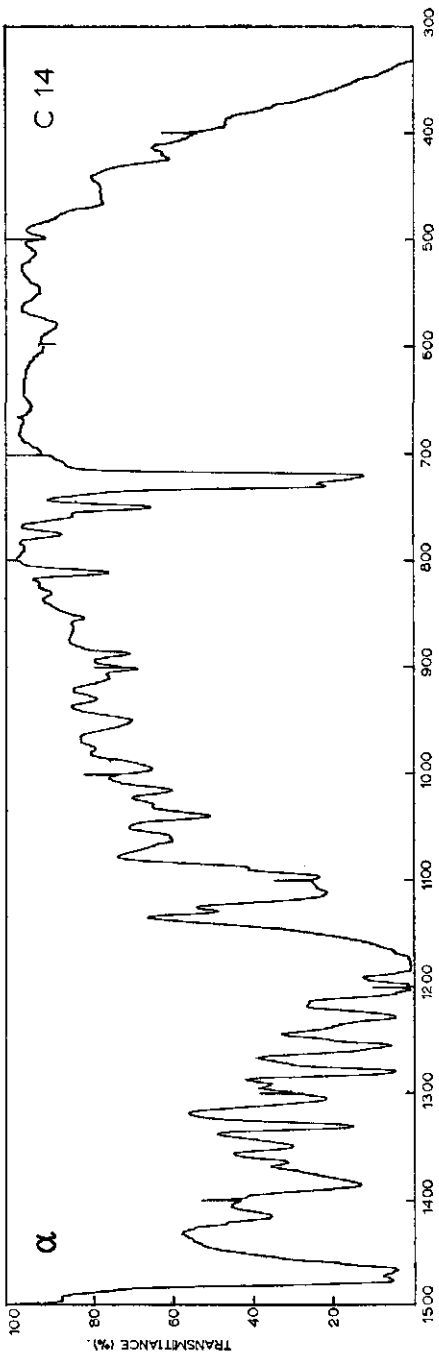
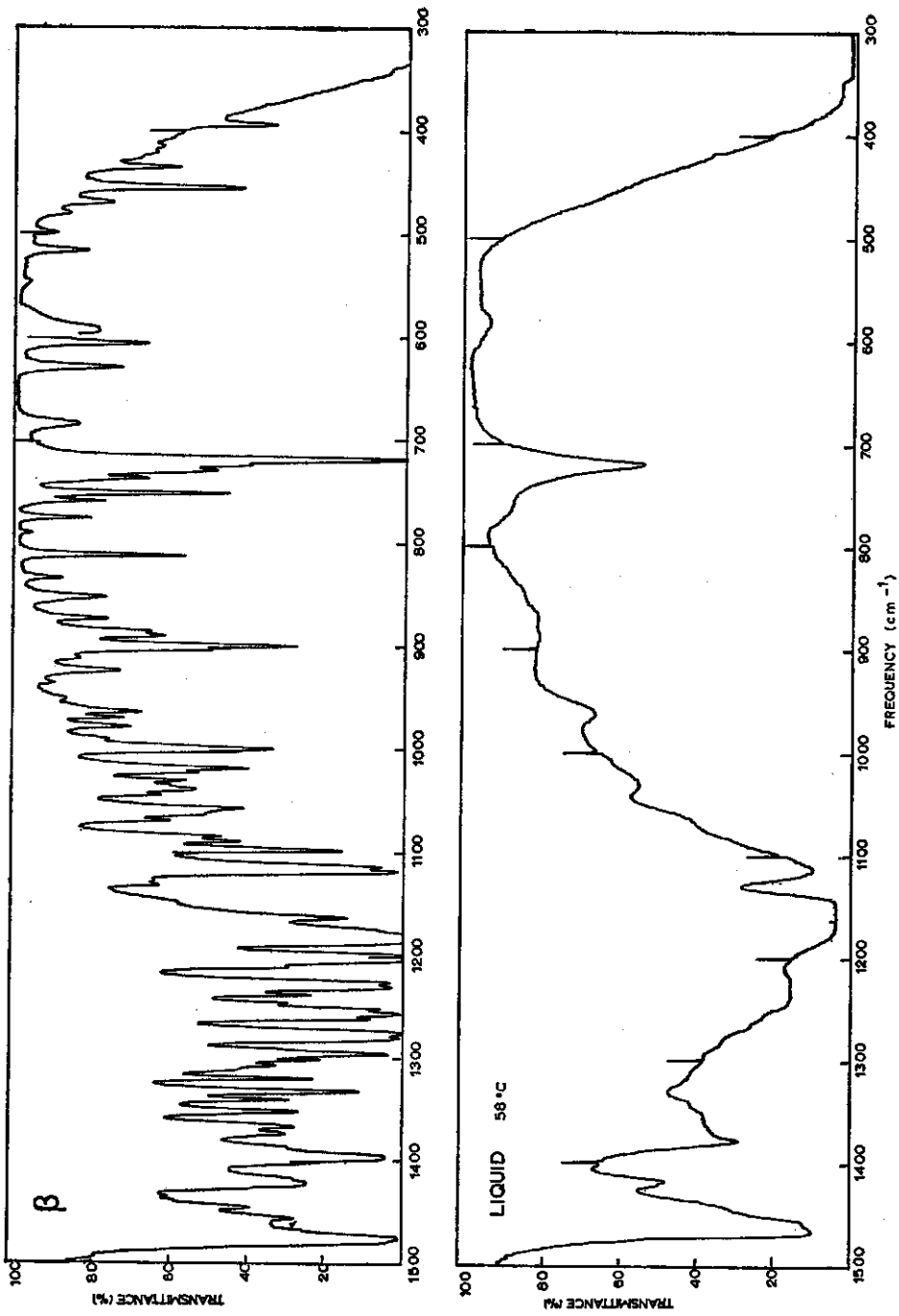
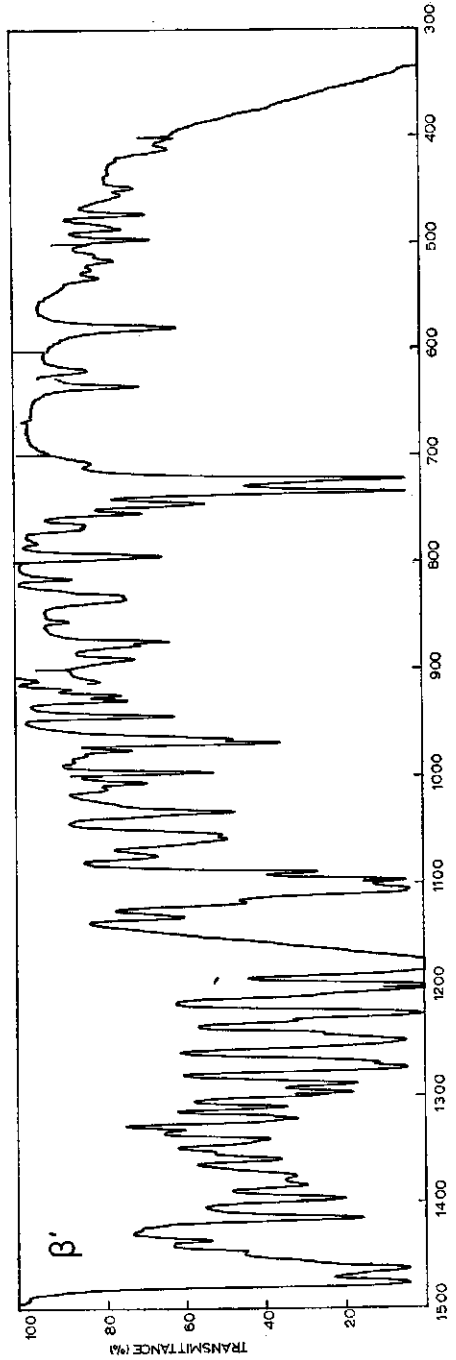
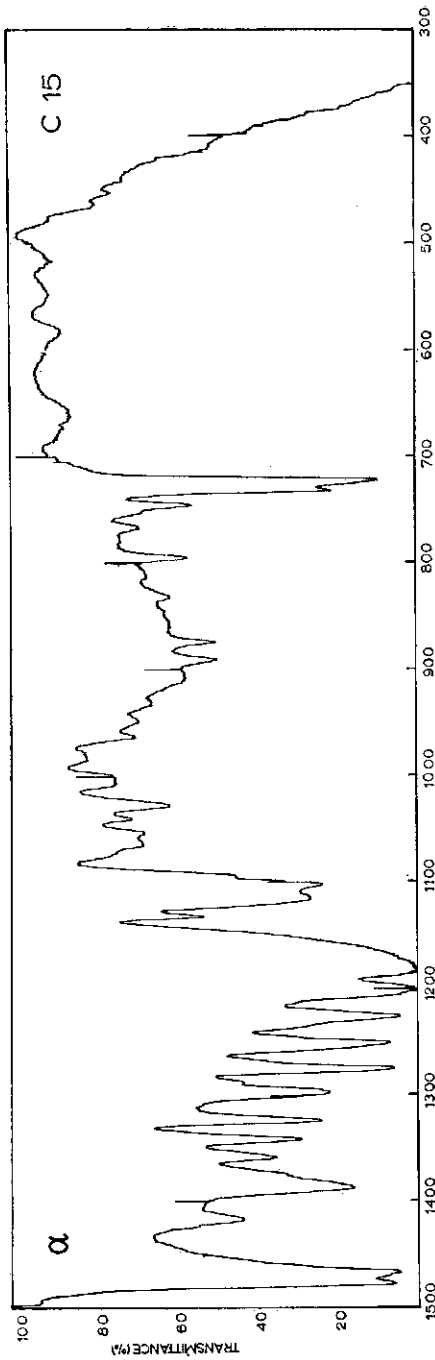


Figure 27a, b, c, d. Infrared spectra of tritridecylin.





3 Figure 28a, b, c, d. Infrared spectra of trimyristin.



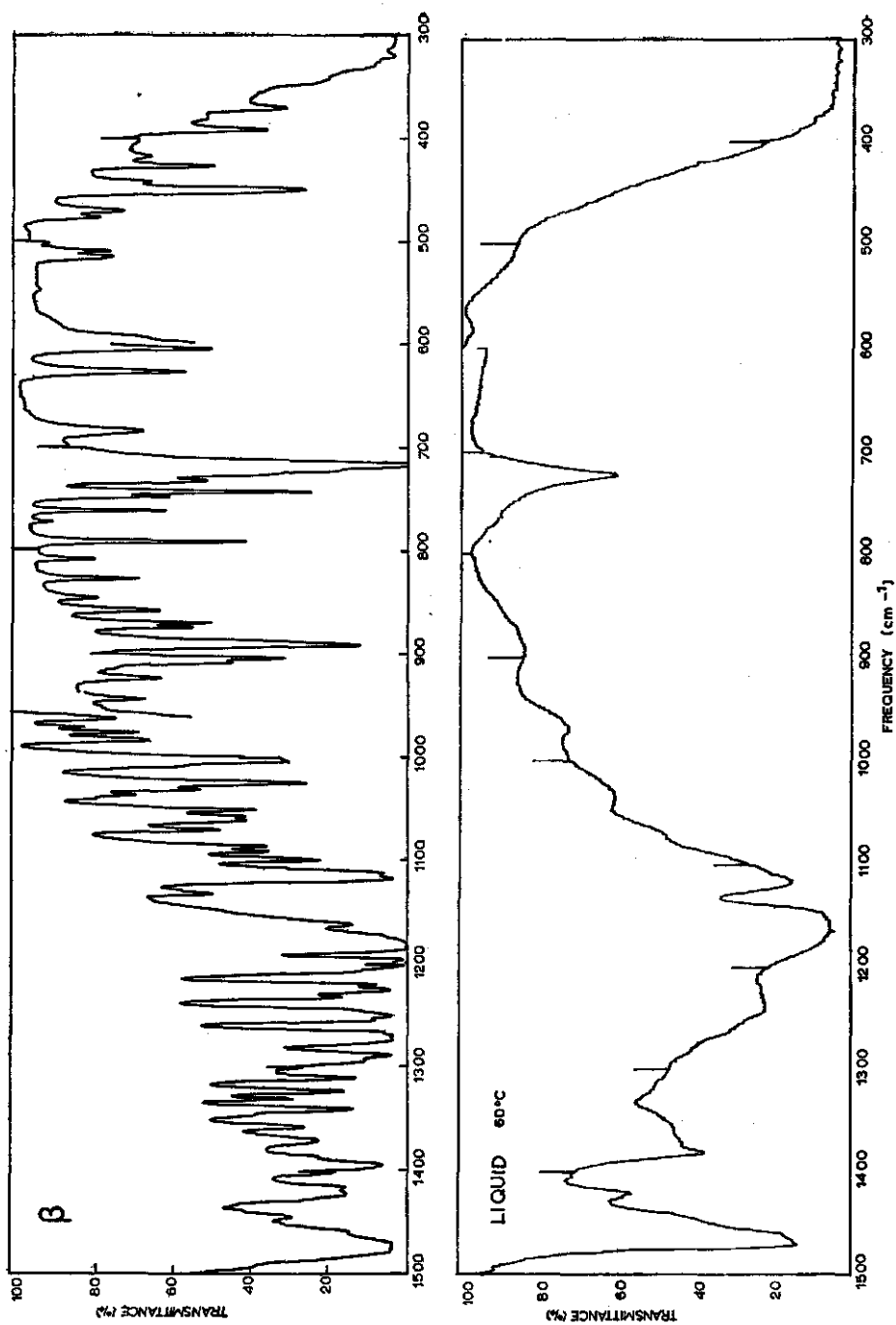
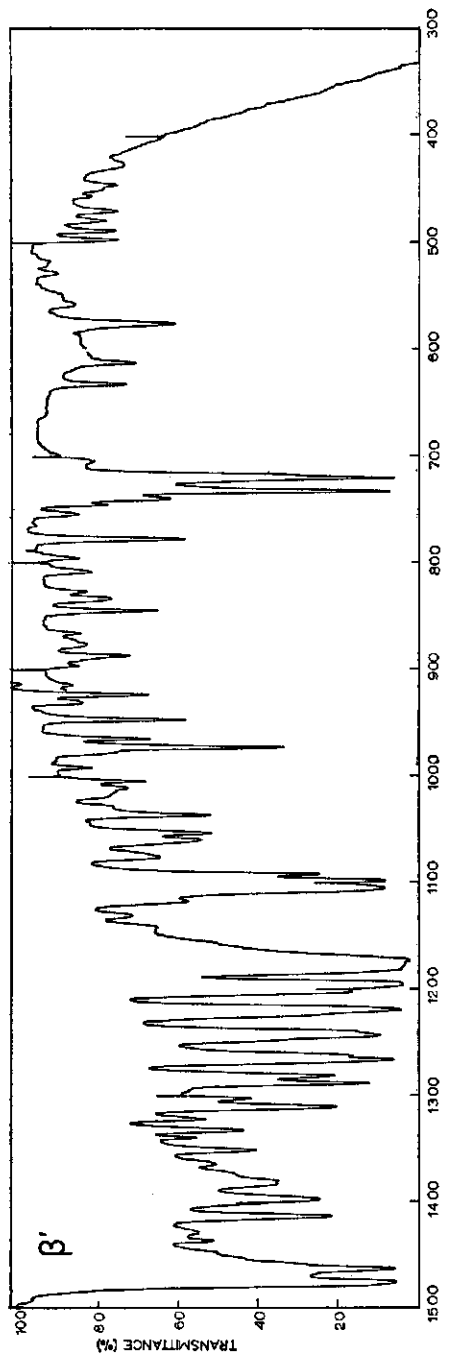
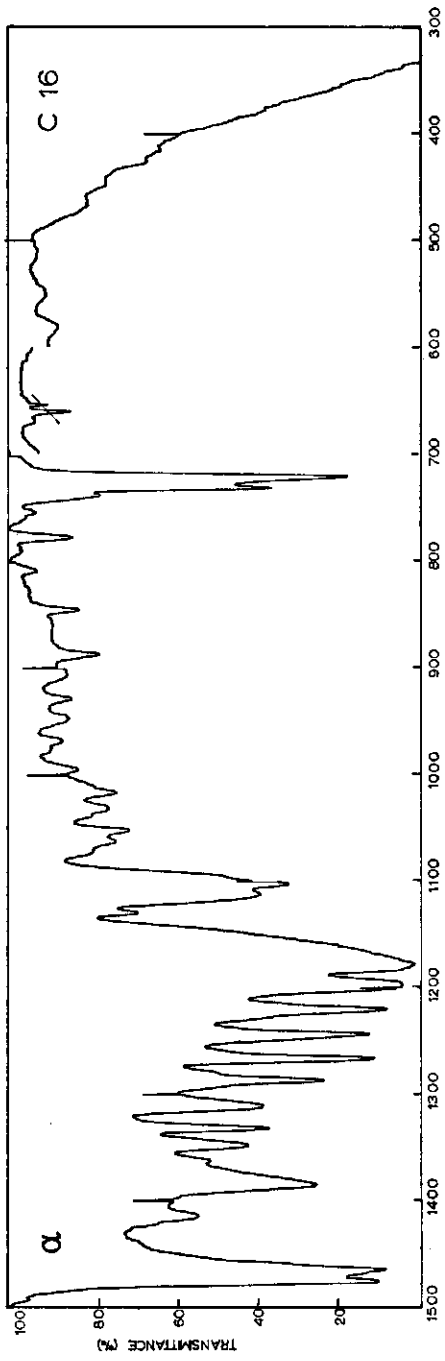


Figure 29a, b, c, d. Infrared spectra of tripentadecylin.



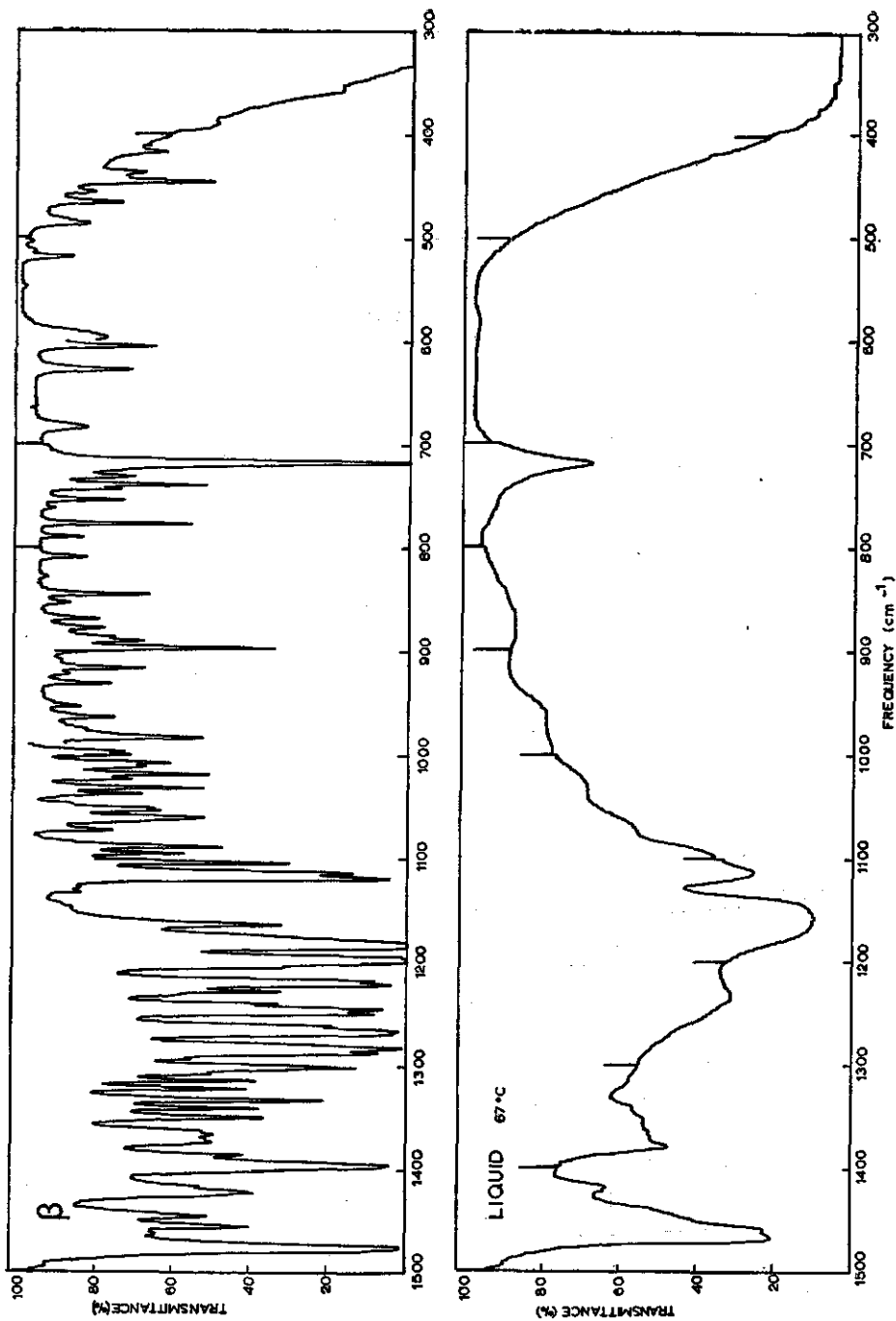
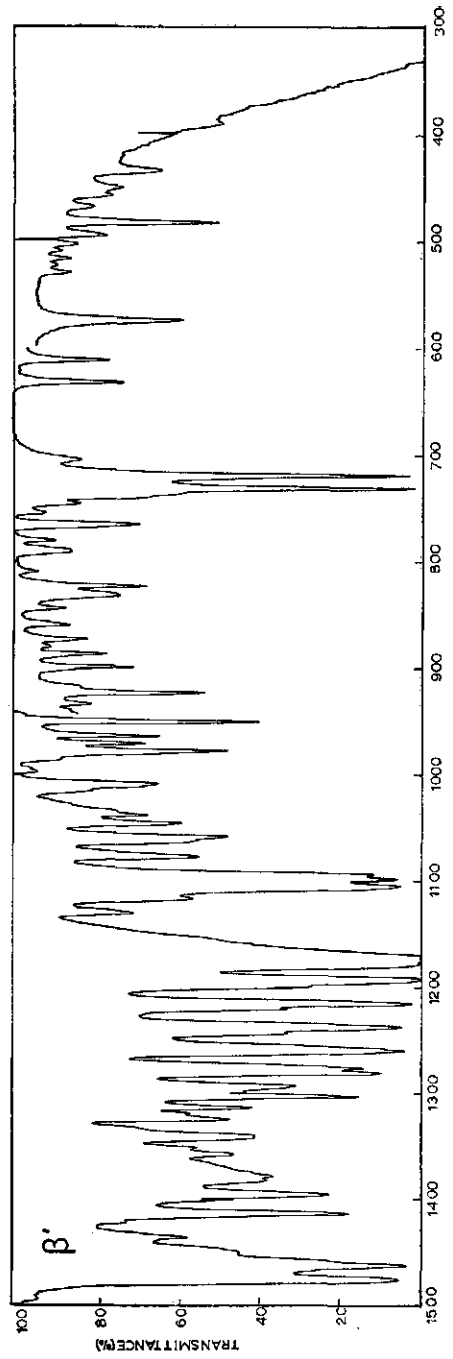
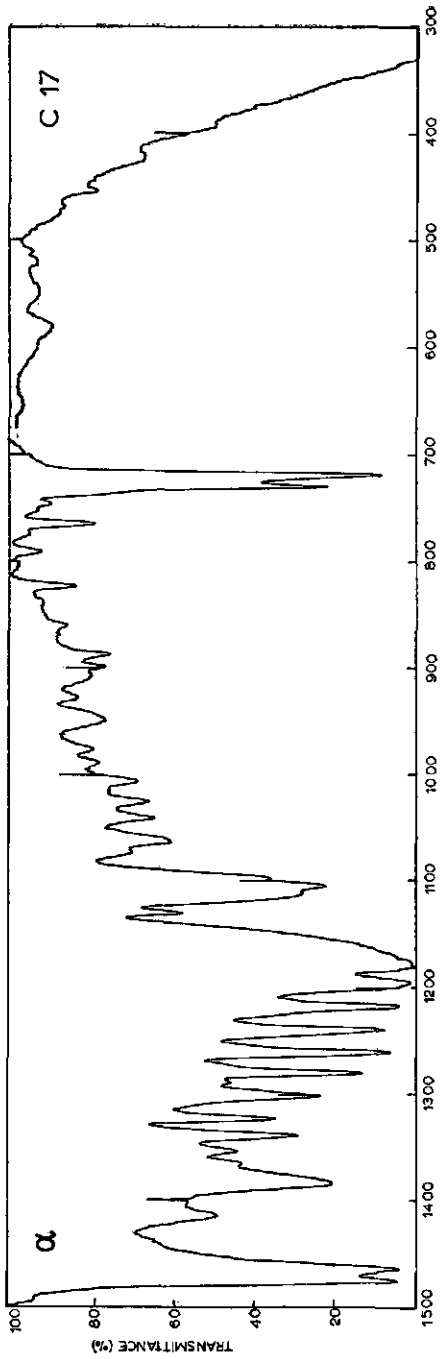
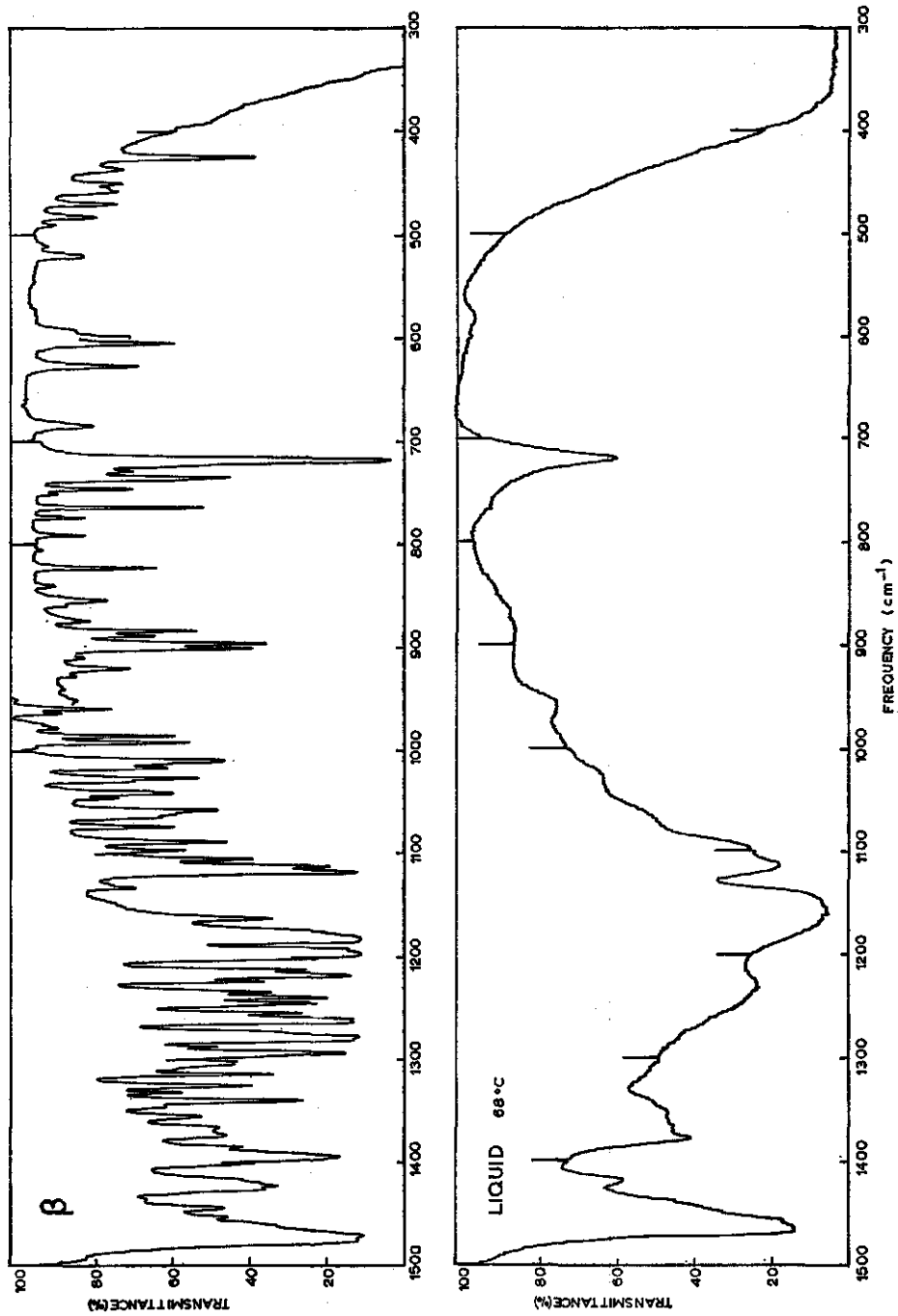
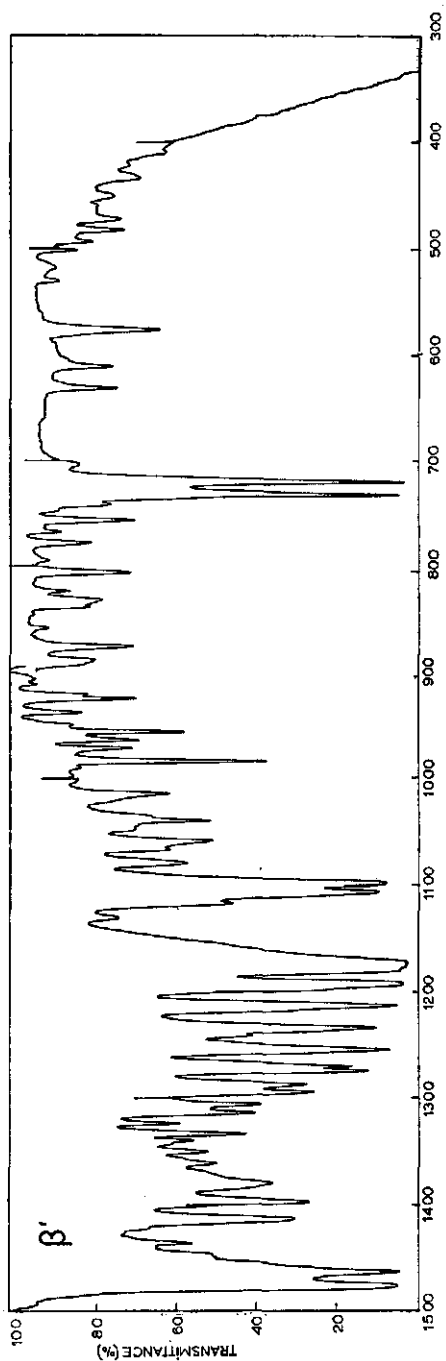
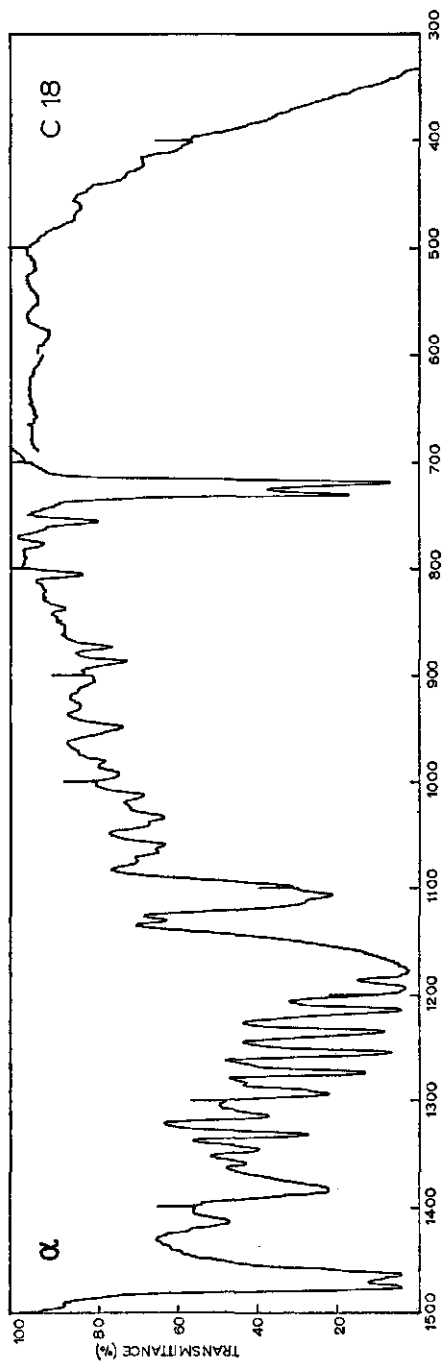


Figure 30a, b, c, d. Infrared spectra of tripalmitin.





③ Figure 31a, b, c, d. Infrared spectra of trimargarin.



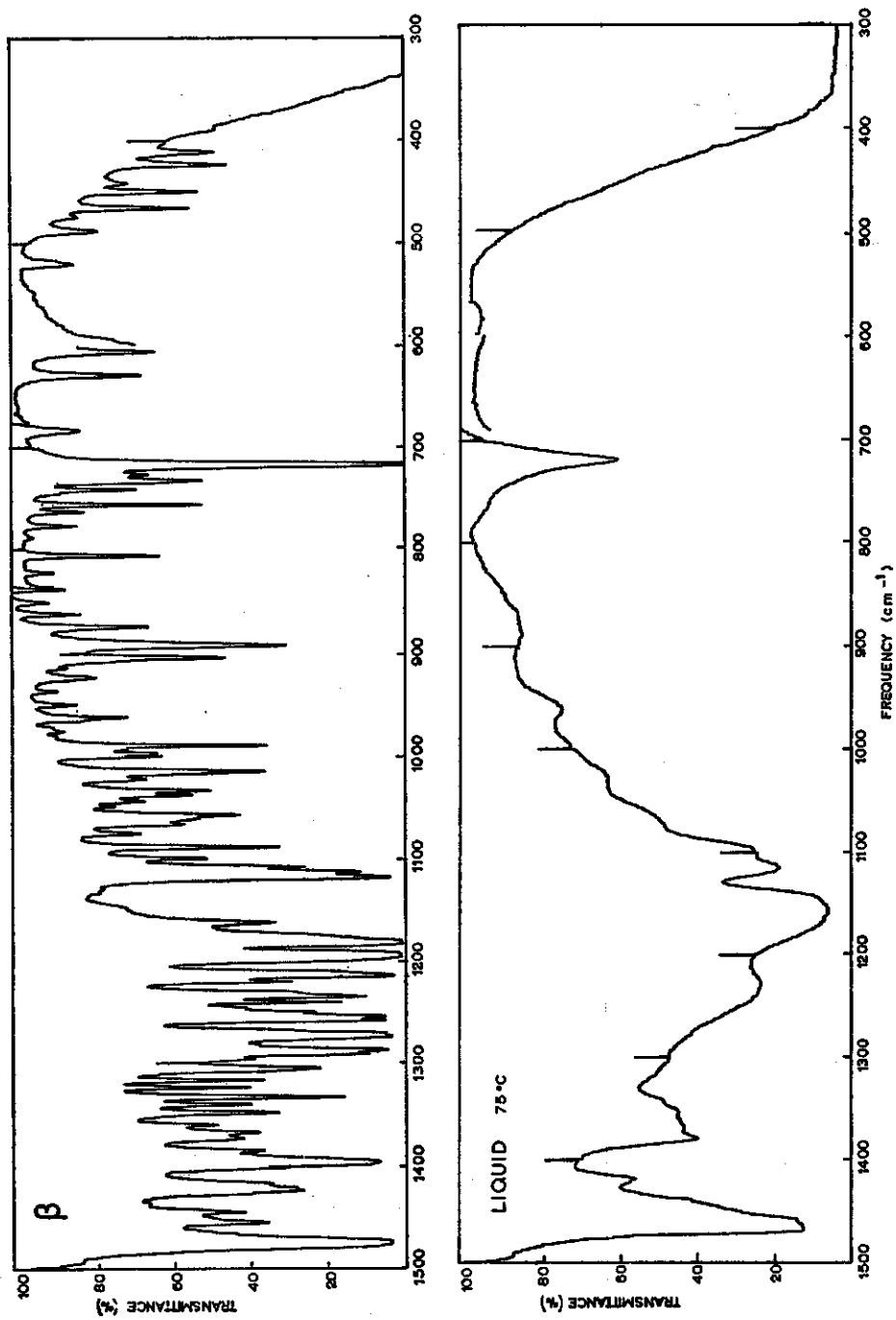
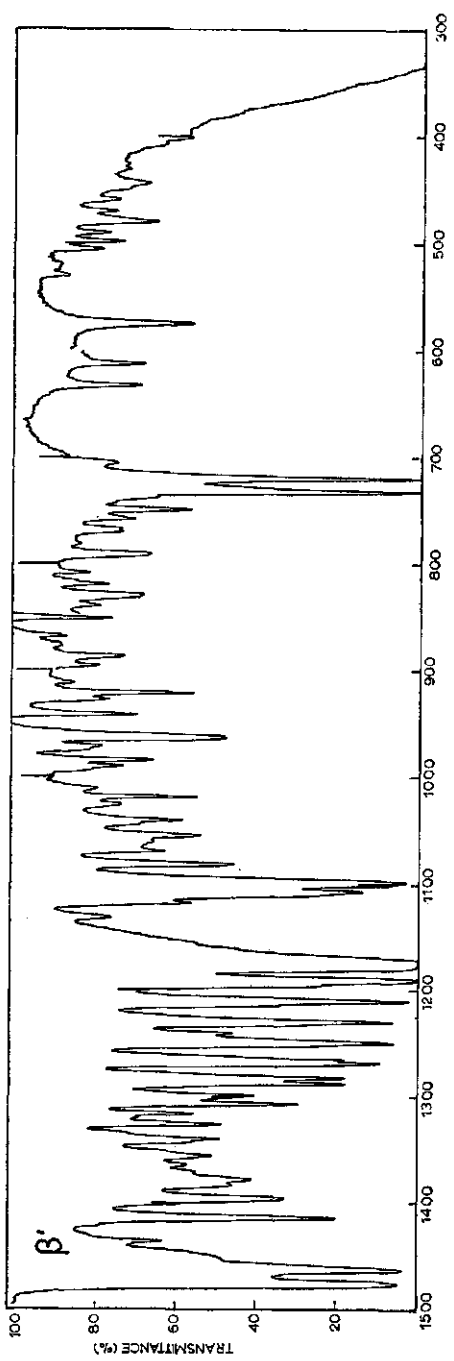
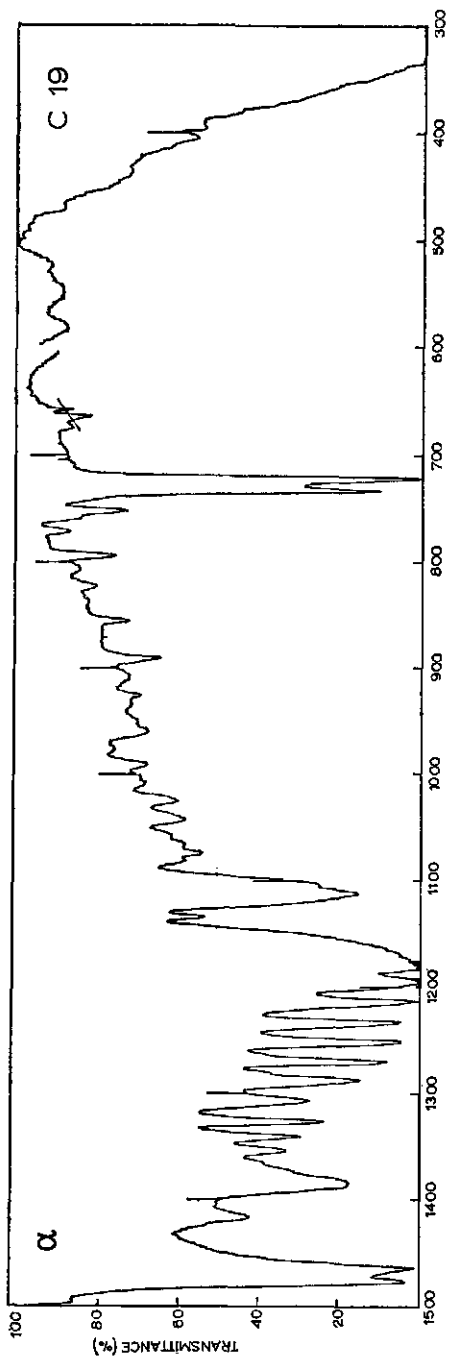


Figure 32a, b, c, d. Infrared spectra of tristearin.



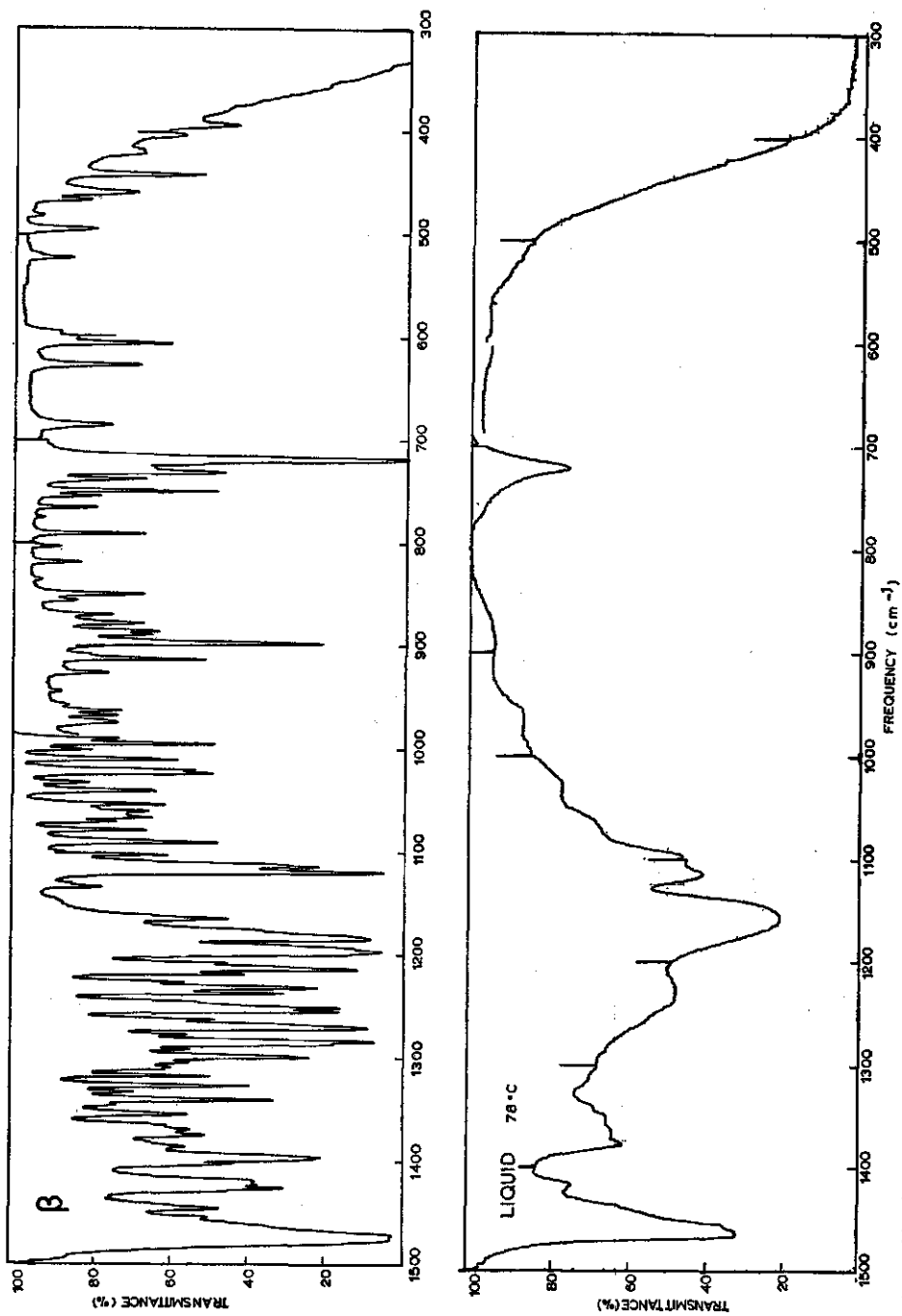
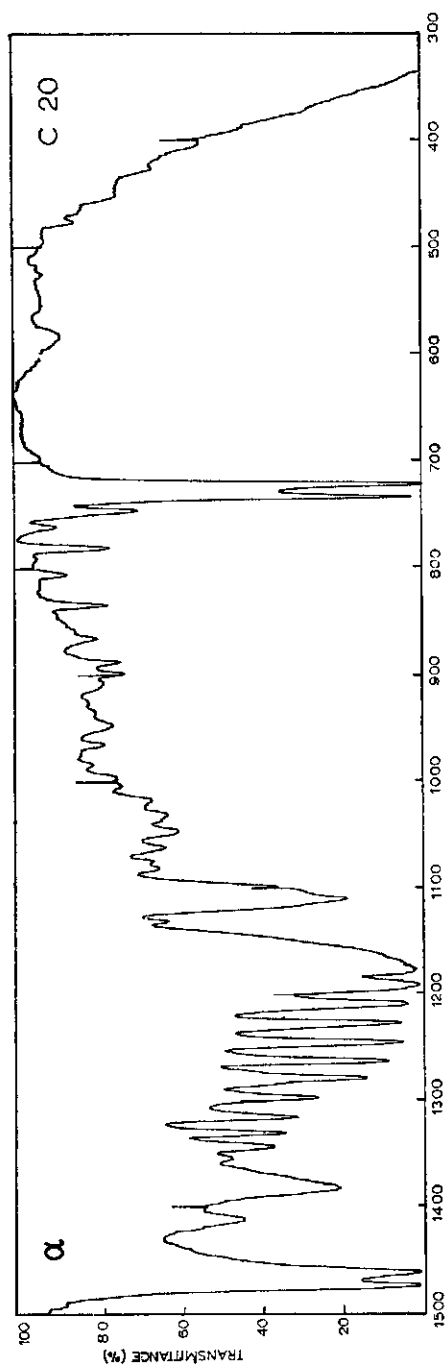


Figure 33a, b, c, d. Infrared spectra of trironadecylin.



β' form omitted

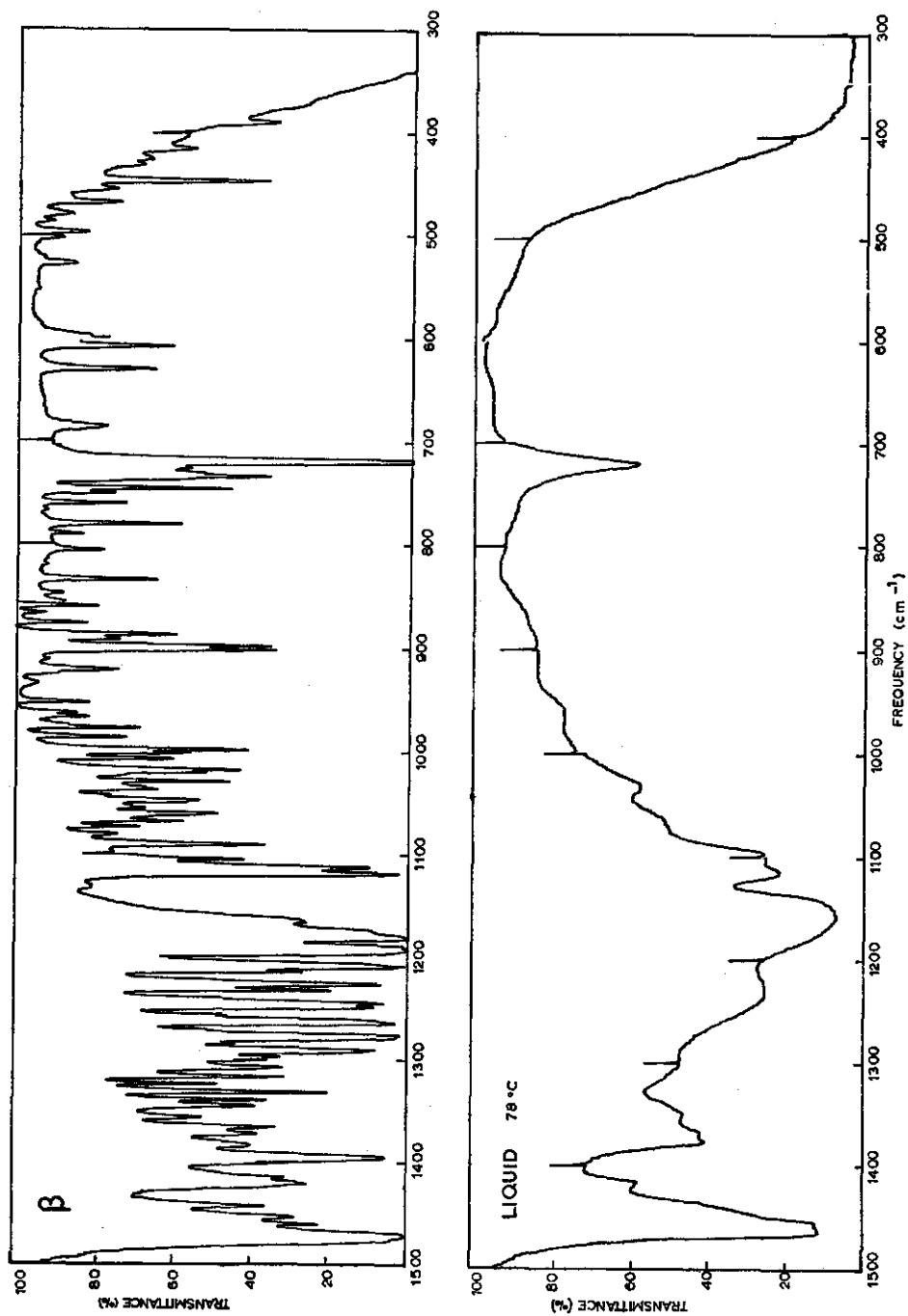
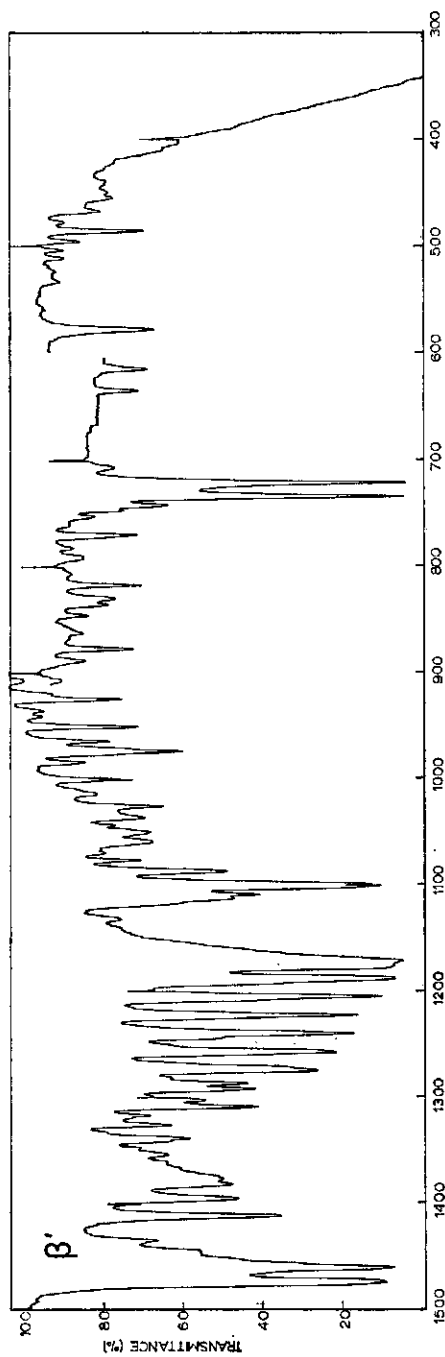
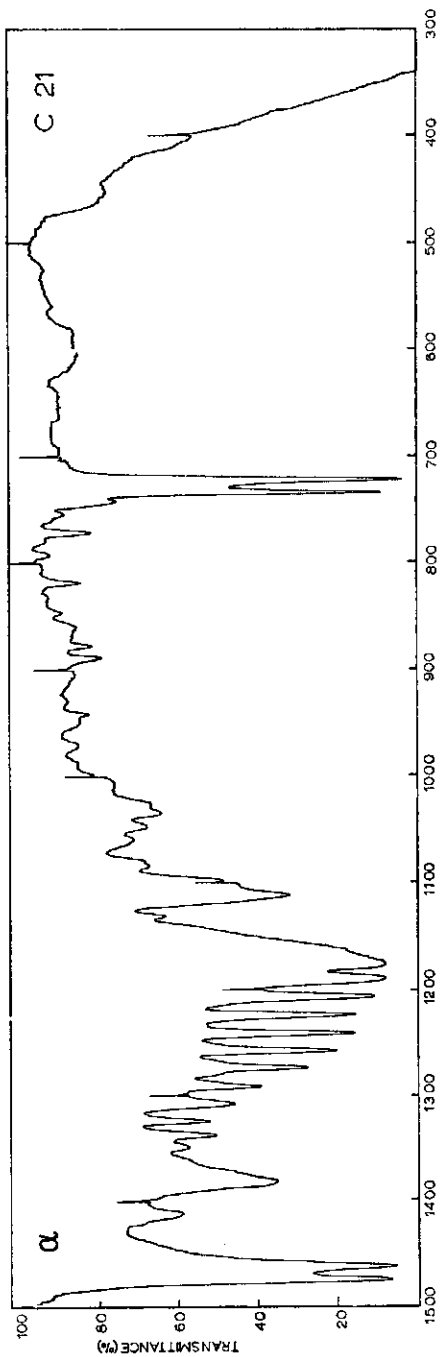


Figure 34a, c, d. Infrared spectra of triarachidin.



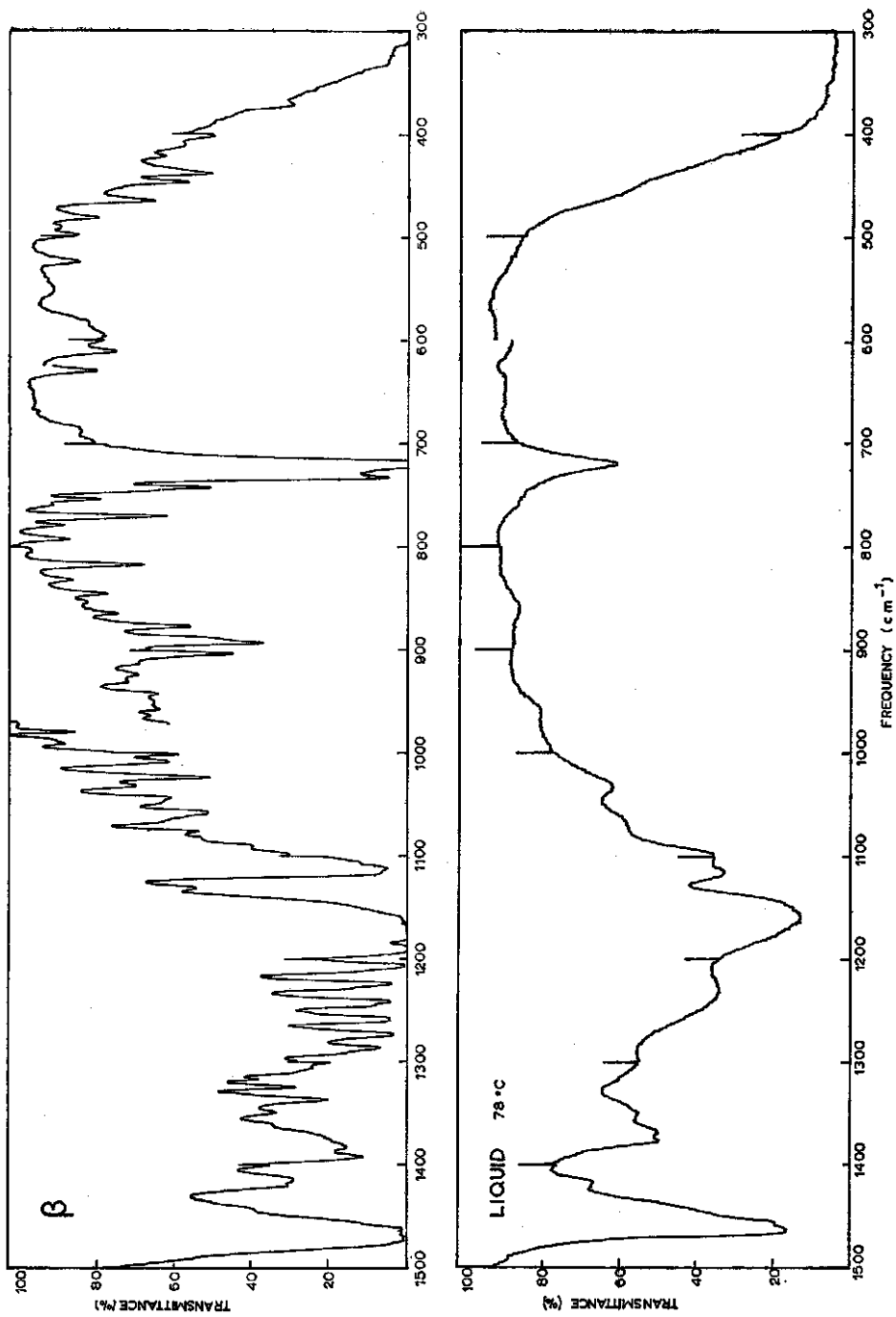
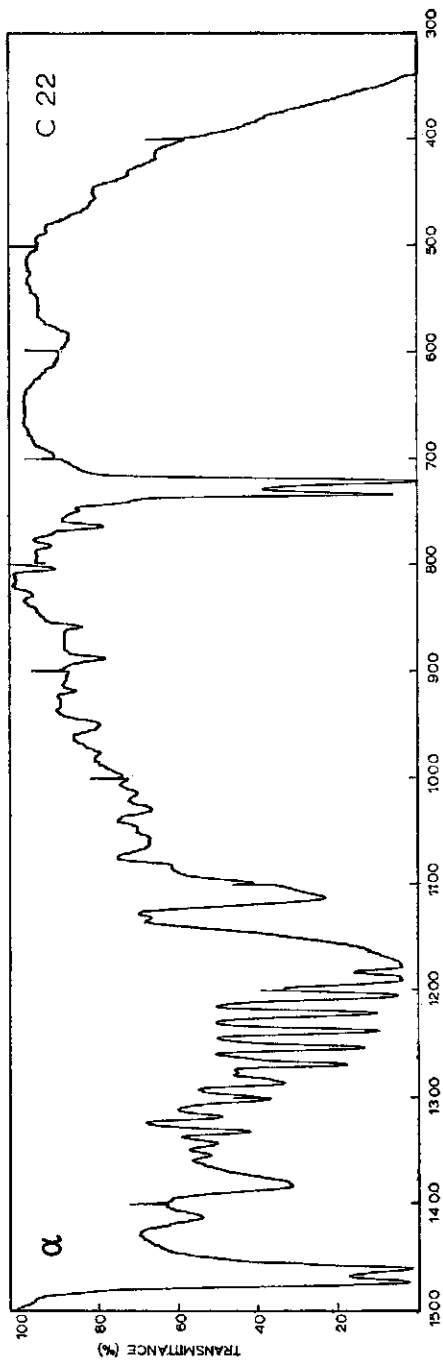


Figure 35a, b, c, d. Infrared spectra of triheicosanoic acid.



β' form omitted

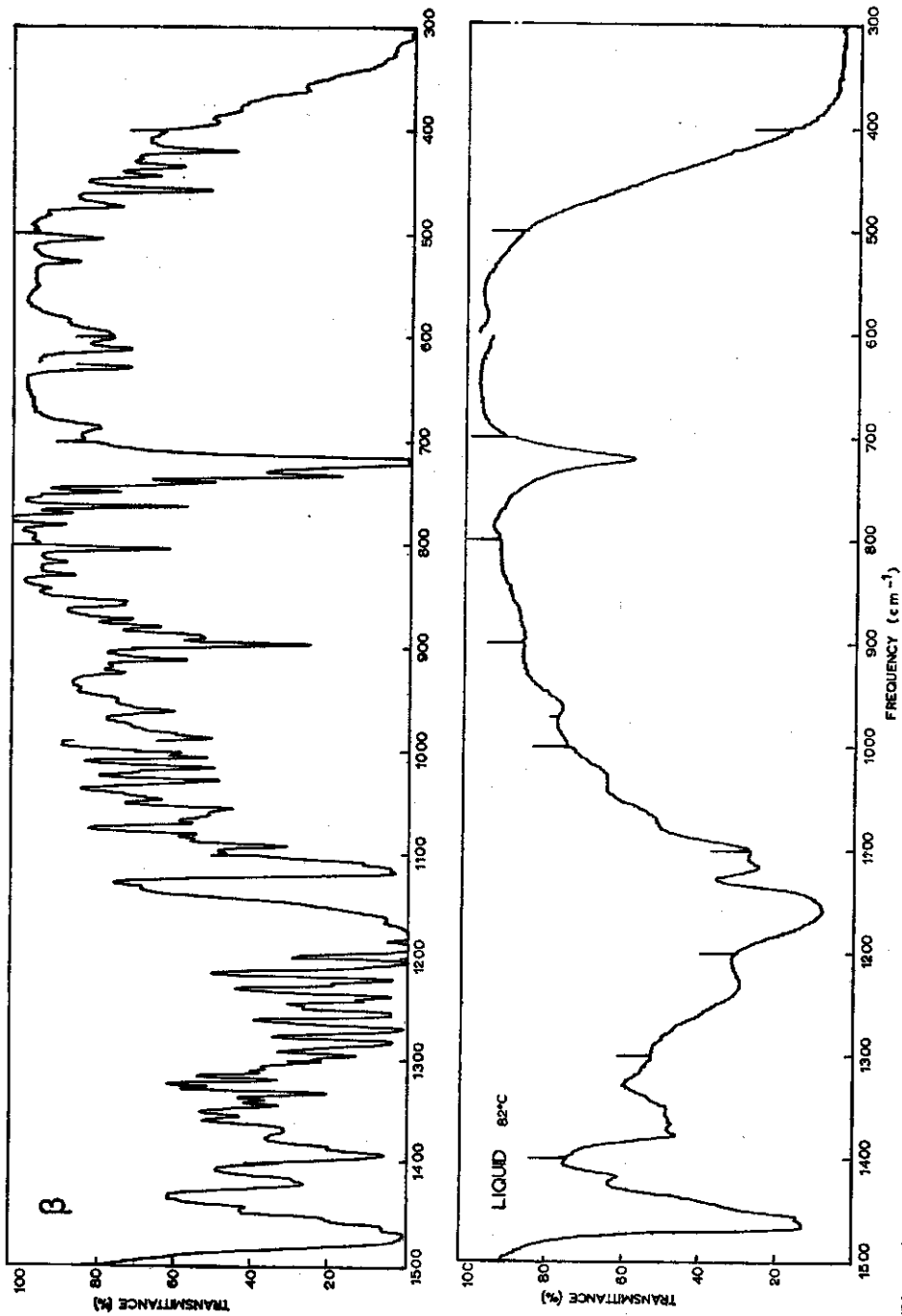
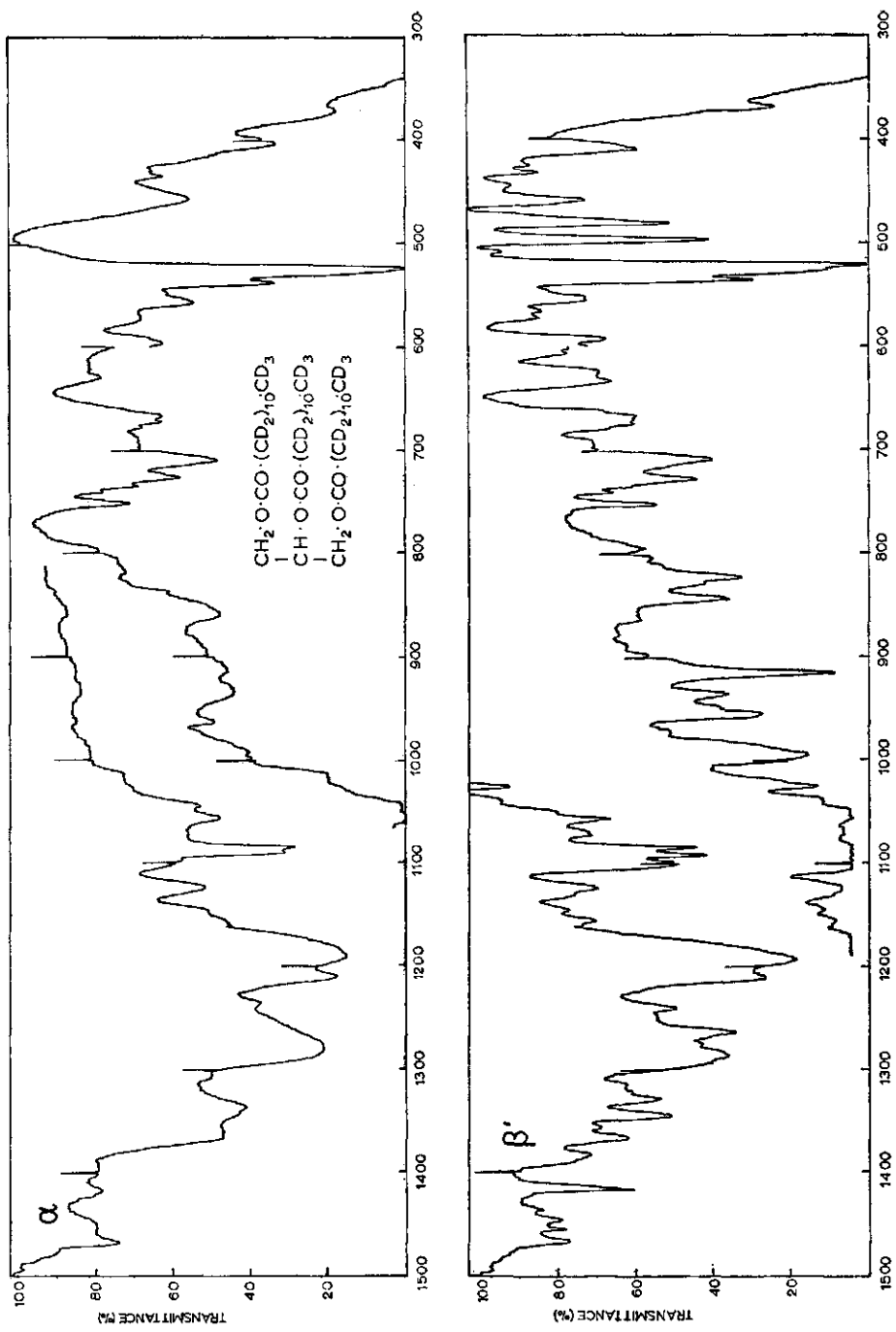


Figure 36a, c, d, Infrared spectra of triphenenin.



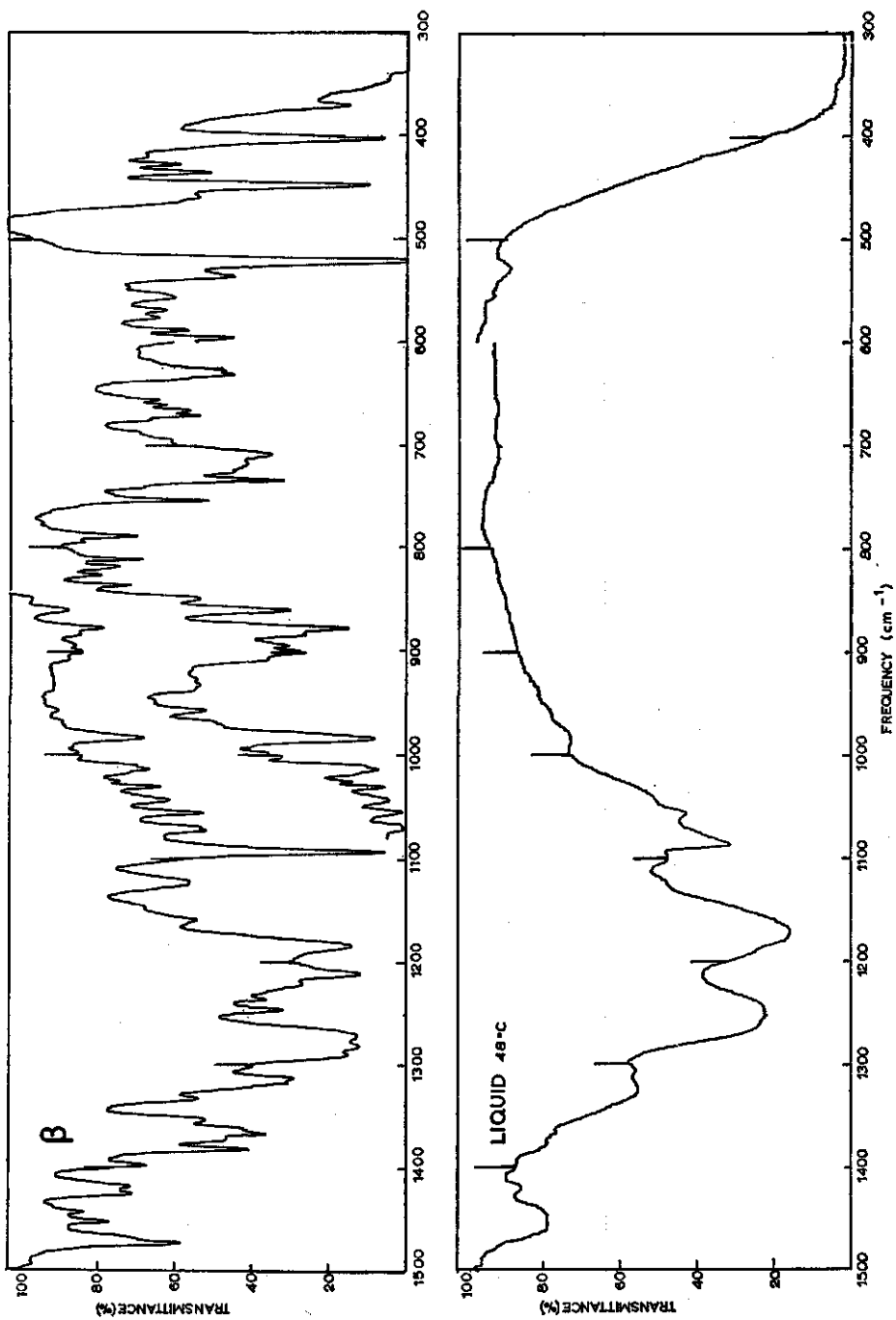


Figure 37a, b, c, d. Infrared spectra of glycerol-tri-(perdeutero-laurate).

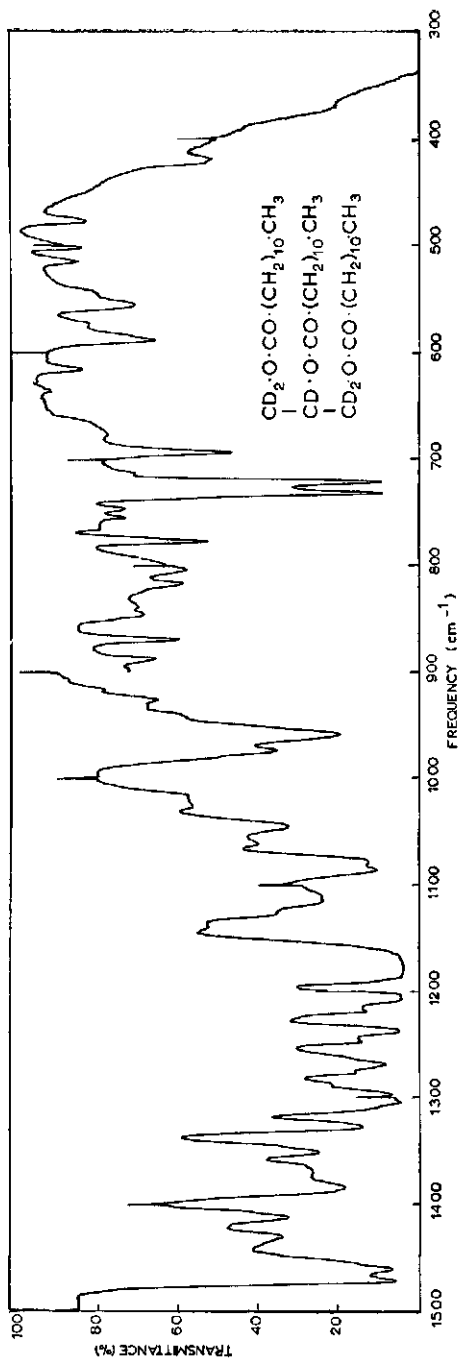
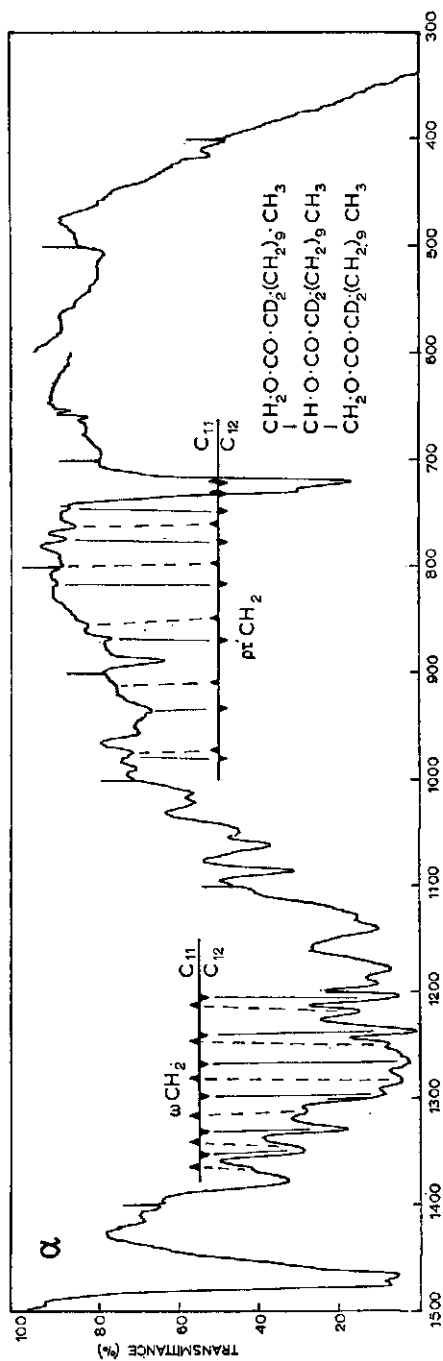


Figure 38. Infrared spectrum of (perdeutero-glycerol)-trilaurate.



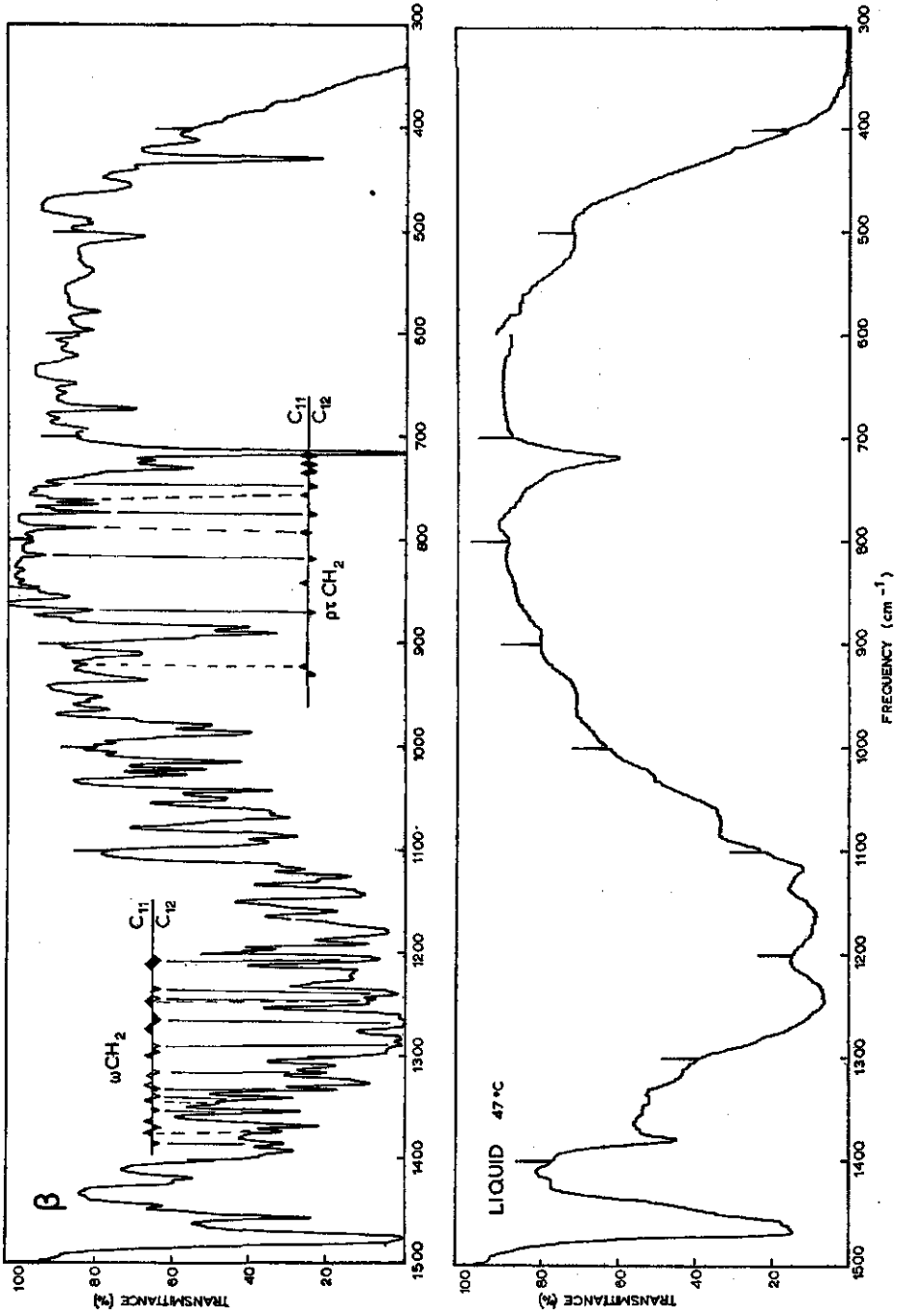


Figure 39a, c, d. Infrared spectra of glycerol-tri-(α -dideutero-laurate).

Explanation of the Tables 10-25

The assigned bands are indicated by abbreviated symbols:

- σ = σCH_2 = methylene scissoring
 σ_a = $\sigma(\alpha\text{-CH}_2)$ = scissoring of the methylene group adjacent to the carbonyl group
 ω = ωCH_2 = methylene wagging
 τ = τCH_2 = methylene twisting-rocking
 ρ = ρrCH_2 = methylene rocking-twisting
 δ_a = $\delta_a\text{CH}_3$ = methyl asymmetric deformation
 δ_s = $\delta_s\text{CH}_3$ = methyl symmetric deformation
 ρCH_3 = methyl rocking
 $\nu_A\text{C-O}$ = $\text{C}-\overset{\wedge}{\text{O}}$ stretching of $\left. \begin{array}{l} \text{---C---O---CH}_2\text{---} \\ || \\ \text{O} \end{array} \right\}$
 $\nu_B\text{C-O}$ = $\text{C}-\overset{\bullet}{\text{O}}$ stretching of $\left. \begin{array}{l} \text{---C---O---CH}_2\text{---} \\ || \\ \text{O} \end{array} \right\}$
A, B = unidentified bands specific for β'
C = unidentified band specific for β
D, E, F = three unidentified bands in β' and β in the 600 cm^{-1} region

vs = very strong

s = strong

m = medium

w = weak

vw = very weak

sh = shoulder

b = broad

Table 10. Trienantoin, glycerol triheptanoate, C₇.

α	β'	β	α	β'	β
1470 s	σ	1475 sh	σ	1469 s	σ
1457 sh	$\delta_a + \sigma$	1467 s	$\delta_a + \sigma$	1459 m	$\delta_a + \sigma$
1439 sh	$\delta_s + \sigma$	1460 sh	$\delta_s + \sigma$	1452 m	$\delta_s + \sigma$
1422 sh	$\delta_s + \sigma$	1453 sh	$\delta_s + \sigma$	1447 w	$\delta_s + \sigma$
1416 m	σ_a	1431 m	σ_a	1443 sh	σ_a
1035 m		1052 s		1062 m	
1012 vw	ν_3	1043 sh	ν_4	1053 s	
1000 w	ν_5	1014 vw	ν_3	1046 m	ν_4
		1003 w	ν_5	1038 w	
				1015 w	ν_3

Table 11. Tricaprylin, glycerol trioctanoate, C₈.

α	β'	β
1470 s	σ	σ
1460 sh	$\delta_a + \sigma$	$\delta_a + \sigma$
1440 sh	σ_a	σ_a
1418 m		
1415 s		
1385 s	$\delta_b + \omega$	$\delta_b + \omega$
1359 m	ω_4	ω_4
1326 s	ω_3	ω_3
1300 w	τ	
1290 sh		
1275 s	ω_2	ω_2
1251 m	τ	
1228 s	ω_1	ω_1
1210 vw		
1175 vs	ν_A C-O	ν_A C-O
1125 sh	$\nu_1?$	ν_1
1117 s	ν_B C-O	ν_B C-O
1100 s		
1185 vs	ν_A C-O	ν_A C-O
1160 sh		
1125 m	ν_1	ν_1
1118 m		
1103 s	ν_B C-O	ν_B C-O
1185 vs		
1163 m		
1149 w		
1127 m	ν_1	ν_1
1120 s		
1114 s		

α	β'	β
698 vw		
632 m	D	D
615 w	E	E
582 m	F	F
550 m		
522 vw		
508 vw		
494 w		
477 m		
468 sh		
451 vw		
441 sh		
429 w		
412 w		
472 w		
448 m		
437 vw		
429 m		
415 sh		
401 m		

1063 W	1061 W	1073 m	2
1050 m	1056 m	1064 W	
1035 W	1045 W	1062 sh	2
1015 m	1028 VW	1058 m	
1000 W	1021 W	1049 W	
	1018 sh	1041 m	
		1036 sh	
		1032 VW	
		1025 sh	
		1018 m	6
		1004 s	
985 W	998 s	993 VW	
935 m	980 s	987 W	
912 m	963 W	966 VW	
	947 s	958 W	
	928 W	950 VW	
	923 W	927 W	5
	912 m	913 W	CH ₃
	907 sh	903 s	C
890 W	897 VW	890 VW	
876 VW	889 VW	882 m	
863 W	874 VW	868 W	
830 m	865 W	853 VW	
	836 m	843 sh	
	831 m	830 W	4
	801 W		
793 m	770 s	795 W	
768 s	747 W	768 s	3
725 vs	738 sh	745 VW	
	730 m	737 m	2
	722 s	727 m	
		720 s	1

1105 s ¹³B C-O

1075 m	¹³ C ₂	1082 m	¹³ C ₂
1062 m	¹³ C ₆	1076 m	
1042 m		1062 m	¹³ C ₆
1033 m	¹³ C ₃	1057 m	
1010 m	¹³ C ₇ + ¹³ C ₃	1047 w	
1005 sh	¹³ C ₄	1039 m	¹³ C ₅
		1036 w	
		1032 w	
		1024 vw	
		1017 sh	
		1011 s	¹³ C ₇ + ¹³ C ₃
		1004 m	¹³ C ₄
985 sh		992 vw	
980 w		988 sh	
965 sh		981 s	
960 sh		967 m	
954 m	¹³ C ₆	954 s	¹³ C ₆
940 vw		936 w	
923 vw		932 vw	
912 vw		923 m	A
		913 vw	
888 w	¹³ C ₃	892 w	¹³ C ₃
868 w		888 sh	
860 m	¹³ C ₅	873 m	
835 vw		869 w	
827 vw		860 s	¹³ C ₅
812 vw		834 m	B
		827 w	
		810 vw	

Table 13. Tricaprin, glycerol tridecanoate, C₁₀.

α	β'	β	α	β'	β
1476 sh	1475 vs	1475 vs	σ	790 vw	792 w
1470 vs	1463 vs	1467 sh	$\delta_8 + \sigma$	772 w	754 m
1465 sh	1458 sh	1462 sh	$\delta_8 + \sigma$	747 sh	750 m
1440 sh	1453 sh	1456 m	$\delta_8 + \sigma$	739 m	741 s
1416 m	1434 w	1445 m	σ_{α}	728 sh	729 m
	1421 sh	1437 sh		722 vs	720 sh
	1414 m	1427 sh	σ_{α}	700 vw	717 vs
		1422 m			
		1415 w			
1384 s	1395 m	1394 s	$\delta_8 + \omega$	631 m	682 m
1372 sh	1382 m	1384 w	ω_7	620 m	628 m
1355 m	1372 sh	1375 sh	ω_6	577 s	610 s
1330 s	1358 m	1371 w	ω_5	523 w	593 m
1310 sh	1347 vw	1366 m	ω_6	512 w	523 vw
	1340 w	1356 s	ω_5	503 vw	508 m
	1328 s	1340 m	ω_4		502 w
	1319 vw	1331 s	ω_4	467 vw	485 vw
	1310 m	1312 s	τ	445 sh	467 s
		1304 w		434 vw	461 sh
1292 s	1292 s	1297 sh	ω_3	415 w	450 vw
1282 vw	1279 s	1292 m	τ		447 s
1265 sh	1268 sh	1282 s	ω_2	425 w	441 sh
1252 s	1253 s	1267 w	τ	420 w	427 vw
1237 w	1241 vw	1259 s	ω_2		413 s
1213 s	1215 s	1239 sh	τ		
		1231 w	ω_1		
		1222 m			
		1213 s	ω_1		

	$\nu_{\text{C-O}}$	ν_{B}	$\nu_{\text{C-O}}$		ν_{B}	$\nu_{\text{C-O}}$
1104 s			1124 sh	1129 w	ν_1	
			1117 sh	1117 } s		ν_{B} C-O
			1102 s	1114 }		
1080 w	ν_2	ν_2	1083 s	1091 s	ν_2	
1065 sh	ν_7	ν_7	1064 sh	1077 s		
1060 w	ν_6	ν_6	1059 s	1063 sh	ν_7	
1036 w	ν_3		1042 sh	1059 s	ν_6	
1017 m	ν_5	ν_3	1034 w	1057 sh		
			1023 sh	1046 vw		
			1016 s	1036 m	ν_3	
				1027 w		
				1017 s	ν_5	
				1007 sh		
993 w	ν_4		997 sh	997 s	ν_4	
987 w		ν_4	992 w	988 w		
953 m	ν_7		982 m	972 m		
930 w		ν_7	962 s	963 m	ν_7	
910 w			953 vw	955 m		
			946 sh	933 w		
			937 w	922 m		
			923 m	910 sh		
			918 sh			
			910 sh			
887 m	$\nu_6 + \nu_{\text{CH}_3}$		897 vw	897 s	C	
855 vw			887 sh	890 w		
840 vw			884 m	884 w		$\nu_6 + \nu_{\text{CH}_3}$
822 m	ν_5		875 w	878 w		
			854 w	862 m		
			834 m	848 w		
			821 s	821 s		ν_5

~	1180	VS	%A C-O	~	1180	VS	%A C-O	1181	VS	%A C-O
	1131	W	%1		1132	W	%1	1174		
	1115	S	%B C-O		1118	sh		1160	W	
					1108	S	%2	1128	W	%1
								1116	S	%B C-O
								1110	m	
								1102	m	%2
	1086	W	%2		1089	S		1089	m	
	1075	VW			1072	m		1080	sh	
	1062	W	%7,8		1058	m	%7,8	1069	VW	
	1045	sh	%3,6		1050	VW		1065	VW	%8
	1033	S	%9		1040	W	%3	1060	sh	%7
	1025	sh			1036	sh	%6	1055	m	
	1007	m			1025	m	%9	1049	sh	
					1013	W		1037	W	
					1005	W		1029	m	%9
								1022	m	
								1010	sh	
								1007	m	
	988	VW	%5		986	VW	%5,4	986	m	
	982	VW	%4		975	S	%8	980	VW	
	970	W	%8		967	W		976	VW	
	949	W			945	m		972	W	%8
	933	W			928	m	A	969	sh	
	915	m			923	sh		962	W	
	908	m	%7		913	m	%7	945	sh	
								942	W	
								923	m	%7
								913	sh	

Table 16. Trinidecyltin, glycerol tritridecanoate, C₁₃.

α		β'		β		α		β'		β						
1476	vs	σ	1475	s	σ	1478	sh	988	vw	p ₆	991	s	p ₆ + e ₁₀ ?	994	s	p ₆ ?
1465	vs	$\delta_8 + \sigma$	1463	vs	$\delta_8 + \sigma$	1472	vs	980	vw	p ₅	982	w		985	w	
1458	sh	$\delta_8 + \sigma$	1458	sh	$\delta_8 + \sigma$	1464	sh	949	w	e ₉	976	m		979	vw	
1445	sh	$\delta_8 + \sigma$	1453	sh	$\delta_8 + \sigma$	1454	sh	938	m		965	m	p ₅	970	vw	p ₅
1427	sh	$\delta_8 + \sigma$	1447	sh	$\delta_8 + \sigma$	1450	sh	927	vw		953	s	e ₉	965	w	p ₅
1421	sh	σ_α	1435	m		1444	m	910	w	e ₈	938	w		961	m	e ₉
1415	m	σ_α	1423	sh		1434	vw				933	w		950	vw	
			1420	sh		1427	sh				924	s	A	939	w	
			1415	sh	σ_α	1423	m				915	vw		923	sh	
			1410	s	σ_α	1417	w							917	m	
														909	vw	
1385	s	$\delta_8 + \omega$	1396	s	$\delta_8 + \omega$	1394	s	887	m	eCH ₃	897	w	e ₈	897	s	e ₈ + C
1372	sh	ω_8	1383	m	$\delta_8 + \omega$	1385	vw	860	w		893	vw		888	w	
1359	m	ω_7	1377	m	$\delta_8 + \omega$	1374	m	836	s	e ₇	884	m	eCH ₃	883	m	eCH ₃
1342	sh	ω_6	1370	sh	ω_8	1369	m				875	w		876	m	
1339	s	ω_6	1360	m	ω_7	1361	w				867	vw		866	m	
1318	s	ω_5	1352	w	ω_7	1349	vw				860	w		862	w	
			1344	s	ω_6	1342	s				836	s	B	835	m	e ₇
			1338	m	ω_6	1329	m				830	sh	e ₇	814	vw	
			1328	w		1321	m				815	w				
			1322	w		1305	s									
			1315	s	ω_5			792	m	e ₆	795	sh		793	w	e ₆
			1306	m	τ			761	s	e ₅	792	m	e ₆	771	w	
1288	s	ω_4	1298	sh		1295	sh	738	sh	e ₄	778	w		760	s	e ₅
1282	sh	τ	1288	s	ω_4	1289	w	730	s	e ₃	761	sh		745	sh	
1272	s	ω_3	1280	s		1283	s	720	vs	e _{1,2}	759	s	e ₅	740	m	e ₄
1257	sh	τ	1267	sh	τ	1268	sh				748	vw		731	m	e ₃
1240	sh	ω_3	1260	s	ω_3	1263	s				741	w	e ₄	725	w	e ₂
1234	s	ω_2	1250	sh	τ	1257	w				734	sh		717	vs	e ₁
1220	vs	τ	1242	w	τ	1247	vw				732	vs		728	sh	e _{1,2,3}
											726	w				

Table 17. Trimyristine, glycerol tritetradecanoate, C₁₄.

α	β'	β
1476 vs	σ	1492 sh
1464 vs	$\delta_a + \sigma$	1479 sh
1460 sh	$\delta_a + \sigma$	1475 vs
1440 sh	$\delta_a + \sigma$	1467 sh
1422 sh	$\delta_a + \sigma$	1460 sh
1415 m	σ_a	1455 w
		1444 m
		1438 sh
		1433 vw
		1422 m
		1416 w
1385 s	$\delta_a + \omega$	1394 s
1365 w	ω_8	1385 sh
1349 m	ω_7	1372 m
1331 s	ω_6	1366 m
1305 m	ω_5	1351 s
		1344 w
		1338 w
		1331 s
		1320 m
		1316 sh
		1306 w
		1300 w
1292 w	τ	1295 s
1280 s	ω_4	1291 sh
1272 sh	ω_3	1280 s
1255 s	ω_3	1275 s
1250 sh	τ	1269 sh
1238 sh	τ	1260 vw
1228 s	ω_2	1254 s
1200 s	ω_1	1251 w
		1245 m

α	β'	β
888 m	ρCH_3	898 s
854 w	ρ_8	889 m
832 vw		884 m
812 m	ρ_7	873 m
		852 m
		833 w
		811 s
776 m	ρ_6	789 vw
758 sh		775 m
750 m	ρ_5	758 m
730 s	ρ_4	750 s
721 vs	$\rho_{1,2,3}$	736 s
		728 m
		723 w
		717 vs
		702 vw
		684 m
		628 m
		610 m
579 w		595 m
		546 vw
		516 m
		513 w
		499 vw
		495 w
		480 w
		469 m

442 VW
424 W
408 W

426 sh
421 W
415 W

1220 s	ω ₂	1224 s	τ	1224 s	ω ₁
1224 sh	τ	1209 sh	τ	1209 sh	τ
1208 W	τ	1204 s	ω ₁	1204 s	ω ₁
1180 vs	τ _A C-O	1198 s	ω ₁	~ 1180 s	τ _A C-O
1165 sh		1182 s	τ _A C-O	1174 sh	
1128 W	τ ₁	1173 vs	τ _A C-O	1161 m	
1112 s	τ _B C-O	1145 sh	τ ₁	1146 sh	
		1128 W	τ ₁	1130 W	τ ₁
		1116 W	τ _B C-O	1126 VW	
		1103 s	τ _B C-O	1117 s	τ _B C-O
				1112 m	τ _B C-O
1096 s		1095 s		1097 s	
1089 sh		1084 s		1088 m	
1060 m	τ _{3,10}	1071 W	τ ₃	1083 m	
1040 m	τ ₉ + τ ₁₂	1061 sh	τ ₁₀	1068 W	τ ₃
1028 VW	τ ₈	1056 s	τ ₉ + τ ₁₂	1061 sh	
1015 m	τ ₄	1044 m	τ ₈	1056 m	τ ₁₀
		1038 VW	τ ₄	1043 W	
		1031 W	τ ₈	1037 m	τ ₉ + τ ₁₂
		1022 m	τ ₄	1033 sh	
		1008 sh		1029 W	τ ₈
				1021 W	
				1017 m	τ ₄
995 m	τ ₇ + τ ₁₁	997 m	τ ₇ + τ ₁₁	998 s	τ ₇ + τ ₁₁
976 VW		988 s		988 VW	τ ₆
950 m	τ ₁₀	973 s		976 W	
930 W		965 m		968 W	
910 VW		957 s	τ ₁₀ ?	962 W	τ ₅
902 m	τ ₉	945 VW		949 VW	τ ₁₀
		937 W		934 VW	
		925 s	A	922 m	
		920 sh		910 VW	τ ₉
		902 m	τ ₉	902 VW	

Table 18. Tripentadecylin, glycerol tripentadecanoate, C₁₅.

α	β'	β
1474 vs	1475 vs	1474 vs
1463 vs	1461 vs	1470 sh
1460 sh	1454 sh	1461 m
1445 sh	1445 w	1453 sh
1420 sh	1435 m	1444 m
1413 m	1425 sh	1437 vw
	1420 sh	1424 m
	1413 s	1415 m
1385 s	1395 m	1394 s
1372 sh	1382 m	1385 w
1356 m	1372 m	1371 m
1339 s	1358 m	1356 m
1321 s	1351 sh	1345 sh
	1342 sh	1340 s
	1339 m	1330 m
	1330 w	1323 s
	1322 sh	1317 sh
	1320 m	1310 s
	1317 sh	1305 vw
	1309 m	
1294 s	1296 s	1294 m
1285 sh	1287 s	1287 s
1272 s	1273 s	1274 s
1254 sh	1268 m	1270 sh
1248 s	1248 s	1266 w
1233 sh	1240 w	1254 m
1224 s	1229 w	1250 s
	1223 s	1245 sh
	1205 sh	1231 m
		1225 s

α	β'	β
998 w	995 m	985 w
981 vw	985 vw	977 w
961 w	980 vw	972 vw
947 vw	974 w	967 w
930 vw	968 s	964 m
906 vw	964 m	946 w
	942 m	943 w
	927 m	926 w
	922 m	915 vw
	916 vw	910 w
	908 vw	906 m
889 m	888 m	893 s
872 m	876 w	891 sh
830 w	872 m	876 w
807 vw	853 vw	871 m
	834 m	859 w
	830 sh	847 vw
	825 sh	835 sh
	814 w	831 m
		813 sh
		811 vw
793 m	793 m	794 s
764 w	781 vw	780 vw
749 sh	767 w	774 vw
744 m	764 w	763 m
731 s	753 w	750 w
720 vs	744 m	744 s
	733 vs	734 m
	725 sh	728 w

01	1202 sh				705 sh
	1201 s				
	1196 s	ω_1			685 w
	1185 vs	$\%A$ C-O			634 sh
	1173 sh	$\%A$ C-O			629 m
	1163 m	$\%A$ C-O			612 m
	1148 sh	$\%A$ C-O			
	1132 m	$\%A$ C-O			597 w
	1128 sh	$\%A$ C-O			590 sh
	1118 s	$\%A$ C-O			575 vw
	1113 m	$\%A$ C-O			529 vw
	1105 vw	$\%A$ C-O			515 w
	1100 m	$\%A$ C-O			509 w
	1093 m	$\%A$ C-O			493 w
	1087 m	$\%A$ C-O			483 sh
	1072 m	$\%A$ C-O			478 vw
	1062 m	$\%A$ C-O			470 w
	1057 m	$\%A$ C-O			453 m
	1052 m	$\%A$ C-O			450 vw
	1041 sh	$\%A$ C-O			443 w
	1036 vw	$\%A$ C-O			
	1032 m	$\%A$ C-O			
	1026 s	$\%A$ C-O			
	1009 vw	$\%A$ C-O			
	1005 s	$\%A$ C-O			
	1001 sh	$\%A$ C-O			

1199 s	ω_1	1197 s		657 w,b
1180 vs	$\%A$ C-O	1180 vs		
1130 m	$\%A$ C-O	1133 m		633 m
1112 s	$\%A$ C-O	1118 w		618 w
1101 s	$\%A$ C-O	1106 vs		
1093 sh	ω_1	1097 s		
1071 sh	$\%A$ C-O	1089 m		
1062 w	$\%A$ C-O	1074 w		
1052 w	$\%A$ C-O	1058 m		
1038 vw	$\%A$ C-O	1053 m		
1025 m	$\%A$ C-O	1032 m		
1004 w	$\%A$ C-O	1024 sh		
998 w	$\%A$ C-O	1011 vw		
	$\%A$ C-O	1005 w		
	$\%A$ C-O	1001 sh		

581	w	576	m	F	596	m	F
549	vw, b	558	vw		547	vw	
512	w	550	sh		518	w	
		529	vw		513	sh	
		517	vw		504	vw	
468	w	497	w		486	w	
448	w	488	w		465	m	
427	w	479	w		455	vw	
416	w	470	w		445	m	
		457	sh		436	w	
		450	sh		417	m	
		446	vw				
		427	vw				

1196	s	ω ₁	1197	s	ω ₁	1199	s	ω ₁
1177	vs	ν _A C-O	1186	vs	ν _A C-O	~1184	vs	ν _A C-O
1129	w	ν ₁	1174	vs	ν ₁	1178	sh	ν _A C-O
1111	m	ν _B C-O	1162	sh	ν ₁	1174	sh	ν _A C-O
1101	s		1157	sh	ν ₁	1163	m	ν _A C-O
			1142	vw	ν ₁	1147	sh	
			1131	w	ν ₁	~1130	w	ν ₁
			1117	sh	ν ₁	1117	s	ν _B C-O
			1106	s	ν ₁	1112	s	ν _B C-O
					ν _B C-O	1103	m	
1093	sh		1098	s		1094	m	
1070	sh	ν ₃	1092	m		1088	m	
1062	w	ν ₁₂	1076	w	ν ₃	1072	w	ν ₃
1051	m	ν ₁₁	1073	sh	ν ₃	1059	m	ν ₁₂
1038	sh	ν ₄	1059	m	ν ₁₂	1053	sh	ν ₁₁
1030	w	ν ₁₀	1053	m	ν ₁₁	1050	m	ν ₁₁
1016	m	ν ₁₃ + ν ₉	1036	m	ν ₁₀	1046	sh	
1008	sh	ν ₈	1027	sh	ν ₁₀	1036	m	ν ₄
			1015	sh	ν ₁₃ ?	1031	m	ν ₁₀
			1011	w	ν ₉	1023	sh	
			1004	w	ν ₈	1018	m	ν ₁₃ + ν ₉
						1011	vw	ν ₈
						1007	m	

621	vW	632	m	685	w
610	vW	616	m	626	m
				609	m
				~ 600	m
569	vW	575	m	592	sh
554	w	530	sh	520	w
544	vW	524	sh	510	vW
523	w	518	m		
		511	m		
		504	sh		
494	w	497	sh	490	vW
474	vW	484	m	482	w
		468	vW	469	w
		459	sh	457	w
		451	vW	453	sh
		435	w	449	w
				436	vW
				424	s

1217	s	ω ₂	1243	m	ω ₃
1202	sh	τ	1240	m	
			1235	w	
			1224	w	
			1218	s	ω ₂
			1212	sh	
1195	s	ω ₁	1197	s	ω ₁
1178	vs	ν _A C-O	1187	sh	
1172	sh		1182	vs	ν _A C-O
1131	m	ν ₁	1174	sh	
1113	w		1162	m	
1105	m	ν _B C-O	1147	sh	
			1133	w	ν ₁
			1117	s	ν _B C-O
			1112	s	
			1105	m	
1098	sh		1097	w	
1074	vW	ν ₃	1088	m	
1063	m	ν ₁₂	1074	m	ν ₃
1041	w	ν ₄	1064	sh	
1025	w	ν ₉	1062	sh	ν ₁₂
1007	w	ν ₈	1058	m	
			1046	vW	ν ₄ + etis?
			1042	m	ν ₁₁
			1040	sh	
			1027	m	ν ₁₀
			1017	w	ν ₉ + Q14
			1010	m	ν ₈

Table 21. Tristearin, glycerol trioctadecanoate, C₁₈.

α	β'	β	α	β'	β
1476 vs	σ	σ	1475 vs	σ	1475 vs
1463 vs	$\delta_8 + \sigma$	$\delta_8 + \sigma$	1463 vs	$\delta_8 + \sigma$	1466 sh
1460 sh			1455 sh		1455 m
1450 sh	$\sigma\alpha$	$\sigma\alpha$	1448 sh	$\sigma\alpha$	1445 m
1415 m			1436 m		1436 vw
			1420 sh		1424 m
			1413 s		1422 sh
					1417 vw
1384 s	$\delta_8 + \omega$	$\delta_8 + \omega$	1397 s	$\delta_8 + \omega$	1397 s
1370 sh	ω_{10}	$\delta_8 + \omega$	1382 sh	$\delta_8 + \omega$	1386 vw
1358 m			1379 m		1374 sh
1346 m	ω_9	ω_{11}	1374 sh	ω_{10}	1368 m
1327 s	ω_8	ω_{10}	1360 w	ω_9	1360 w
1314 m	ω_7		1357 sh		1348 m
			1350 w		1340 w
			1343 sh		1333 s
			1340 w		1324 m
			1333 m		1316 m
			1323 w		1305 m
			1314 m		
			1305 m		
1293 s	ω_6	τ	1294 m	τ	1296 sh
1283 sh	ω_5	ω_6	1287 m	ω_6	1291 sh
1273 s			1274 s		1287 s
1266 sh	ω_4	ω_5	1270 m	ω_5	1282 sh
1254 s			1254 s		1274 s
1233 s	ω_3	τ	1240 sh	ω_5	1271 s
1214 s	ω_2	ω_3	1234 s	ω_3	1268 sh
		ω_2	1212 s	ω_2	1258 s
					1254 s

α	β'	β	α	β'	β
993 w	$\nu_{5,8,7}$		990 vw		
981 vw	ϱ_{13}	ν_6	985 s	ν_6	989 s
948 m			962 w		965 sh
928 vw			953 w		962 m
904 w	$\varrho_{12}?$	ϱ_{13}	945 m	ϱ_{13}	950 w
			934 w		937 vw
			922 m	A	923 w
			917 sh		913 sh
			907 vw		904 s
			903 vw		
886 m	ϱCH_3		890 w	ϱCH_3	892 s
873 m	ϱ_{11}		885 m	ϱ_{11}	874 m
862 w	ϱ_{10}		855 vw		862 w
806 m	ϱ_9		832 sh	ϱ_{10}	850 vw
			828 m	B	839 w
			820 w		822 vw
			803 m	ϱ_9	806 m
778 w	ϱ_8		792 vw		789 vw
764 sh	ϱ_7	ϱ_8	775 w	ϱ_8	777 w
756 m			765 vw		763 w
745 sh	ϱ_6		754 m	ϱ_7	756 s
730 s	ϱ_{1-5}	ϱ_6	745 sh	ϱ_6	741 m
718 vs			740 w		732 s
			730 vs	ϱ_{1-5}	727 w
			718 vs		717 vs
			701 vw		
630 m	D	D	630 m	D	682 w
615 m	E	E	615 m	E	627 m
					D

549 W	530 VW	520 W
516 W	518 VW	
	501 VW	
462 W	493 VW	488 W
436 W	482 W	474 VW
423 W	472 W	466 m
	450 VW	449 m
	433 W	442 VW
	422 VW	423 m
	410 VW	411 m

1235 s	ω_3	1235 s	ω_3
1230 sh		1230 sh	
1220 w	τ	1220 w	
1214 s	} ω_2	1214 s	
1210 sh		1210 sh	
1195 s	ω_1	1195 s	ω_1
1183 vs	ρ_A C-O	1183 vs	ρ_A C-O
1162 m		1162 m	
1147 sh		1147 sh	
1130 w	ρ_1	1130 w	ρ_1
1118 s	ρ_B C-O	1118 s	ρ_B C-O
1113 m		1113 m	
1108 m		1108 m	
1100 m		1100 m	
1089 s		1089 s	
1075 w	ρ_3	1075 w	ρ_3
1067 sh	ρ_{13}	1067 sh	ρ_{13}
1061 sh	ρ_4	1061 sh	ρ_{13}
1057 m		1057 m	ρ_4
1049 w	ρ_{11}	1049 w	ρ_{11}
1044 w	$\rho_{10,9} + \rho_{15}$	1044 w	ρ_{12}
1038 w		1038 w	
1034 m	ρ_{11}	1034 m	ρ_{11}
1022 w	ρ_{10}	1022 w	ρ_{10}
1015 s	$\rho_9 + \rho_{15}$	1015 s	$\rho_9 + \rho_{15}$
1000 w	$\rho_{5,8}$	1000 w	$\rho_{5,8}$
1193 s	ω_1	1198 sh	
1176 vs	ρ_A C-O	1193 s	ω_1
1130 w	ρ_1	1173 vs	ρ_A C-O
1113 sh	~	1155 sh	
1106 s	ρ_B C-O	1130 w	ρ_1
1101 sh		1117 w	
		1107 s	
1075 w	ρ_3	1097 s	
1066 w	ρ_{13}	1080 w	
1058 m	ρ_4	1067 VW	ρ_{13}
1040 sh		1059 m	ρ_4
1033 m	ρ_{11}	1048 sh	
1024 VW		1040 m	ρ_{11}
1013 w	$\rho_{10,9} + \rho_{15}$	1035 sh	
		1014 m	$\rho_{10,9} + \rho_{15}$
		1102 VW	

Table 22. Trinonadecylin, glycerol trinonadecanoate, C₁₉.

α		β'		β		α		β'		β	
1477	vs	σ	1477	vs	σ	1476	vs	σ	990	m	ϱ_{15}
1463	vs	$\delta_a + \sigma$	1463	vs	$\delta_a + \sigma$	1473	vs	$\delta_a + \sigma$	976	w	$\nu_{6,7}$
1455	sh		1450	sh		1463	sh		ϱ_{14}		
1445	sh	σ_a	1445	sh	σ_a	1454	sh	σ_a	958	m	ν_8
1417	m		1437	w		1446	w		ν_6		
			1422	sh		1428	sh		968	w	ν_7
			1414	s		1426	m		963	w	ϱ_{14}
						1422	m		958	vw	
						1419	sh		945	vw	
1385	s	$\delta_s + \omega$	1395	m	$\delta_s + \omega$	1390	m	$\delta_s + \omega$	927	w	ϱ_{13}
1373	sh	ω_{12}	1384	w	$\delta_s + \omega$	1386	w	ω_{12}	913	m	
1365	sh	ω_{11}	1379	m	ω_{12}	1374	m	ω_{11}	908	sh	
1353	m	ω_{10}	1372	sh	ω_{12}	1369	w	ω_{11}	898	s	
1340	m	ω_9	1364	w	ω_{11}	1365	sh	ω_{10}	890	w	$\nu_{12} + \nu_{13}$
1327	m	ω_8	1356	w	ω_{10}	1354	m	ω_{10}	886	w	
1307	m	ω_7	1342	sh	ω_9	1346	vw	ω_9	878	w	
			1340	m	ω_9	1341	sh	ω_9	870	w	
			1335	sh	ω_8	1333	w	ω_8	857	vw	
			1326	m	ω_8	1327	s	ω_8	850	m	ϱ_{11}
			1317	m	ω_7	1317	m	ω_7	837	vw	
			1307	m	ω_7	1312	vw	ω_7	819	w	ϱ_{10}
						1308	w	τ	804	vw	
						1304	w	τ			
1287	s	ω_6	1299	m	ω_6	1298	s	ω_7			
1281	sh	$\tau?$	1288	s	ω_6	1292	w	τ			
1270	s	ω_5	1282	s	ω_6	1287	sh	ω_6	794	m	ϱ_9
1263	sh	τ	1268	s	ω_5	1283	s	ω_5	772	w	ϱ_8
1251	s	ω_4	1266	sh	τ	1277	w	τ	758	sh	
1232	s	ω_3	1249	s	ω_4	1270	s	ω_5	752	m	ϱ_7
1212	s	ω_2	1241	w	τ	1263	w	τ	733	s	ϱ_{1-6}
			1229	s	ω_1	1255	s	ω_1	722	vs	
									792	m	ϱ_9
									775	vw	
									767	w	ϱ_8
									754	w	
									749	m	ϱ_7
									738	w	

722 911 } 21-3

733 VS } 21-6
 720 VS }
 706 W }
 633 m D
 618 m E
 686 m
 627 m D
 617 m E
 600 m F

575 s F
 530 VW
 520 VW
 506 W
 497 W
 490 W
 480 m
 470 W
 459 W
 449 sh
 444 W
 431 VW
 425 VW
 400 W

582 W
 550 W
 525 W
 471 W
 435 W
 400 W

1232 s ω_3
 1227 W
 1218 m τ
 1213 s ω_2
 1208 VW

1197 s } ω_1
 1193 sh }
 1184 s } $\%A$ C-O
 1176 sh }
 1165 m }
 1150 sh }
 1134 W } $\%1$
 1131 sh }
 1119 VS } $\%B$ C-O
 1113 m }
 1103 m }

ω_1
 $\%A$ C-O

1196 sh
 1190 s
 1175 VS
 1163 sh
 1155 sh
 1145 sh
 1132 W
 1118 W
 1108 s

ω_1
 $\%A$ C-O
 $\%1$
 $\%B$ C-O

1195 s
 1181 VS
 1133 W
 1111 s
 1104 m

$\%B$ C-O

1098 s
 1082 m
 1070 W
 1062 sh
 1055 m
 1045 sh
 1041 m
 1026 W
 1019 m
 1011 W
 1000 VW

$\%3$
 $\%14$
 $\%4,13$
 $\%12,11$
 $\%10+\%16$
 $\%9,5$

1081 W
 1074 m
 1065 W
 1058 W
 1041 m
 1025 m
 1008 W

1091 m $\%3$
 1079 m
 1072 W
 1067 W
 1061 W $\%14$
 1057 sh
 1054 m $\%13$
 1042 m $\%12$
 1033 W $\%11$
 1024 m } $\%10+\%16$
 1021 m }
 1011 m $\%9$
 1000 W $\%5$

Table 23. Triarachidin, glycerol triicosanoate, C₂₀.

α	β' omitted	β
1473 vs	σ	1476 sh
1462 vs	$\delta_8 + \sigma$	1473 vs
1455 sh		1460 m
1440 sh	σ_{12}	1453 m
1420 sh		1442 m
1412 m		1420 m
		1414 w
1383 s	$\delta_8 + \omega$	1395 s
1355 w	ω_{11}	1383 w
1343 m	ω_{10}	1372 w
1331 m	ω_9	1370 m
1316 m	ω_8	1356 w
		1344 m
		1338 m
		1331 s
		1323 w
		1317 m
		1307 m
		1300 w
1297 m	ω_7	1297 w
1284 sh	τ	1290 s
1279 s	ω_6	1284 w
1273 sh		1278 sh
1262 s	ω_5	1276 s
1245 s	ω_4	1271 sh
1227 s	ω_3	1264 s
1209 s	ω_2	1262 sh
		1257 w
		1248 s
		1245 s
		1241 s
		1237 w
		1233 w
		1229 w
		1225 w
		1221 w
		1217 w
		1213 w
		1209 w
		1205 w
		1201 w
		1197 w
		1193 w
		1189 w
		1185 w
		1181 w
		1177 w
		1173 w
		1169 w
		1165 w
		1161 w
		1157 w
		1153 w
		1149 w
		1145 w
		1141 w
		1137 w
		1133 w
		1129 w
		1125 w
		1121 w
		1117 w
		1113 w
		1109 w
		1105 w
		1101 w
		1097 w
		1093 w
		1089 w
		1085 w
		1081 w
		1077 w
		1073 w
		1069 w
		1065 w
		1061 w
		1057 w
		1053 w
		1049 w
		1045 w
		1041 w
		1037 w
		1033 w
		1029 w
		1025 w
		1021 w
		1017 w
		1013 w
		1009 w
		1005 w
		1001 w
		997 w
		993 w
		989 w
		985 w
		981 w
		977 w
		973 w
		969 w
		965 w
		961 w
		957 w
		953 w
		949 w
		945 w
		941 w
		937 w
		933 w
		929 w
		925 w
		921 w
		917 w
		913 w
		909 w
		905 w
		901 w
		897 w
		893 w
		889 w
		885 w
		881 w
		877 w
		873 w
		869 w
		865 w
		861 w
		857 w
		853 w
		849 w
		845 w
		841 w
		837 w
		833 w
		829 w
		825 w
		821 w
		817 w
		813 w
		809 w
		805 w
		801 w
		797 w
		793 w
		789 w
		785 w
		781 w
		777 w
		773 w
		769 w
		765 w
		761 w
		757 w
		753 w
		749 w
		745 w
		741 w
		737 w
		733 w
		729 w
		725 w
		721 w
		717 w
		713 w
		709 w
		705 w
		701 w
		697 w
		693 w
		689 w
		685 w
		681 w
		677 w
		673 w
		669 w
		665 w
		661 w
		657 w
		653 w
		649 w
		645 w
		641 w
		637 w
		633 w
		629 w
		625 w
		621 w
		617 w
		613 w
		609 w
		605 w
		601 w
		597 w
		593 w
		589 w
		585 w
		581 w
		577 w
		573 w
		569 w
		565 w
		561 w
		557 w
		553 w
		549 w
		545 w
		541 w
		537 w
		533 w
		529 w
		525 w
		521 w
		517 w
		513 w
		509 w
		505 w
		501 w
		497 w
		493 w
		489 w
		485 w
		481 w
		477 w
		473 w
		469 w
		465 w
		461 w
		457 w
		453 w
		449 w
		445 w
		441 w
		437 w
		433 w
		429 w
		425 w
		421 w
		417 w
		413 w
		409 w
		405 w
		401 w
		397 w
		393 w
		389 w
		385 w
		381 w
		377 w
		373 w
		369 w
		365 w
		361 w
		357 w
		353 w
		349 w
		345 w
		341 w
		337 w
		333 w
		329 w
		325 w
		321 w
		317 w
		313 w
		309 w
		305 w
		301 w
		297 w
		293 w
		289 w
		285 w
		281 w
		277 w
		273 w
		269 w
		265 w
		261 w
		257 w
		253 w
		249 w
		245 w
		241 w
		237 w
		233 w
		229 w
		225 w
		221 w
		217 w
		213 w
		209 w
		205 w
		201 w
		197 w
		193 w
		189 w
		185 w
		181 w
		177 w
		173 w
		169 w
		165 w
		161 w
		157 w
		153 w
		149 w
		145 w
		141 w
		137 w
		133 w
		129 w
		125 w
		121 w
		117 w
		113 w
		109 w
		105 w
		101 w
		97 w
		93 w
		89 w
		85 w
		81 w
		77 w
		73 w
		69 w
		65 w
		61 w
		57 w
		53 w
		49 w
		45 w
		41 w
		37 w
		33 w
		29 w
		25 w
		21 w
		17 w
		13 w
		9 w
		5 w
		1 w

Table 24. Triheneicosanoin, glycerol triheneicosanoate, C₂₁.

α		β'		β		α		β'		β			
1474	vs	σ	1474	vs	σ	1479	sh	985	w	ν_9	992	w	ν_9
1461	vs	$\delta_n + \sigma$	1460	vs	σ	1474	vs	974	m	ν_8	988	sh	
1455	sh	$\delta_n + \sigma$	1456	sh	$\delta_n + \sigma$	1464	s	971	sh		980	w	ν_8
1445	sh	σ_α	1453	sh	$\delta_n + \sigma$	1459	sh	965	w	ϱ_{15}	972	sh	
1412	m	σ_α	1445	sh	σ_α	1444	sh	951	m		964	vw	
			1435	w		1422	m	942	vw	ϱ_{15}	958	vw	
			1412	s		1416	m	936	vw		950	vw	
1382	s	$\delta_s + \omega$	1395	m	$\delta_s + \omega$	1393	s	925	m	A	942	vw	ϱ_{15}
1370	sh	ω_{11}	1382	m	$\delta_s + \omega$	1384	m	920	sh		931	vw	ϱ_{15}
1362	sh	ω_{10}	1376	sh	$\delta_s + \omega$	1374	sh	907	vw	ϱ_{14}	924	vw	
1350	w	ω_{11}	1367	sh	ω_{12}	1362	sh	889	w	ϱCH_3	913	sh	
1338	m	ω_{10}	1362	sh	ω_{11}	1350	w	877	m	ϱ_{13}	903	m	ϱ_{14}
1325	m	ω_9	1354	w	ω_{10}	1337	m	863	vw		893	s	C
1308	m	ω_8	1348	vw	ω_9	1325	m	846	vw	ϱCH_3	890	sh	ϱCH_3
			1342	sh		1317	w	836	w		877	m	ϱ_{13}
			1338	w	ω_{10}	1310	sh	832	vw	ϱ_{12}	865	vw	
			1333	sh	ω_{11}	1300	m	832	vw		853	vw	
			1327	w	ω_9			830	w	B	845	w	ϱ_{12}
			1320	sh				819	m	ϱ_{11}	832	vw	
			1317	w				805	vw		817	m	ϱ_{11}
			1309	m	ω_8			807	vw		817	m	ϱ_{11}
			1303	w							804	vw	
1292	m	ω_7	1292	m	ω_7	1292	sh	797	vw	ϱ_{10}	792	w	ϱ_{10}
1288	sh		1287	m	ω_7	1287	m	783	vw		779	w	
1280	sh		1282	vw	ω_6	1273	s	770	m	ϱ_9	770	m	ϱ_9
1273	s	ω_6	1275	s	ω_6	1267	sh	763	vw		759	sh	
1268	sh	ω_5	1272	sh	ω_6	1259	s	754	vw	ϱ_8	753	w	ϱ_8
1258	s	ω_5	1258	s	ω_5	1252	sh	747	vw		745	sh	
1252	sh	ω_4	1256	sh	ω_5	1245	sh	743	w	ϱ_7	742	m	
1241	s	ω_4	1245	sh	ω_4	1242	s	734	vs	ϱ_{1-6}	733	s	ϱ_7
								722	vs		720	vs	ϱ_{1-6}

Tabel 25. Tribehenin, glycerol tridocosanoate, C₂₂.

α	β omitted	β	α	β omitted	β
1472 vs	σ	1476 s	889 m	ϱCH_3	897 s
1460 vs	$\delta_a + \sigma$	1469 vs	860 w	ϱ_{13}	891 w
1455 sh		1465 sh	830 vw	ϱ_{12}	888 sh
1445 sh	σ_a	1450 sh	817 vw	ϱ_{11}	880 w
1412 m		1442 w	805 m		873 vw
		1419 m		859 sh	ϱ_{13}
		1414 sh		856 w	
				844 vw	
1382 s	$\delta_a + \omega$	1392 s		830 w	ϱ_{12}
1354 w	ω_{12}	1385 sh		819 vw	
1343 w	ω_{11}	1368 m		805 m	ϱ_{11}
1332 m	ω_{10}	1355 w			
1318 w	ω_9	1344 w	793 sh		
1301 m	ω_8	1338 w	784 w	ϱ_{10}	
		1332 m	766 m	ϱ_9	
		1326 w	751 vw		
		1319 w	735 vs	ϱ_{1-8}	763 m
		1312 sh	721 vs		749 w
		1308 sh		740 w	ϱ_7
				734 s	ϱ_6
				720 vs	ϱ_{1-5}
1287 m	ω_7	1295 m			
1283 sh		1282 s			687 w
1277 vw		1270 s		628 m	D
1269 s	ω_6	1263 sh		613 m	E
1253 s	ω_5	1257 s		601 w	F
1238 s	ω_4	1253 s			
1222 s	ω_3	1248 sh			
1206 s	ω_2	1243 w			
		1238 m			
		1228 w	583 w		583 sh
		1223 s	548 vw		551 vw,b
		1211 sh	526 vw		527 vw
			501 vw		505 w

486 VW
456 VW
434 VW
419 VW
474 W
458 m
448 W
434 W
427 VW
420 m

1178 VS }
1162 m }
1132 sh }
1118 s }
1113 sh }
1108 sh }
PB C-O

1093 m
1085 VW
1081 W
1070 W P4
1063 sh
1057 m
1048 W
1045 sh
1042 sh
1029 m P5,12,13
1021 sh
1017 m P11
1007 m }
1002 W }
P6,10

1160 sh }
1132 W }
1113 s }
1101 sh }
P1
PB C-O

1083 sh
1064 W P4
1057 VW
1047 sh
1032 W P5,12,13
1016 VW P11
1001 VW

984 W Q9
979 sh
975 sh
962 W Q17
951 sh Q16
939 VW
924 W Q15
918 VW
912 W
977 VW Q17
951 W Q16
931 VW
919 W Q15

5.2 Assignments of absorption bands in the triglyceride spectra

For the assignments of bands as reported in Tables 10-25 the spectra of the following series of compounds were compared.

- The homologous series of the triglycerides and the hydrocarbons, the latter mainly as assigned by Snyder & Schachtschneider (1963).
- The α , β' , and β form of each of the triglycerides.
- The homologous series of the α forms.
- The homologous series of the β' forms.
- The homologous series of the β forms.
- Some normal and deuterated triglycerides of the same chain length.

Attention was paid both to the position of the bands and their shapes. Sometimes intensity calculations were helpful in detecting corresponding bands.

The first conclusion is that in the triglyceride spectra the absorption pattern of *n*-paraffins are recognizable, especially for the higher triglycerides (Section 5.3). This agrees with the results mentioned in Chapter 4 for fatty acids and their salts and methyl esters. But the triglyceride spectra are more complicated, due to the greater number of possible vibrations. In fact, *the hydrocarbon chain can be considered as 'characteristic group' in the triglyceride molecule*, in the same way as, e.g. the carbonyl group.

In triglyceride spectra two band collections can be considered: one originating from the hydrocarbon chains and another consisting of bands due to the glycerol 'head', including the carboxyl groups. The hydrogen part of the spectra will vary throughout the homologous series, but it may be expected that the vibrations arising from the glycerol head will be constant in number and approximate position. Intra- and intermolecular effects give rise to additional complications.

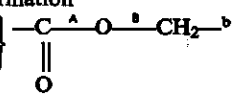
Secondly, the spectra of the α , β' and β forms are different: each of the crystallization phases has its own appearance throughout the homologous series.

In the field of infrared spectroscopy it is often just assumed, that a compound has its characteristic spectrum. This is a dangerous proposition, and the triglyceride spectra shown here are a convincing example that the infrared spectra are not only dependent on the molecular composition, but also on the molecular structure and on the relation between the molecules and their surroundings.

In the spectra of all crystallized triglycerides a number of strong to medium absorption bands were observed, which show only minor variations for various triglycerides, as well as for the various polymorphic forms of the same triglyceride. The major part of these bands have already been interpreted (Table 26).

The remaining absorption pattern as a whole is dependent both on kind of triglyceride and polymorphic form, in number and position of bands. Therefore in the following sections the homologous series in the α , β' and β form will be discussed separately.

Table 26. Characteristic bands in the spectra of triglycerides.

Approximate frequency (cm ⁻¹)	Intensity	Assignment
2925	very strong	methylene asymmetric stretching
2850	very strong	methylene symmetric stretching
1740	very strong	C=O stretching
1475	strong	methylene scissoring
1470	strong	combination methylene scissoring
1460-1440	some shoulders	+ methyl asymmetric deformation
1415	medium	α -methylene scissoring ^a
1385	strong	methyl symmetric deformation
1180	very strong	C ^a -O stretching of } 
1115	strong	C ^b -O stretching of }
890	medium	methyl rocking

a. Corish & Chapman (1957), Sinclair (1952a).

b. Thompson & Torkington (1945), Tschamler (1953).

5.3 Assignments of spectra of the α forms

In Chapter 4 molecular vibrations due to methylene chains in *n*-paraffins, alkyl halides, polymethylene halides, fatty acids and their salts and methyl esters are discussed. These vibrations resulted in various series of band progressions.

I have found that corresponding band progressions also do occur in triglyceride spectra. In spite of the more complicated structure, the vibrations of the hydrocarbon chains evidently exist almost unaltered in triglyceride spectra.

When it is taken into account that in *n*-paraffins some vibrations are forbidden by symmetry considerations, the number of bands or band progressions and their position in triglycerides agree well with those of *n*-paraffins. *For this agreement it proved to be necessary to compare a triglyceride with n methylene groups in the fatty acid chains with an n-paraffin having n - 1 methylene groups* (See further discussion in Section 4.7).

I succeeded in assigning band progressions due to methylene wagging, methylene rocking-twisting and skeletal vibration modes.

The *methylene wagging modes* in the region between 1385 and 1185 cm⁻¹ form a series of regular medium to strong bands. These bands are much more intense than the corresponding ones in *n*-paraffin spectra. They mask the progression of the methylene twisting-rocking modes, which occurs in the same range (Section 4.5).

Some additional weak bands or shoulders are probably twisting-rocking bands, but they could not be combined into a regular progression.

As a consequence of the presence of the polar group at the head of the hydrocarbon chain the methylene wagging modes become much stronger while the inten-

sities of the methylene twisting-rocking modes do not alter. This means that the dipole moment change in the wagging mode is strongly influenced by the polar end, signifying presumably that a considerable movement of the carbonyl group is involved in this normal mode. The alternative explanation, that the strong intensity might be due to the wagging of an induced dipole in the α -CH₂ is extremely unlikely since in that case the twisting-rocking modes would have an increased intensity as well.

The methylene wagging region is bounded by the strong CH₃ symmetric deformation band at about 1385 cm⁻¹ and the very strong C-O stretching band at 1180 cm⁻¹. Snyder and Schachtschneider have calculated that, theoretically, the methylene wag-

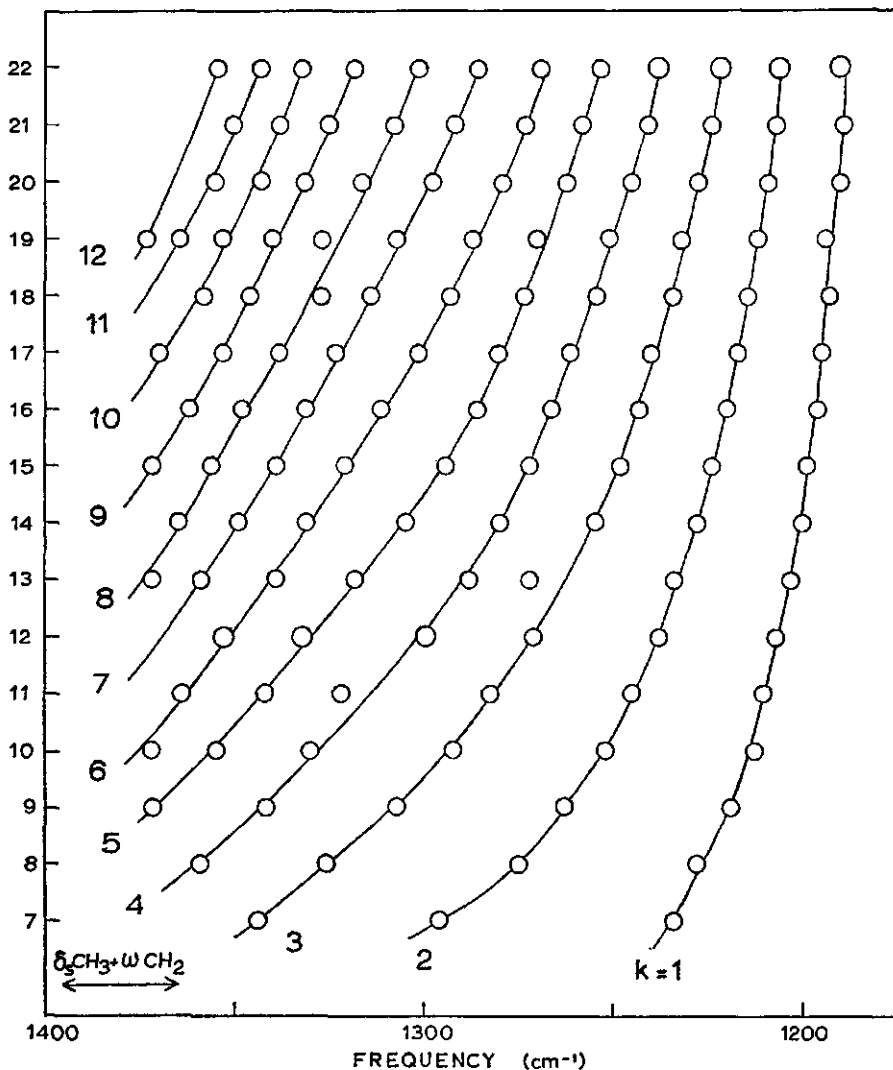


Figure 40. Methylene wagging mode array for triglycerides C₇-C₂₂.

ging mode frequencies should go up to 1420 cm^{-1} , but the high frequency modes are masked by and coupled with the CH_3 symmetric deformation band. The most in-phase methylene wagging mode ($k = 1$, Section 4.3 and 4.7) is situated adjacent to the C-O band. It shifts from 1234 cm^{-1} in C_7 to 1190 cm^{-1} in C_{22} .

Throughout the homologous series, when the chain lengthens, even new bands appear by shifts to lower wavelenghts, first as a shoulder on the $\delta_s\text{CH}_3$. The 'rule of two' relationship of Meiklejohn et al. (1957) drawn up for solid fatty acids and soaps (Section 4.6) obviously does not hold for triglycerides. E.g. for C_{18} ten bands and a small shoulder are found. The appearance of the shoulders are moreover dependent on the recording temperature of the samples and on the resolution of the spectrometer.

The array of methylene wagging bands is shown in Figure 40. All k values are allowed for all triglycerides, contrary to n -paraffins, where for even numbered ones the even k values are forbidden (Snyder & Schachtschneider, 1963).

As mentioned above no regular *methylene twisting-rocking* distribution is observed, for these bands are masked by the much stronger methylene wagging modes. It may be expected that in the Raman spectra the reverse will be the case, so that in a further study using Raman spectroscopy this distribution can be found. In the tables 10-25 some uncertain assignments of methylene twisting-rocking bands are indicated.

The region between 1150 and 950 cm^{-1} includes the *C-C stretching vibrations*. Their pattern is rather irregular; Section 4.5 already indicates that their frequency-phase diagram will have a minimum. Further complications are the overlap of the high frequency methylene rocking-twisting vibrations below 1060 cm^{-1} and the presence of a strong C-O stretching vibration at 1115 cm^{-1} and of other vibrations of the triglyceride molecules with intensities similar to those of the C-C stretching vibrations. Nevertheless a number of absorption bands could be assigned tentatively to the C-C stretching vibrations with a satisfactory degree of certainty.

Figure 41 shows the array of skeletal stretching vibrations. Again all k values are allowed in the triglycerides, whereas for even n -paraffins only $k = \text{even}$ values are allowed.

The *methylene rocking-twisting modes* in the region 1060 - 720 cm^{-1} are mixtures of fundamental rocking and twisting modes (Section 4.5). In the triglyceride spectra all rocking-twisting modes are allowed, the $k = \text{odd}$ are the more intense, whereas in paraffins the $k = \text{even}$ modes are forbidden. The number of bands and their positions in C_n paraffins agree well with the $k = \text{odd}$ bands in the C_{n-1} triglycerides.

The array of methylene rocking-twisting modes for triglycerides is shown in Figure 42.

A band about 890 cm^{-1} in all spectra is assigned to the methyl rocking mode (Chapman, 1965b).

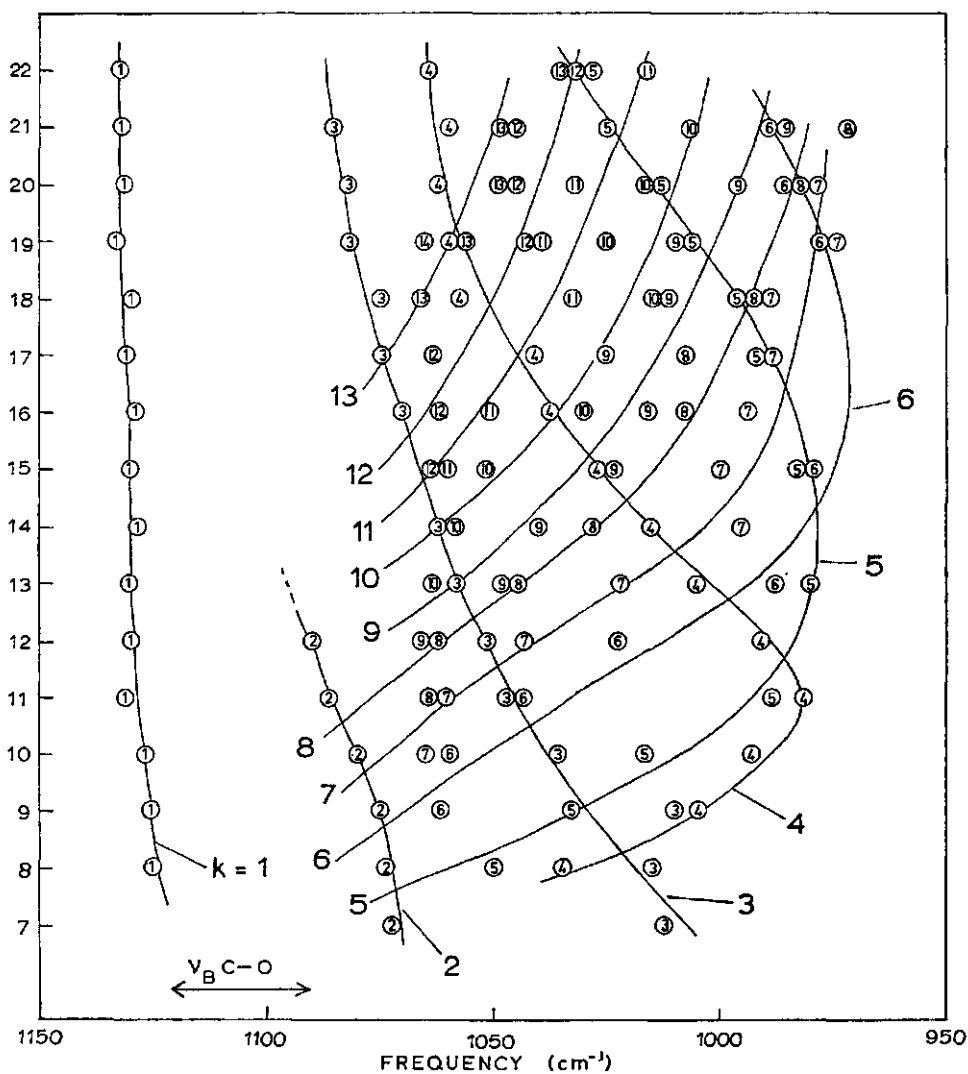


Figure 41. Skeletal stretching mode array for triglycerides $\text{C}_7\text{-C}_{22}$.

Skeletal bending vibrations should be present in the region below 700 cm^{-1} . However, the observed bands in this region, so far could not be assigned to definite vibration modes.

5.4 Assignments of the spectra of the β' and β forms

The transition of the α form into the β' and the β forms results in changes in the infrared spectra, of which sharpening of the absorption bands is most obvious: the peaks are higher and narrower, though the integrated area is approximately the same.

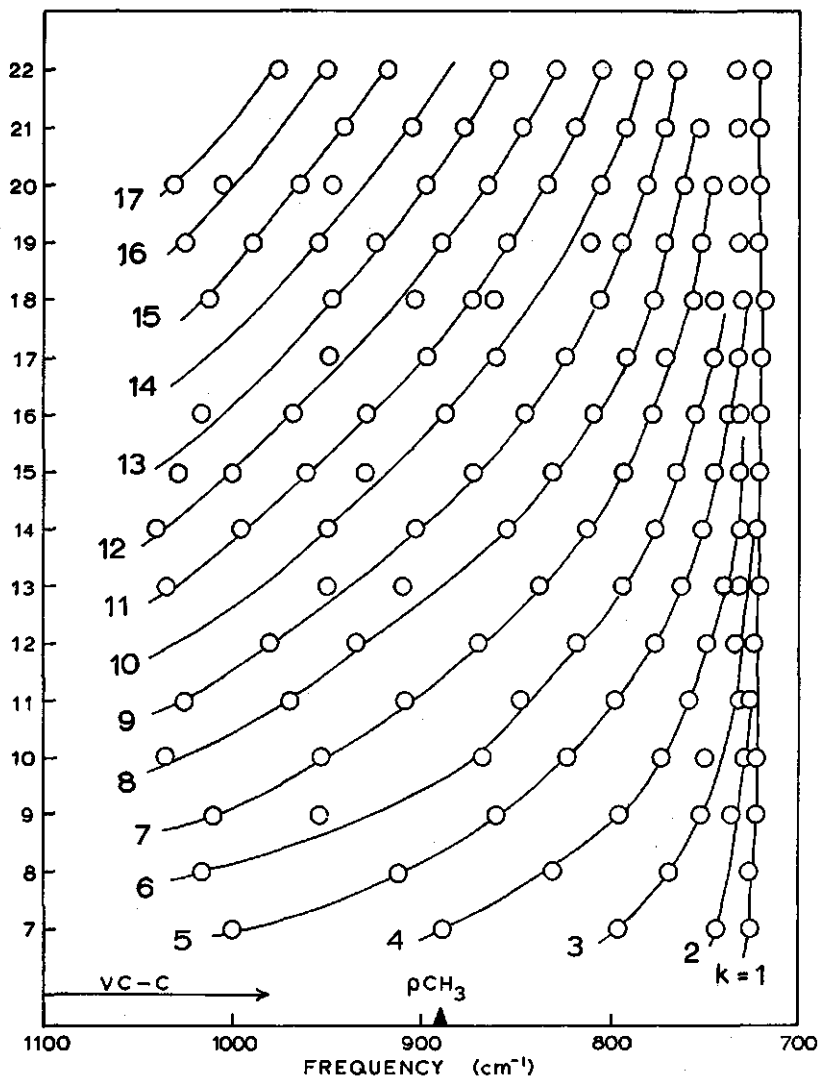


Figure 42. Methylene rocking-twisting mode array for triglycerides C₇-C₂₂.

Again, in the β form the bands are sharper than in the β' form. As sharp bands are correlated with a well-defined structure, these phenomena show that the α -crystals are the less well-formed, and the β -crystals are the most regularly shaped ones.

In Chapter 2 some marked differences of some triglycerides between the three crystallization forms have already been mentioned. The main rocking band has proved to be especially characteristic for the various polymorphic forms (α : 720 cm⁻¹; β' : 726 and 719 cm⁻¹; β : 717 cm⁻¹). Further differences are reported in the 1250 cm⁻¹ region. A strong band near 900 cm⁻¹ was present in the β form only.

These observations were confirmed by the examinations of the whole series of

Table 27. Intercomparison of the infrared spectra of the polymorphs of triglycerides.

	α	β'	β
Quantity of absorption bands	less bands	more bands	still more bands
Appearance of bands	not sharp	sharp	very sharp
σCH_2	1475	ditto	ditto
$\delta_s\text{CH}_3 + \sigma\text{CH}_2$	1470-1450	ditto ¹	ditto ¹
$\sigma(\alpha\text{-CH}_2)$	1418 m	1436 extra band 1415 s	1439 extra band 1425-1415 m doublet or triplet
$\delta_s\text{CH}_3$	1380 ¹ broad	1395 sharp 1380 ¹ broad or doublet	1395 ¹ sharp
ωCH_2	1385-1185 regular band progression	ditto splitting up, irregularities	ditto more splitting up or new bands, more irregularities
$\nu_{\text{A}}\text{C-O}$	1178	1175 ¹	1180 ~ 1160 extra band
$\nu_{\text{B}}\text{C-O}$	1115	1115	1115
$\nu_{\text{C-C}}$	1495-950	ditto differently shaped	ditto differently shaped
$\nu_{\text{r}}\text{CH}_2$	1060-720	ditto	ditto
Other bands	~ 950	~ 975 m ~ 950 m ~ 925 m ~ 835 m	~ 900 s
A		several weak bands	several weak bands
B		sharper bands, a.o.:	sharper bands, a.o.:
C		~ 635	~ 635
720-400 cm^{-1}	broad bands	~ 610 weakest	~ 610 strongest
D		~ 575 strongest	~ 600 weakest
E			500-400: several medium bands
F			

1. Shoulders or weak bands at the lower frequency side of the band.

investigated triglycerides. The more detailed results are included in Tables 10-25 and summarized in Table 27.

The very regular methylene-wagging band progression in the 1385-1185 cm^{-1} region in the α form (Section 5.3) I found to become less regular in the β' and β forms; some bands seem to be split up and new ones have arisen.

The methyl symmetrical deformation band is split up into a doublet in the β' form only; in the β form this band is shifted to higher frequencies.

In the β' form and still more in the β form a number of weak bands have arisen, especially in the region 1100-700 cm^{-1} . In this region I observed medium to strong

bands at about 975, 950, 925 and 835 cm^{-1} in the β' form; the strong band at about 900 cm^{-1} in the β form has been reported above (A, B and C in tables 10-25).

In the region 700-400 cm^{-1} a number of medium peaks are found in the β' and especially in the β form, which are not observed in the α form. Remarkable are the three sharp peaks at about 600 cm^{-1} (listed as D, E and F in tables 10-25). These bands have different positions and intensities in the β' and in the β forms.

5.5 Deuterated triglycerides

For further identification of bands and confirmation of assigned bands I have investigated some deuterated triglycerides, prepared as described in Chapter 3.

As the mass of deuterium is twice that of normal light hydrogen, the frequency of a C-D vibration will be $\frac{1}{\sqrt{2}}$ times that of the corresponding C-H vibration, according to Hooke's law (Section 4.3). That means that all C-H vibrations of the deuterated part of the molecule will shift by a factor 0.7 to lower frequencies. This offers the possibility of distinguishing between C-H vibrations and other vibrations. As the other bands in the spectrum keep their position, overlapping and masking of bands can be removed in this way.

The spectra of the following compounds were compared with each other.

Glycerol-tri-(perdeutero-laurate) $\text{C}_3\text{H}_5[\text{O}-\text{CO}-(\text{CD}_2)_{10}-\text{CD}_3]_3$

(Perdeutero-glycerol)-trilaurate $\text{C}_3\text{D}_5[\text{O}-\text{CO}-(\text{CH}_2)_{10}-\text{CH}_3]_3$

Glycerol-tri-(α -dideutero-laurate) $\text{C}_3\text{H}_5[\text{O}-\text{CO}-\text{CD}_2-(\text{CH}_2)_9-\text{CH}_3]_3$

'Normal' trilaurin $\text{C}_3\text{H}_5[\text{O}-\text{CO}-(\text{CH}_2)_{10}-\text{CH}_3]_3$

Deuterated in these compounds are thus successively: the side chains, the glycerol head, and the methylene groups adjacent to the carbonyl group.

5.5.1 Glycerol-tri-(perdeutero-laurate)

From this compound four different infrared spectra were obtained (Fig. 37a, b, c, d), attributed to the α , β' and β forms and the liquid, respectively.

In these spectra the CD_2 scissoring and CD_3 asymmetric deformation band combinations are found at about 1095 cm^{-1} , the symmetric CD_3 deformation at 990 cm^{-1} . In trilaurin the corresponding bands are situated at about 1475 and 1380 cm^{-1} . A relatively weak CH_2 scissoring band is left at 1475 cm^{-1} due to the glycerol methylene groups.

The CD_2 main rocking mode is shifted from 720 to $\sim 525 \text{ cm}^{-1}$. The other methylene rocking-twisting modes are difficult to assign.

Probably the strong absorption bands at 1280 and 1190 cm^{-1} are the two C-O stretching vibrations, which are found at 1180 and 1115 cm^{-1} in normal triglycerides. These bands are shifted to longer frequencies, due to an unexpected interaction of the $\alpha \text{ CD}_2$ (cf. Section 5.5.3).

Interesting is the beautiful band progression between 1100 and 1000 cm^{-1} observed in the spectrum of the β form (Figure 37c). Undoubtedly these bands have to be assigned to the C-C stretching vibration modes. This distribution lies in this region, but its bands are in normal triglycerides masked by and coupled with C-H and C-O vibration modes.

5.5.2 (Perdeutero-glycerol)-trilaurate

This compound is, as it were, the reverse of the first one. Only one polymorphic form could be obtained, which resembles most to the α form (Figure 38).

A doublet at 1085-1075 cm^{-1} is assigned to the CD_2 scissoring. The surprising relatively strong intensity should be caused by induction from oxygen. Methyl and methylene vibrations due to the side chains resemble very close those of trilaurin, which confirms the assignments of these vibrations. More definite conclusions could not be drawn, as the sample after purification still contained free lauric acid. This resulted in a strong absorption band at 960 cm^{-1} , and some other less intense bands a.o. at 1305, 690 and 555 cm^{-1} .

No shift of the C-O stretching vibrations is observed for this compound.

5.5.3 Glycerol-tri-(α -dideutero-laurate)

As the methylene group adjacent to the carbonyl group ($\alpha\text{-CH}_2$) occupies a particular position, a triglyceride was synthesized in which these groups only have been deuterated. Spectra of the α and the β forms and of the liquid have been obtained. In conformity with the expectations, the spectra of this deuterated compound most of the three resembles trilaurin (compare Fig. 39a,c,d with Fig. 26a,c,d).

The $\alpha\text{-CH}_2$ scissoring band at 1415 cm^{-1} in trilaurin is replaced by an $\alpha\text{-CD}_2$ scissoring band and shifted to 1085 cm^{-1} .

The C-O stretching vibrations are also shifted. They are probably observed at 1280 and 1180 cm^{-1} , and thus are shifted in the same way as in the perdeutero-laurate compound (Section 5.5.1).

A very interesting phenomenon is observed for the methylene band progression. In the deuterated compound methylene rocking-twisting and methylene wagging band progressions are found, both in the α and the β form, resembling those of trilaurin (indicated as C_{12} in Figure 39a,c). They are, however, interlaced with a second band progression which resembles that of glycerol triundecanoate, indicated as C_{11} in Figures 39a,c. (Although no definite conclusions can be drawn from the ill-defined methylene wagging progressions in the β form, these tend to the same conclusion.)

The meaning of the phenomenon described is, that in the deuterated compound the methylene rocking-twisting and wagging modes are partly concerned with the methylene chain including the $\alpha\text{-CD}_2$, but partly are 'reflected' from the $\alpha\text{-CD}_2$.

The phenomenon demonstrates that in non-deuterated compounds for the methylene wagging and rocking-twisting modes the $\alpha\text{-CH}_2$ behaves like the other methylenes.

6 Introduction of the concept 'diathesis' of chemical compounds

In infrared spectroscopy one often thinks in terms of an unambiguous correlation between chemical compound and infrared spectrum. A well defined chemical compound shows a definite spectrum, and vice versa, an infrared spectrum is characteristic for one definite compound. With this concept it is taken for granted, that the spectrum is dependent on the state of the compound. A change in temperature, phase or crystallization state and also sample preparation and scanning conditions can alter the infrared spectrum.

The absorption patterns of different compounds can also show a surprising similarity. Some examples of this will be mentioned here.

a. Mizushima (1954) showed that in Raman spectra of long-chained aliphatic hydrocarbons, absorption bands occurred that were also in the spectra of corresponding hydrocarbons with shorter chains. The latter were matched until the length of the long-chained molecules was reached, by combining $C_{12} + C_4$, $C_{11} + C_5$, $C_{10} + C_6$ and $C_9 + C_7$. He concluded that the combination had caused a bend in the otherwise straight chain of the molecule, the two parts vibrating as independent units because the coupling across a *cis*-single band is weaker than that of a *trans*-single band.

b. Broad bands are found in the infrared spectra of organic compounds with flexible chains, such as aliphatic compounds in the liquid state. Compounds with rigid skeletons, on the other hand, show narrower sharper bands, as in aromatic and cyclic compounds, steroids, and in general solids.

c. Kirby et al. (1965) determined the length of polymethylene chains in salts of saturated and unsaturated fatty acids from infrared spectra using the number and frequencies of the methylene wagging modes in the region $1380-1170\text{ cm}^{-1}$ and from the methylene rocking modes between 1070 and 710 cm^{-1} (see Section 4.6). In case of the methylene wagging modes, only the carboxylate segment is found. No coupling occurs over the double bond. For the methylene rocking modes the same rule is observed for the *cis*-unsaturated compounds. The *trans*-form, on the contrary, behaves as the corresponding saturated compound.

d. From my investigations the infrared spectra of the solid *n*-paraffins could be found in the infrared spectra of solid monoacid triglycerides. The acid radical chains in the triglyceride molecules behave almost as independent units. With the help of data from *n*-paraffin spectra, the chain length of monoacid triglycerides can therefore be determined.

e. The infrared spectrum of cyclohexadecane is remarkably similar to that of hexane. Although the cyclohexadecane spectrum (Fig. 43) is more complex, the absorption

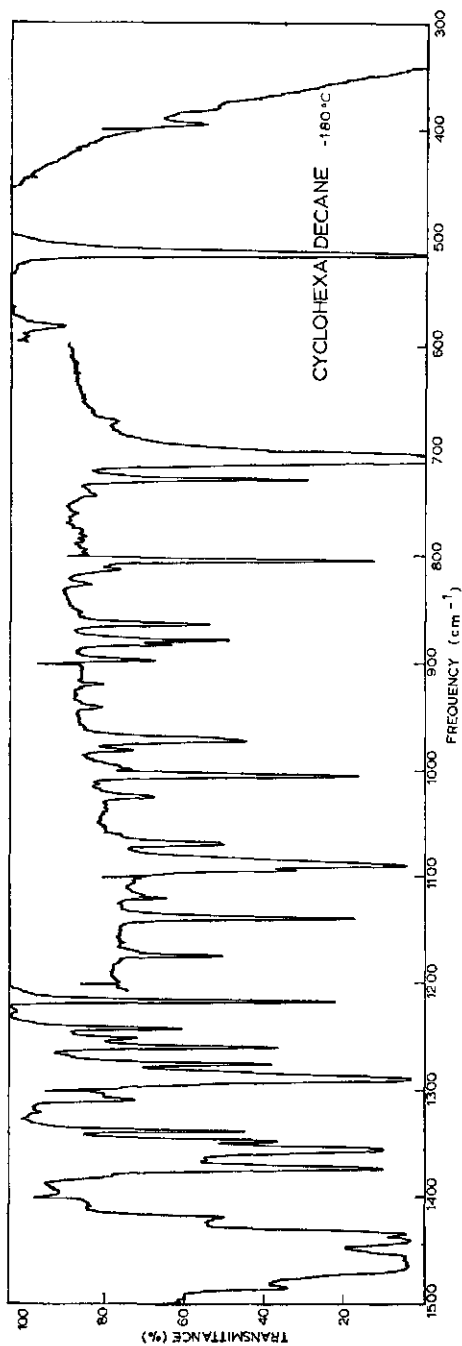


Figure 43. Infrared spectrum of cyclohexadecane.

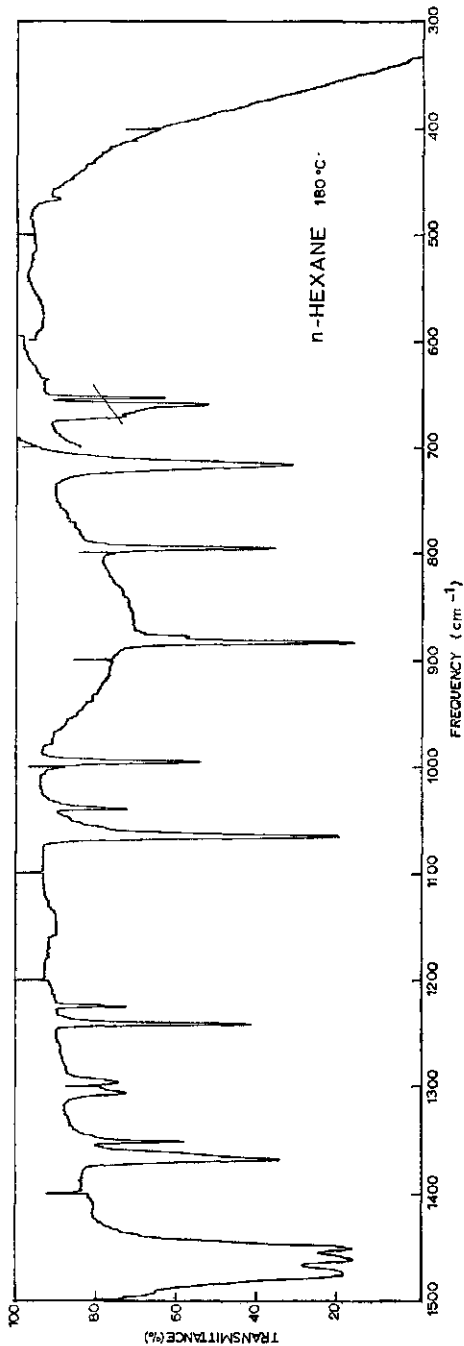


Figure 44. Infrared spectrum of *n*-hexane.

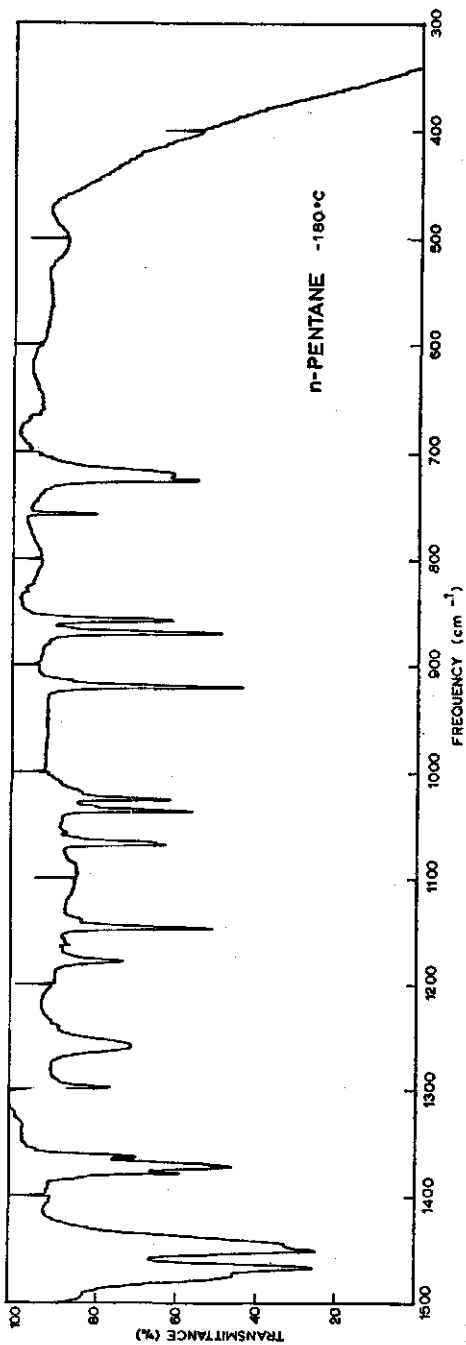


Figure 45. Infrared spectrum of *n*-pentane.

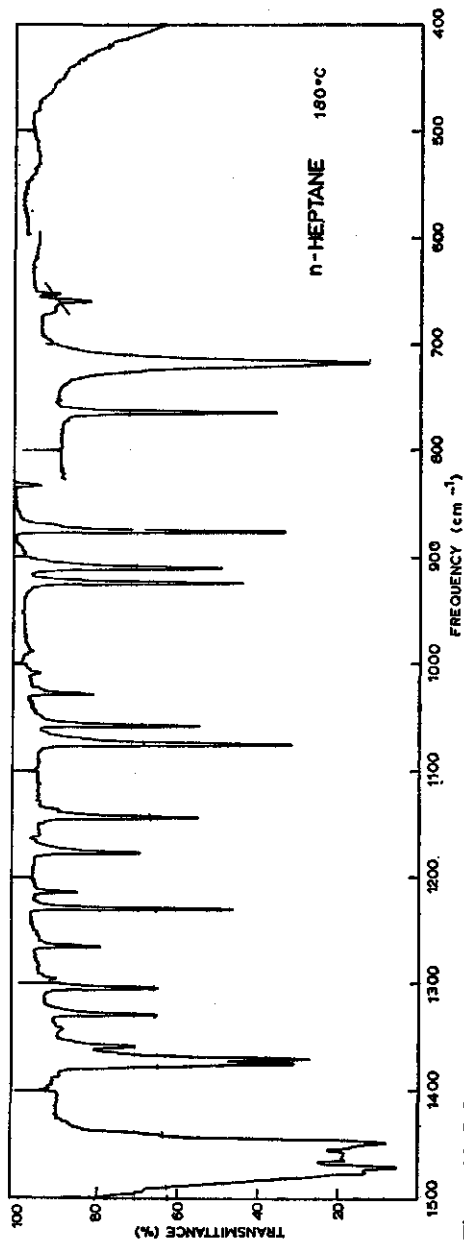


Figure 46. Infrared spectrum of *n*-heptane.

bands of hexane (Fig. 44) can be found in it, very close to their positions; this correspondence does not exist between the spectra of cyclohexadecane and, e.g. pentane (Fig. 45) and heptane (Fig. 46). A confirmation is the absence in cyclohexadecane of the 890 cm^{-1} band of hexane, assigned to the methyl rocking. Cyclohexadecane has a zinc sulphide structure and is folded in four $(\text{CH}_2)_4$ groups. In this case too, a bend in the molecule prevents coupling.

We can, with this in mind, restore the unambiguous relation between the infrared spectrum and the physical entity by stating that each shape a molecule can assume is a different physical entity as far as vibrations are concerned. For these entities the qualifications of 'configuration' and 'conformation' may be used; these have so far been restricted to more or less stable atomic arrangements but we may extend usage of the word conformation to cases where the lifetime is only long enough to allow a few vibrations.

Following this usage we conclude that a compound with flexible chains in the liquid state exists in various conformations; the infrared spectrum of the liquid consists of a superposition of the spectra of these conformations.

These spectra show considerable differences. Parts of molecules in each conformation show absorption bands or band progressions characteristic for that specific spatial arrangement of atoms. It therefore seems both sensible and convenient to introduce a new term for such a spatial arrangement of atoms. I suggest the term 'diathesis' ($\delta\iota\acute{\alpha}\theta\epsilon\sigma\iota\varsigma$ = placing in order, arrangement, plan (of a building), bodily state, condition).

The use of the term may be illustrated by the following examples.

- a. The cetane molecule can display various diatheses, i.e. the diathesis of C_4 , C_5 , C_6 , C_7 , C_9 , C_{11} and C_{22} .
- b. A flexible chain has a number of conformations. Each of these has one or more diatheses, which are apparent in the spectra.
- c. In case of C_{18} unsaturated fatty acid salts (one double bond between C_9 and C_{10}) the *cis*-configuration possesses the same diathesis as saturated C_9 ; the *trans*-configuration also does so for the methylene wagging, but for the methylene rocking its diathesis corresponds to the diathesis of saturated C_{18} .
- d. The diathesis of a solid monoacid C_n triglyceride corresponds with that of solid C_{n-1} *n*-paraffin for all normal vibrations.
- e. The diathesis of solid cyclohexadecane appears to be identical with the diathesis of solid hexane.

The definition of 'diathesis' is: A group of atoms joined together in a spatial arrangement so that at least one vibrational mode exists in which all atoms are involved.

7 Applications to the analysis of natural fats

7.1 Identification of pure triglycerides and of the crystalline state of triglycerides

The infrared spectra with absorption band tables of all even and odd saturated monoacid triglycerides from C_2 to C_{22} , can be used for the identification of these compounds (Figures 16-36, Tables 10-25). The spectra are recorded for the various crystalline forms as well as for the liquid state.

From the infrared spectra the crystalline state, α , β' or β form can be deduced (cf. Sections 2.4 and 5.4). Besides the doublet at about 720 cm^{-1} a handy distinguishing mark of the β' form of natural fats proved to be two medium absorption bands at 922 and 835 cm^{-1} being absent in the β form, and a strong band at 890 cm^{-1} in the β form being absent in the β' form. The α form is easy to recognize from the appearance of the whole spectrum, having less and broader bands than the β' and β forms (Table 27).

The chain length of the fatty-acid radical in the triglyceride can be deduced from the number and the position of certain bands which are found in the solid state spectra. The band progressions that have arisen from the methylene wagging and the methylene rocking-twisting modes, between 1385 and 1185 cm^{-1} , resp. 1060 and 720 cm^{-1} , can be used. The α forms which are obtained after melting followed by solidification below the melting point of the α form (Table 3), were most useful. These bands are compiled from Tables 10-25 in Table 28.

7.2 The detection of beef tallow in milkfat

When molten milkfat and beef tallow are solidified at low temperatures they crystallize in the α form. When heated slowly they first become β' form and then they melt. No β form is observed in this way. When solidified at room temperature the β' form is obtained directly. For the detection of beef tallow in milkfat I found it best to use the absorption bands B and C of the β' forms at 922 and 835 cm^{-1} .

In Figure 47 and 48 a-c the infrared spectra between 1000 and 900 cm^{-1} of beef tallow and of milkfat in the α and β' form and the liquid state are shown. This is a sloping part of the fingerprint region (cf. Figure 10). For the experiments I utilized a flatter curve, which is obtained by compensating the slope of the spectrum of the solid fat with the same fat in the liquid state in the reference beam (Figures 47d and 48d).

In the following experiments I compared the compensated spectra between 1000

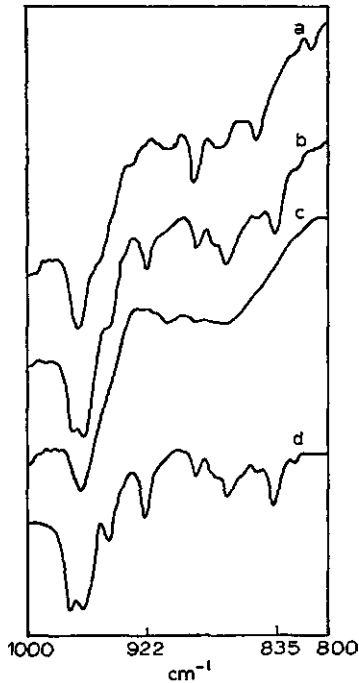


Figure 47a, b, c, d. Infrared spectra of milkfat.
 a. Solid milkfat, α form; -40°C
 b. Solid milkfat, β form; 8°C
 c. Liquid milkfat; 30°C
 d. Solid milkfat, β' form; 8°C , compensated with the same milkfat, in the liquid state; 30°C



Figure 48a, b, c, d. Infrared spectra of beef tallow.
 a. Solid beef tallow, α form; 20°C
 b. Solid beef tallow, β' form; 14°C
 c. Liquid beef tallow; 55°C
 d. Solid beef tallow, β' form; 14°C , compensated with beef tallow in the liquid state; 55°C

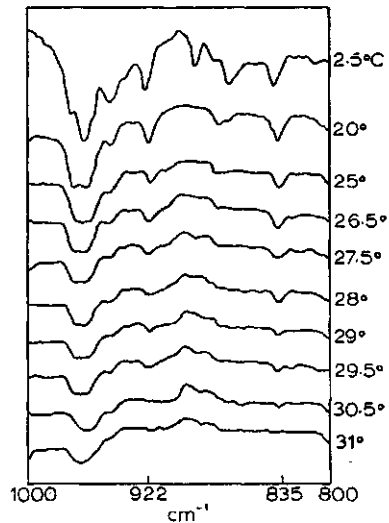
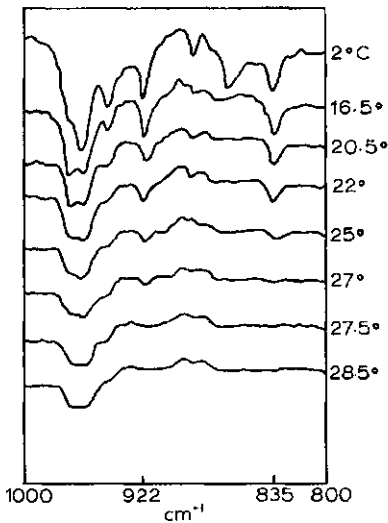


Figure 49. Infrared spectra of pure milkfat and of the same milkfat with 10% beef tallow at various temperatures.

Table 28. List of absorption bands in the α forms of pure triglycerides, useful for identification.

Triglyceride	Methylene wagging (cm^{-1})						Methylene rocking-twisting (cm^{-1})							
C ₇	1344	1296	1234				796							
C ₈	1359	1326	1275	1228			830	768						
C ₉	1342	1307	1263	1219			954	860	795	751				
C ₁₀	1355	1330	1292	1252	1213		953	887	822	722	739			
C ₁₁	1364	1342	1332	1282	1245	1210	908	847	797	758				
C ₁₂	1353	1332	1299	1271	1238	1207	869	818	776					
C ₁₃	1359	1339	1318	1288	1272	1234	910	836	792	761				
	1203													
C ₁₄	1365	1349	1331	1305	1280	1255	950	902	854	812	776	750		
	1228	1200												
C ₁₅	1356	1339	1321	1294	1272	1248	961	930	872	830	793	764		
	1224	1199					744							
C ₁₆	1348	1331	1311	1286	1266	1243	929	844	808	776	737			
	1220	1196												
C ₁₇	1353	1338	1323	1301	1280	1261	948	898	860	823	791	770		
	1240	1217	1195											
C ₁₈	1358	1346	1327	1314	1293	1273	948	904	873	862	806			
	1254	1233	1214	1193			778	756						
C ₁₉	1353	1340	1327	1307	1287	1270	990	958	925	855	822	794		
	1251	1232	1212	1195			772	752						
C ₂₀	1343	1331	1316	1297	1279	1262	965	947	898	866	834	806		
	1245	1227	1209	1191			781	746						
C ₂₁	1350	1338	1325	1308	1292	1273	942	878	847	819	793	772		
	1258	1241	1224	1207	1189		754							
C ₂₂	1354	1343	1332	1318	1301	1287	860	830	805	784	766			
	1269	1253	1238	1222	1206	1190								

and 900 cm^{-1} of pure milkfat with the same fats with 10% beef tallow added. The technique and apparatus described in Chapter 3 was used. I did not cool, however, to -180°C .

The spectra were studied at a gradually increasing temperature, and it was examined at which temperature the absorption bands at 922 and 835 cm^{-1} disappeared (Figure 49).

The results of three samples of milkfats without and with beef tallow are collected in Table 29. A temperature interval existed for these samples, where the pure milkfats showed no more these bands, and in the samples with 10% beef tallow absorption still existed. For the 922 cm^{-1} this region is between 27.5 and 29.5°C , for the 835 cm^{-1} band from 29.5 to 30.5°C . The samples were arbitrarily chosen. For a general validity

Table 29. Temperature range ($^{\circ}\text{C}$) for the disappearance of absorption bands at 922 and 835 cm^{-1} in pure milkfat and in milkfat with 10% beef tallow.

Absorption band	922 (cm^{-1})		835 (cm^{-1})	
	Milkfat pure	Milkfat + 10% beef tallow	Milkfat pure	Milkfat + 10% beef tallow
Sample I	27.0-27.5	29.5-30.5	25.0-27.0	30.5-31.0
Sample II	27.0-27.5	29.5-30.0	28.0-29.5	32.0-33.5
Sample III (Fig. 54)	26.0-27.5	33.0-37.5	27.5-28.0	31.0-33.0

Table 30. Detection of beef tallow in milkfat, using the 922 and 835 cm^{-1} absorption bands.

Beef tallow added (%)	Beef tallow observed (%)
0	-
10	~ 5
5	5-10
4	< 5
2	< 5
0	-

of the method the seasonal variations and perhaps the origin of the samples should be taken into account, as I did before (De Ruig, 1968). From Dutch milkfat production-data and origin are always known.

In another laboratory experiment samples of milkfat were mixed with 0-10% beef tallow. The absorption bands at 922 and 835 cm^{-1} were recorded at room temperature with the pure milkfat in the reference beam. Using the presence of these bands, it proved that less as 2% of beef tallow was semiquantitatively detectable (Table 30).

7.3 The detection of beef tallow in lard

The infrared spectra of lard differs from that of beef tallow. There is, however, no distinct difference between the spectra of pure lard and lard which contains a few per cent of beef tallow. So, the spectra of the fats themselves are not suitable for the detection of adulteration.

A more favourable situation occurred when instead of the fats the so-called Bömerglycerides thereof were studied. The Bömerglycerides consist of saturated triglycerides, obtained by crystallizing the fat sample twice from diethyl ether according to a standard procedure.

Table 31. Composition of the saturated fractions of beef tallow and of lard in % of total fat (Jurriens, 1966).

Triglyceride	Beef tallow	Lard	Melting points		
			α	β'	β
PMS	1.0				
PPP	1.7				
PPS	3.6	2.0	47	57	62.5 ¹
SPS	1.8	2.0	51.8	[69.0]	68.5 ²
PSP	1.6		47	69	[65.5] ³
PSS	3.2		50.5	61.5	65.0 ¹
SSS	1.6				
Rest (each < 1%)	3.9	2.6			
Total	18.4	6.6			

Melting points reported by (1) Chapman (1957a); (2) Hugenberg & Lut-
ton (1963); (3) Lutton & Hugenberg (1960).

[] = forms not obtained unless special precautions.

Table 32. Crystallization behaviour of pure beef tallow, pure lard and lard with 6% beef tallow.

Pure beef tallow:	$\alpha \xrightarrow{43^\circ} \beta' \xrightarrow{57^\circ} \text{liquid}$
Pure lard:	$\alpha \xrightarrow{42-48^\circ} \beta \xrightarrow{63^\circ} \text{liquid}$
Lard + 6% beef tallow:	$\alpha \xrightarrow{43-45^\circ} \beta' \xrightarrow{45-47.5^\circ} \beta \xrightarrow{63^\circ} \text{liquid}$

The composition of these saturated fractions of beef tallow and lard differs from each other (Table 31). In beef tallow, the main triglycerides¹ are PPS and PSS, and in lard SPS and PPS. Chapman (1957a) already demonstrated that for some mixed triglycerides normally only two crystallizing forms are found: for SPS the β' , and for PSP the β form is omitted. PPS and PSS show all three. The melting points of the various forms are indicated in Table 31. Under special conditions β' SPS and β PSP were prepared by Lutton & Hugenberg (1960) and Hugenberg & Lutton (1963).

From these observations and the composition of the Bömerglycerides the reported crystallization behaviour (beef tallow: β' , lard: β) indeed is plausible. I have found that beef tallow admixed to lard tends the fat to crystallize into the β' form, like beef tallow, but unlike pure lard, and I believe that this phenomenon offers a tool for the detection of beef tallow in lard.

1. In the following means M = myristate, P = palmitate, S = stearate, SPS = glycerol-1,3-distearate-2-palmitate, etc.

The following results were obtained when a sample of lard was admixed with 6% beef tallow. The α forms of the pure fats and of the mixture were obtained by chilling the samples down to 0° C. When slowly warmed up, the pure sample of beef tallow changed from α form into β' form into liquid, the pure sample of lard from α into β into liquid while for the mixture three transitions were observed: $\alpha \rightarrow \beta' \rightarrow \beta \rightarrow$ liquid (Table 32). Whether a β' or a β form is present can be concluded from the infrared spectra by the distinguishing criteria mentioned before (Sections 7.1, 2.4 and 5.4).

The method is still under investigation, but already it can be expected that under proper conditions amounts as little as 5% of beef tallow in lard can be detected by infrared spectroscopic determination of the crystallization state of the Bömerglycerides.

Summary

Natural fats have been characterized by using 'characteristic values'. One of the modern techniques for analysing fats is infrared spectroscopy. Analytical chemists must now relate modern technical data to classical results.

Classical and modern techniques have been used to detect adulterating of fats. But as yet no satisfactory way has been found of detecting animal fats adulterating other animal fats.

At the Netherlands Government Dairy Station at Leiden infrared spectroscopy of natural fats indicated that infrared spectra needed further fundamental study.

Natural fat consists of 95% or more triglyceride. An interesting characteristic of triglycerides is their polymorphism, i.e. they can crystallize into three forms: α , β' and β (Chapter 2). Chapman's idea (1962, 1965b) that these forms can be deduced from infrared spectra, is confirmed (Chapter 5, Section 7.1).

A number of absorption bands in the infrared spectra of triglycerides have already been assigned to molecular vibrations. For a further interpretation, vibrational analyses of other long chain compounds were considered and applied to triglycerides. The number of bands in band progressions has been theoretically considered. It is concluded from experimental results that the methyl end groups probably contribute to these band progressions (Chapter 4).

The list of infrared spectra between 1500 and 400 cm^{-1} of all saturated monoacid triglycerides from C_7 to C_{22} , includes the crystalline and liquid states (Figs. 21-36). Infrared spectra of C_2 to C_6 in the liquid form are also given (Figs. 16-20). The frequencies of the absorption bands in the crystalline forms are given and the majority of the strong and medium bands were assigned to molecular vibrations (Tables 10-25, Chapter 5).

From some deuterated compounds additional information about molecular vibrations could be obtained (Sections 3.4 and 5.5).

To describe the intramolecular behaviour as apparent from vibrational spectra, the concept 'diathesis' of chemical compounds is introduced (Chapter 6).

The presented infrared spectra of triglycerides (Figs. 21-36, Tables 10-25) can be used for the identification of these compounds.

The chain length of the fatty acid radicals of triglycerides can be read from the number and position of certain bands in the solid-state spectra. The band progressions due to methylene wagging and rocking-twisting modes (between 1385 and 1185 cm^{-1} , and between 1060 and 720 cm^{-1} , respectively) can be used for this purpose (Table 28).

Some applications of solid-state infrared spectra for the detection of beef tallow in milk fat and in lard are elaborated.

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Curriculum vitae

De schrijver van dit proefschrift behaalde in 1950 het diploma HBS-B aan de 1e Chr. HBS-B te Amsterdam. In hetzelfde jaar begon hij zijn academische studie aan de Vrije Universiteit te Amsterdam. Het candidaatsexamen, letter e, werd afgelegd in juli 1954; het doctoraalexamen met hoofdvak organische chemie en bijvakken chemische fysiologie en bedrijfseconomie in februari 1958.

Gedurende de vervulling van zijn militaire dienstplicht is hij een jaar als bio-chemicus werkzaam geweest in het klinisch laboratorium van het Centraal Militair Hospitaal te 's-Gravenhage.

In 1960 kwam hij in dienst bij N.V. Philips Gloeilampenfabrieken te Eindhoven, als medewerker op het Natuurkundig Laboratorium.

Sinds 1963 is hij verbonden aan het Rijkszuivelstation te Leiden. Hier is hij thans hoofd van de afdeling Radiologie en Spectrofotometrie.