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A STUDY OF PALMITIC-STEARIC TRIGLYCERIDES AND THEIR BINARY MIXTURES BY DIFFERENTIAL THERMAL ANALYSIS (DTA) – I – PURE TRIGLYCERIDES

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The cryothermograms of the six pure triglycerides derived from palmitic and stearic acids have been determined by DTA

As well as revealing itself to be an excellent method of distinguishing between the positional isomers of the mixed triglycerides, DTA also showed that cooling the triglycerides from the melt at a rate of $1.2 \,^{\circ}$ C/min yielded an α_L form (except PSP), which on subsequent heating gave the β_L form with the symmetrical triglycerides, but the β'_L form with the non-symmetrical triglycerides.

In the process of cooling melted triglycerides, various forms may appear depending on the rate of cooling. The symmetrical triglycerides, with the exception of SSS, give stable forms more easily than the non-symmetrical triglycerides.

Further, a sub- $\beta'_{\rm L}$ form can be detected in the case of PSP, PSS and SPP.

For many years, the attention of numerous workers was drawn to the highly complex polymorphism of glycerides, and an important number of works deal with this subject.

Among them it is convenient to recall here those of Lutton¹⁻³), Malkin⁴⁻⁶) and their schools, and also the studies of Bailey et al.⁷), Filer et al.⁸), Ralston⁹), Vaeck¹⁰) and Ravich et al.¹¹). The essential aspects of these works were first assembled by Bailey¹²), and then particularly well commented on by Chapman^{13,14}); see also Larsson¹⁵).

These studies on polymorphism are based mainly upon two methods of examination, (a) the measurement of melting or solidifying temperatures, (b) the use of X-ray diffraction.

The results so obtained have gradually permitted an understanding of the phenomena concerned, but progress in this field was held up for a long period because of a vigorous controversy between Lutton and Malkin.

This controversy concerns the existence of the vitreous form, and discussions were further complicated by the fact that to represent the several polymorphic forms, these authors used similar symbols which did not designate the same species.

Furthermore, the purity of the investigated materials remains very questionable.

In recent years, new methods have been employed for a study of the problem, such as dielectric constant measurements^{16–18}), X-ray diffraction of a monocrystal of β -trilaurin^{19–21}) and tricaprin^{22, 23}), dilatometry^{24, 25}), infra-red spectrometry^{26–36}), nuclear magnetic resonance^{37–39}) and differential thermal analysis^{40, 41}), while modern separation techniques (chromatography, zone melting) have provided compounds of much greater purity.

The sum of the results thus obtained has provided sufficiently convincing arguments to break the deadlock, and finally confirms Lutton's views.

Although pure glycerides have been widely studied, glyceride mixtures have been but little investigated, perhaps on account of the extremely complex structures to be expected.

Partial results on this subject have been published by Joglekar⁴²), Efremov^{43,44}), Kerridge⁴⁵), Lutton⁴⁶), Moran⁴⁷), Lavery⁴⁸), Haighton and Hannewijk⁴⁹), and Loncin⁵⁰).

Very recently, however, the study of binary mixtures of mono-, di- and triglycerides derived from palmitic and stearic acids has been undertaken by Lutton $^{51, 52}$) and Goto and Asada 53).

The question remains one of the major problems in the study of lipids. For the major part these lipids are in fact triglycerides, resulting from the esterification of long chain carboxylic acids with glycerol. Every oil or fat, of vegetable or animal origin, always contains several fatty acids, and the various combinations of these acids with glycerol, in each case result in an extremely complex glyceridic composition, though nature seems to limit the number by respecting certain rules of association which exclude a strictly random-distribution.

One can understand that even a thorough knowledge of the structure and thermal and mechanical behaviour of each pure glyceride, themselves presenting various aspects not yet completely understood, cannot suffice to describe the physical properties of such mixtures, which to a large extent, condition the role that lipids play in life.

In the last few years, we have attempted to provide a new contribution to this subject, studying different mixtures of very pure glycerides, and increasing their complexity as the research progressed.

Further, differential thermal analysis (DTA), a particularly attractive method in great development at the present time, appeared to be an excellent tool of investigation to approach the problem, on account of its great ability to detect transitions and its sensitivity.

Moreover, in contrast with most other methods, DTA operates in a dynamic manner with respect to the temperature and shows how the thermal events detected follow upon one another, while it can eventually give a quantitative appreciation of them.

We first developed various DTA systems suitable for carrying out our measurements, and then we constructed an automatic apparatus specially conceived for the study of organic compounds⁵⁴), and furthermore we established a graphical method to determine the melting point by DTA⁵⁵).

More recently we have examined the mixtures of mono, di and tri stearins, and constructed the transition temperature/molar concentration diagrams for the three types of binary mixtures⁵⁶) and the diagram of the ternary mixtures⁵⁷).

These diagrams, specially that of ternary mixtures, are quite complex.

In all cases, under the experimental conditions adopted, we have detected only two polymorphic forms for the pure substances and their mixtures, which we designated by I and II. These we interpret as two main forms of glycerides, i.e., the unstable form I attributable to the α_L form, and the socalled stable form II, which corresponds to the forms β'_L or β_L of Lutton.

Our latest work deals with the study of the fifteen binary mixtures possible from the six triglycerides derived from palmitic and stearic acids. For ease of expression and writing, we shall design these triglycerides in the text by the six following arbitrary symbols:

PPP tripalmitin
SSS tristearin
SPP 1-stearo dipalmitin
PSS 1-palmito distearin
PSP 2-stearo dipalmitin
SPS 2-palmito distearin

As the presentation of the results obtained requires a large number of figures and is a relatively important development we are publishing them in two papers.

In this first part, we specify the conditions of DTA measurements, then describe and comment the recorded cryothermograms for the six pure triglycerides, and finally we describe the methods used to prepare these triglycerides.

DTA, apart from being perfectly appropriate for the studied phenomena, showed that under the conditions adopted (heating and cooling rate: $1.2^{\circ}C/min$) the tested triglycerides can be classified into two groups from the point of view of the recorded transitions. The symmetrical triglycerides compose

one group and give, on heating of the α_L form, the stable form with maximum temperature of melting (β_L form). The other group is composed of the unsymmetrical triglycerides which give the stable form with the minimum melting temperature (β'_L form).

PSP is an exception to this rule, as it gives an α_L form only when important rates of cooling are applied, and a β'_L form on slower cooling of the melt, or by heating of the α_L form.

On cooling the melted triglycerides at various rates, it has been shown that different forms will crystallize depending upon the particular cooling rate employed. It was shown that the symmetrical triglycerides (except SSS) and especially PSP, yield a stable form more easily than the non-symmetrical triglycerides.

A sub- $\beta'_{\rm L}$ form seems to exist for PSP, PSS and SPP.

Finally, DTA is an excellent analytical method for distinguishing between positional isomers of glycerides.

Conditions of DTA measurements

The entire study was carried out with the apparatus constructed in our laboratory 54), which offers the possibility of operating at the same heating and cooling rates.

The various samples examined were first heated up to 20 °C above their maximum melting points, in order to destroy any crystalline nuclei, then a cryogram was recorded at the rate of $1.2 \degree$ C/min, the recording being pursued down to 10 °C. Immediately after, a thermogram of the transformations of the species thus formed was recorded, on heating at the same rate until completely melted (paper speed: 6 mm/min, ΔT scale: $1\degree$ C/14.5 mm, marginal marking for each 2°C).

For each sample, the two recordings were combined by coinciding their scales, this constituting a particularly exploitable diagram, which we have named elsewhere "cryothermogram" ⁵⁸).

In order to evaluate the temperatures of transition, we used when possible, that is to say when the transformations gave a non-composite peak, the method which we have previously established⁵⁵). In the other cases, the evaluation was made by estimating the probable aspect of the overlapping peaks, and then applying the method (see below).

For the exothermic phenomena of crystallization on cooling, we adopted as a measure of the temperature of transformation, the value deduced from a geometrical construction identical to that proposed for melting⁵⁵), the elongation ΔT being added from the T_p value in this case.

The temperatures for the different rearrangements obtained on heating were taken as the maximum temperatures of the corresponding peaks.

DTA of the six pure triglycerides

Figs. 1-6 show the cryothermograms obtained for the six pure trigly-cerides.

In these figures, in the case of overlapping of the thermal effects we have drawn with dashed lines, the probable curves which result in the recorded effects.

These curves are only indicative, and were obtained by systematically drawing an endothermic peak of the same elongation as that corresponding to the melting peak of the stable form, and located in the same interval of temperature as that in which the composite figure is registered.

The drawing was facilitated when the beginning of the peak was really recorded.

The exothermic peak was then deduced from this peak and the composite figure.

The relatively great expansion of the endothermic peak recorded for SPS led us to slightly modify the drawing of the indicative endothermic peak.

The overlappings are especially associated with the melting of forms I, more or less immediately followed by a crystalline rearrangement (formation of stable forms II). The recrystallization curves are shown by the dotted and dashed lines.



Fig. 1. Cryothermogram of PPP



Fig. 3. Cryothermogram of SPP

Under the conditions of DTA adopted, and in accordance with the preceding results obtained from DTA by Chapman^{13,40}) on the saturated monoacid triglycerides, we have never detected more than two main forms for each triglyceride, which we continue to note I and II (except PSP which shows an unusual behaviour).



The form I is only generated on cooling of the melt (the triglycerides studied are monotropic) producing the recorded exothermic peak. This form, undoubtedly similar to the α_L form of Lutton, presents in the thermograms the beginning of an endothermic peak (melting). The resulting liquid,

eminently unstable, almost immediately solidifies, yielding a stable form II.

This transformation is accompanied by a strong exothermic effect, but this is combined with the endothermic effect of melting of I, resulting in the composite figure recorded, which varies according to the intensity and the degree of simultaneity of these effects.



Fig. 6. Cryothermogram of PSP

The probable curves related to each separate effect are shown on the cryothermograms as indicated above.

Moreover, Barral and Guffy⁴¹) have recently recorded by DTA of SSS a small endothermic peak ($\simeq 47$ °C) which precedes the melting of the α_L form. They attributed this peak to the transition orthorhombic \rightarrow hexagonal (α_L), it would seem, however without having cooled the substance below 0 °C, though the orthorhombic form named sub- α is obtained around -50 °C^{13, 59}).

We did not observe this transition. In this connection, and in accordance with the results of Chapman^{13,14}) in DTA, a reversible transition at about -50 °C corresponding to the formation of this sub- α form was not recorded, confirming the views of this author, and those of Larsson¹⁵) that this transition appears to be a second order phenomenon.

Except for PSP, the correspondence on the cryothermograms between the crystallization peaks and the beginning of melting of forms I, clearly indicates that these forms solidify without supercooling. The melting temperature, or better, that of the liquid-solid equilibrium, is located inside the melting peak, and so outside the crystallization peak on the higher temperature side of this peak, as would be expected from our study on the determination of melting temperature by DTA⁵⁵).

The beginning of the crystalline rearrangement from the form I in the course of melting corresponds to a hump, or a flattening of the melting peak.

It will be noticed that the rather special case of PPP, for which there is complete simultaneity between the melting of the form I and its rearrangement to a more stable form, implies that the liquid so obtained is completely unstable.

For the other triglycerides the instability is less strongly marked, and the melting peak can be partially recorded.

In this respect, it is well to remark that if the liquid obtained by melting of the form I is always very unstable, conversely the liquid in the course of cooling near the crystallization of this form, or in equilibrium with the solid, is not unstable, since it does not transform into form II. It is possible to conclude from these facts that these two types of liquid possess very dissimilar structures.

Apart from the above phenomena, it should be noted that PSS and PSP which will be examinated separately, before the melting of the stable form, present an anomaly in the registered curve. This is characterized by a small exothermic effect, followed by a similar endothermic effect, producing a slight hump in the large melting peak.

The different anomalies, difficult to detect on the figures produced, are indicated on the cryothermograms of PSS, PSP (and PPP), by small arrows, and exemplified at double scale in fig. 4 for PSS.

We shall see later that the stable form realized is very probably the β'_{L} form of the two compounds.

Consequently, the two minor effects detected, which by their aspects denote the formation and the breaking down of a crystalline species, are to be connected with the transient existence in the temperature gradient of a sub- β' form. They cannot be a first order phenomenon which for example could be related to the rotation of the hydrocarbon chains, which in this case could only give an endothermic peak.

With this hypothesis, it would be this form which has normally been described and not the real $\beta'_{\rm L}$ form.

On the cryothermogram of PPP, a very slight anomaly of the same kind can perhaps be revealed, but it is difficult to take into account.

For SPP the peak which corresponds to the formation of the stable form passes without discontinuity into the peak corresponding to the melting of this form, and a sub- $\beta'_{\rm L}$ form cannot be detected in this case.

However, it should be pointed out that on cooling more slowly it is possible to show the existence of this form for SPP. It is interesting to note that in mixtures of triglycerides which will be examined later, the special thermal manifestations due to these sub- β' forms seem to remain independant of mixture, as we have encountered them every time for PSS or PSP.

In other respects, the differences between the temperatures of the crystalline rearrangement of forms I (temperatures of the maximum of the exothermic peak) and the melting temperatures of forms II, indicate the degree of thermal stability of the different stable forms II for each triglyceride. One can note the unstable character of the form II of SPP and more generally, it is possible to remark, but with reservations, that the non-symmetrical mixed triglycerides PSS and SPP show for this form a much more restricted field of existence, in comparison with the symmetrical compounds PPP, SSS and SPS.

Moreover, the aspects of the cryothermograms of SPS and SSS are practically identical, and therefore the forms II are equally stable.

The determination of the transition temperatures were made as previously indicated. In the case of the melting of forms I, the evaluation was only approximate, as the temperatures were deduced from the endothermic peak drawn.

A geometrical construction identical to that proposed in a preceding paper ⁵⁵) was used to evaluate the temperatures of crystallization; in this case the elongation Δt is added and not substracted from the $T_{\rm P}$ value. The so evaluated temperatures are those reported on the cryothermograms.

The various temperatures of transition so obtained are reported in table 1. The temperature related to exothermic peak is that corresponding to its maximum, which corresponds to that of the exothermic peak of the composite figure.

Triglycerides	Crystallization	Temperatures of transition (°C)					
	(°C)	Forms I	Exothermic peak	Forms II			
PPP	45.8	45.5-46	47.1	64.9			
SSS	56.1	56.5-57	59.6	71.6			
SPP	48.5	48 -48.5	52.6	57.1			
PSS	51.7	51.5-52	53.2	60.8			
SPS	51.7	51.5-52	55.2	67.5			
PSP	51.9	-	-	67.3			

Identification of the forms detected

For the moment this identification is based upon a comparison between

the evaluated temperatures of transition and the data given in the literature. An X-ray diffraction study is being performed at the present time both on the triglycerides and their mixtures to furnish more complete results from this point of view.

Adopting the nomenclature of Lutton and the temperatures of transition given by this author, and consulting the data assembled by Chapman¹⁴), the forms regularly obtained in our DTA experiments are as reported in table 2.

Triglycerides	This work		Ch	Probable		
	Forms I (cryst. temp.)	Forms II	α	β'	β	Forms II
РРР	45.8	64.9	44.7	56.6	66.4	$\beta_{\rm L}$
SSS	56.1	71.6	54.0	64.0	73.1*	$\beta_{\rm L}$
SPP	48.5	57.1	47.4	57.7 — 61.7	62.7	β' L
PSS	51.7	60.8	50.6	61.1 — 65.0	65.2	β' L
SPS	51.7	67.5	51.8		68.2	β _L
PSP		67.3	46.5	68.6	-	$\beta'_{\rm L}$

TABLE 2 Stable forms II obtained by DTA $(1.2^{\circ}C/min)$ for the six triglycerides studied

* β form obtained by solvent crystallization and determination of the melting point in capillary tube.

The identification of stable forms with the known β'_{L} or β_{L} forms is made without ambiguity.

The concordance of our results with those found in the literature is very satisfactory, considering that the measurements were carried out under very different conditions.

The appraisal of the phenomena being unquestionably more hazardous using other methods, we consider our own results from DTA as more accurate, at least for the melting of stable forms.

An important feature can be deduced from the preceding identification. Under the conditions of our DTA measurements, it is easy to see that the symmetrical triglycerides provide a form II related to β_L (except PSP), whereas the unsymmetrical triglycerides regularly give β'_L .

Only PSP is an exception to this rule, both with regards to the existence of a single stable β'_L form, and the absence of α_L form. It is the only glyceride among those studied to possess a central chain longer than the two located on the external positions of the glyceride. It is interesting to relate this fact with the particular behaviour of this compound.

The β'_L form was also the only stable form observed by other workers, such as Lutton⁶⁰) and Chapman³⁰).

The latter demonstrated by infra-red study of the main rocking bands of the CH₂ groups that PSP shows only two forms, and not four as was previously claimed by Malkin and Meara⁶¹), and at the same time, he confirmed the absence of a β' form for the pure SPS. This form was, however, more recently obtained by Hugenberg and Lutton⁶²) in hexane by slow nucleation with the aid of succinic acid, these authors having previously produced the β_L form of PSP in a similar manner⁶³). Larsson¹⁵) has shown that the β'_L form of PSP only differs from the β'_L forms of the homogeneous triglycerides by the length of the *c* axis. Concerning the α_L form which we did not obtain by DTA, Lutton et al.⁶⁰) and Chapman³⁰) formed it on rapid cooling of the melt to 0°C. The melting temperature was evaluated by observation of the variation of opacity at the beginning of melting (m.p. α_L form: 46.5 °C⁶⁰) and 47 °C³⁰)).

By cooling of the melt in liquid nitrogen, we also obtained this form, which shows only a short spacing at 4.2 Å in its X-ray diffraction pattern (hexagonal form, and not the sub- α variety which could appear under these conditions).

Crystallization experiments

As we have remarked earlier, the formation of an α_L form for PSP depends essentially on the cooling rate. It seems interesting to compare this fact with the well known property of triglycerides to give stable forms and not α_L forms on slow cooling of the liquid.

Various experiments have been undertaken on this subject for all the glycerides except PSP, recording the cryograms for cooling rates progressively smaller and smaller. The thermograms subsequently showing the form produced during the cooling have been recorded for the normal rate of 1.2° C/min. The cryothermograms obtained are represented in fig. 7.

In the case of SSS, it was only at a cooling rate of 0.08 °C/min that the $\beta'_{\rm L}$ form could be obtained, alongside of $\alpha_{\rm L}$, since under normal heating conditions the $\alpha_{\rm L}$ form does not give a $\beta'_{\rm L}$. This implies then, that the above $\beta'_{\rm L}$ form is produced more or less at the level of recrystallization of the $\alpha_{\rm L}$ form. On heating it transforms into $\beta_{\rm L}$ with melting and a rapid rearrangement of the unstable liquid, as for $\alpha_{\rm L}$.

For a cooling of 0.04 °C/min, only nuclei of $\beta_{\rm L}$ were obtained around 63 °C (delay in the crystallization denoted by the sharp peak).

For PPP at a cooling rate of $0.34 \,^{\circ}C/\text{min}$, slow crystallization between 50.8 $^{\circ}C$ and 46.5 $^{\circ}C$ produced nuclei of β'_{L} , these transforming to β_{L} on heating.



Fig. 7. Cryothermograms of triglycerides (except PSP) as a function of the rate of cooling θ (determined at 1.2 °C/min.)

At a rate of 0.27 °C/min a sharp crystallization was recorded at 53.2 °C denoting in DTA an important delay in the crystallization. As in the thermogram which followed only the $\beta_{\rm L}$ was detected, it follows that at this latter cooling rate the PPP had directly crystallized into $\beta_{\rm L}$ form.

With SPS, it is only at a rate of 0.15 °C/min that the β_L form was directly crystallized (with a delay at 57 °C) as in the preceding instance. At higher rates the β'_L form never appeared.

For PSS a stable crystallized form was only recorded for a rate of $0.04 \,^{\circ}C/$ min. This crystallization is situated rather exactly at the level of transformation of sub- β'_{L} , a form which was always detected at several superior cooling rates. It is important to note that the transformations corresponding to this form also exist in the thermogram, and thus on cooling the sub- β'_{L} form was obtained either directly, or after a subsequent slight cooling after the production of the β'_{L} . Finally for SPP, at a rate of $0.11 \,^{\circ}C/min$ the α_L form thus crystallized provided a double peak on heating, attributable to two β'_L forms, which again allows us to show the presence of a sub- β'_L form for this triglyceride. The presence of this form, resulting from the rearrangement of the liquid after melting of the α_L (the α_L did not undergo any apparent modifications on DTA) can be explained, as in the case of the presence of β'_L of SSS on cooling at 0.08 °C/min by the fact that the glyceride had partially crystallized in the sub- β'_L alongside of the α_L , and at the level of crystallization of the latter.

At a rate of 0.02 °C/min some of α_L is still produced, but it is possible that the sub- β'_L form is suppressed to the benefit of the β'_L form, which crystallized with α_L (the simple peak, however, prevents us from being absolutely definite on this point, but at slightly faster cooling rates we have observed that the peak attributable to a sub- β'_L form diminishes in size to give way to a β'_L peak of increasing importance as the rate of cooling employed was decreased).

To summarize, these experiments at various cooling rates, as well as establishing that a sub- β'_L form can exist in the cases of SPP, PSP, PSS, have also shown that the production of a given form from the liquid triglyceride is essentially dependant upon the cooling rate employed. According to the rate employed, crystalline nuclei form in the liquid on cooling, the nuclei which are the precursors of a stable form being more difficult to obtain in this manner than those which are the precursors of less stable forms.

The crystallization of the liquid can therefore take place either in a zone of temperature close to the melting of one of the stable forms, with a more or less marked delay, or at a temperature which is practically that at which the arrangement of the α_L forms take place on melting, giving in this latter case the stable form normally produced by this arrangement, or a mixture of α_L together with this stable form (β'_L or sub- β'_L).

Concerning this double crystallization, this may be explained by there not being a sufficient quantity of nuclei of the stable form to carry along the total crystallization in this direction. A cooling rate not sufficiently slow would further contribute to this phenomenon.

The particularly unstable character of the liquid resulting from melting of the α_L form as opposed to the stable liquid close to the crystallization of the same form has been understood earlier on. The preceding experiments reveal, in fact, that the latter liquid is only stable at sufficiently high cooling rates, and the building of an α_L form, imperative at a certain temperature, corresponds to the least elaborate structure which may be obtained. This confirms well X-ray diffraction data and density measurements.

On the other hand, for slower cooling rates, nuclei specific to a stable

form may appear in the liquid and bring about crystallization of the mass at various temperatures above that at which the α_L form is set up. In the case where this crystallization is brought about at a temperature close to the latter, the liquid in which it takes place presents the same characteristics of instability as that resulting from the melting of α_L , and thus the crystallization is registered by DTA at the level of the crystalline rearrangement $\alpha_L \rightarrow \beta'_L$.

The phenomenon is especially clear in the case of PSP. In fact the cryothermogram of fig. 6 shows that the crystallization takes place close to the melting temperature of α_L (m.p.: 46.5 °C), but slightly above it (51.9 °C), in the region where the crystalline rearrangement $\alpha_L \rightarrow \beta'_L$ should take place. It should be note that it is the sub- β'_L form which is thus formed.

The results obtained on varying the cooling rate are summarized in table 3. This table shows further that it is possible to introduce a new classification of the triglycerides studied, as a function of the ease with which they produce stable forms on cooling the liquid.

In fact, the symmetrical triglycerides, with the exception of SSS, appear to produce a stable form on cooling the liquid more easily than the nonsymmetrical ones. PSP, which has also been taken into account in table 3 here falls normally into the class of the symmetrical triglycerides, whilst nevertheless showing a greater tendency than the others to yield a stable

Forms obtained	Rate of cooling (°C/min)							
	I°20	0°34	0°27	0°15	0 °11	0°08	0°04	0°02
β L (or sub- β L)	PSP	PPP					PSS	
$\alpha_{\rm L} + \beta'_{\rm L}$ (or sub- $\beta'_{\rm L}$)					SPP	SSS		SPP
$\beta_{ m L}$			РРР	SPS			SSS	

 TABLE 3

 Appearance of stable forms for the six triglycerides, as a function of cooling rate

form. Moreover, we have finally been able to demonstrate the existence of a sub- β'_L form for the three glycerides PSP, PSS and SPP. We can remark here that it is rather the mixed triglycerides which present this form, PSP entering into the classification as it produces exceptionally a β'_L form instead of β_L form at a cooling rate of 1.2 °C/min.

Conclusions

The construction of the cryothermograms for the six triglycerides has

shown that cooling of these triglycerides from the melt at a rate of $1.2 \,^{\circ}\text{C}/$ min yielded an α_L form (except PSP), which on subsequent heating at the same rate gives the β_L form with the symmetrical triglycerides, but the β'_L form with the non-symmetrical triglycerides.

Experiments carried out at lower cooling rates have enabled us to establish that the symmetrical triglycerides studied, except SSS, yield stable forms more easily than the unsymmetrical triglycerides, PSP having the greatest facility in this respect.

Furthermore, a sub- β' form was detected for PSP, PSS, and SPP, these three triglycerides being those which produce a β'_{L} form on heating of the α_{L} form.

Finally, DTA has shown itself to be an excellent method for distinguishing between the positional isomers of the triglycerides studied.

Experimental part

The six triglycerides were prepared either by direct esterification for the homogeneous compounds PPP and SSS, or from 1-mono or 1-3 diglycerides for mixed triglycerides.

Preparation of monoacid triglycerides

The apparatus consisted of a distillation column with a reflux condenser attached to a round flask. The drops of condensed liquid were collected by a lateral tube fixed on the column which leads the liquid, after passing through a second small condenser, to fall on a cartridge filled with anhydrous K_2CO_3 . The liquid is then returned to the flask by means of a siphon.

1 mole of glycerol (heated for 3 hr and then distilled in vacuo) and 3 mole +5% of fatty acid were put in the flask with 5% (by weight of fatty acid) of *p*-toluenesulfonic acid and 500 ml of CHCl₃ free of ethanol. The system was refluxed during 6 hr.

The resulting liquid was first washed with distilled water, then with a 5% K_2CO_3 aqueous solution, then again with water to reach neutrality.

Finally, the solution was dried and evaporated. The glycerides so obtained were first crystallized in ethanol to remove monoglycerides. Elimination of diglycerides was realized by several crystallization in hexane. The purification was followed by thin-layer chromatography on silica gel. The product was finally crystallized from acetone.

Preparation of diacid triglycerides

The 1-monoglycerides were prepared by the method of Hartman⁶⁴) using the apparatus described above.

The 1-3 diglycerides were synthesized by the method of Hartman⁶⁵), and

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the resulting diglycerides crystallized by the same procedure employed for monoacid triglycerides.

The triglycerides were then obtained as described by Craig et al.⁶⁶), and recrystallized as above.

The purity of the six triglycerides was checked by G.L.C.⁶⁷).

Bibliography

- 1) E. S. Lutton, J. Am. Chem. Soc. 67 (1945) 524
- 2) E. S. Lutton, J. Am. Oil Chemists' Soc. 27 (1950) 276
- 3) E. S. Lutton, J. Am. Oil Chemists' Soc. 35 (1958) 11
- 4) C. E. Clarkson and T. Malkin, J. Chem. Soc. (1934) 666
- 5) T. Malkin and M. R. E. Shurbagy, J. Chem. Soc. (1936) 1628
- 6) T. Malkin, Progress in chemistry of fats and other lipids, Pergamon Press, London, 1954, Vol. 2
- 7) A. E. Bailey, M. E. Jefferson, F. B. Kreeger and S. T. Bauer, Oil and Soap, 22 (1945) 10
- L. J. Filer, S. S. Sidhu, B. F. Daubert and J. E. Longenecker, J. Am. Chem. Soc. 68 (1946) 167
- 9) A. W. Ralston, Fatty acids and their derivatives, Wiley, New York, 1948, p. 545
- 10) S. V. Vaeck, Mededel. Vlaam. chem. Ver. 10 (1948) 225
- 11) G. Ravich, C. Zurimov, V. Volova and V. Petrov, Acta Physicochim., U.R.S.S. 21 (1946) 101
- 12) A. E. Bailey, Melting and solidification of fats, Interscience Pub. Inc., New York, 1950
- 13) D. Chapman, Chem. Rev. 62 (1962) 433
- 14) D. Chapman, The structure of lipids, Methuen and Co Ltd., London, 1965
- 15) K. Larsson, Ark. Kemi. 23 (5) (1964) 35
- 16) R. W. Crowe and C. P. Smyth, J. Am. Chem. Soc. 72 (1950) 5281
- 17) R. W. Crowe and C. P. Smyth, J. Am. Chem. Soc. 73 (1951) 2040
- 18) R. W. Crowe and C. P. Smyth, J. Am. Chem. Soc. 72 (1950) 4427
- 19) V. Vand and I. P. Bell, Acta Cryst. 4 (1951) 465
- 20) K. Larsson, Proc. Chem. Soc. (1963) 87
- 21) K. Larsson, Ark. Kemi. 23 (1) (1964) 1
- 22) K. Larsson, Proc. Chem. Soc. (1963) 87
- 23) L. H. Jensen and A. J. Mabis, Nature, 197 (1963) 681
- 24) E. S. Lutton and F. L. Jackson, J. Am. Chem. Soc. 70 (1948) 2445
- 25) A. T. Gros and R. O. Feuge, J. Am. Oil Chemists' Soc. 2 (1957) 239
- 26) R. T. O'Connor, E. F. Du Pre and R. O. Feuge, J. Am. Oil Chemists' Soc. 32 (1955) 88
- 27) D. Chapman, Nature, 176 (1955) 216
- 28) D. Chapman, J. Chem. Soc. (1956) 55
- 29) D. Chapman, J. Chem. Soc. (1956) 2522
- 30) D. Chapman, J. Chem. Soc. (1957) 2715
- 31) D. Chapman, J. Chem. Soc. (1958) 4680
- 32) D. Chapman, J. Chem. Soc. (1958) 3186
- 33) D. Chapman, J. Am. Oil Chemists' Soc. 37 (1960) 73
- 34) D. Chapman, Nature, 176 (1955) 216
- 35) D. Chapman, Spectrochim. Acta, 11 (1957) 609
- 36) D. Chapman, J. Chem. Soc. (1957) 2715
- 37) D. Chapman, R. E. Richards and R. W. Yorke, J. Chem. Soc. (1960) 436
- 38) H. Nakajima, J. Phys. Soc. Japan, 16 (1961) 1778
- 39) D. Chapman, J. Chem. Soc. (1963) 131

- 40) D. Chapman and M. J. Hayes, unpublished work (1960) cited by Chapman (see ref. 14)
- 41) E. M. Barrall II and J. C. Guffy, Am. Chem. Soc., Div. Petrol. Chem. Preprints 11 (3) (1966) 261
- 42) R. B. Joglekar and H. E. Watson, J. Indian. Inst. Sci. A 13 (1930) 119
- 43) N. N. Efremov, Ann. Inst. Polytechn. Oural, 6 (1927) 155
- 44) N. N. Efremov, Akad. Nauk S.S.S.R. 16 (1948) 142
- 45) R. Kerridge, J. Chem. Soc. (1952) 4577
- 46) E. S. Lutton, J. Am. Oil Chemists' Soc. 32 (1955) 49
- 47) D. P. J. Moran, J. appl. Chem. (1963) 91
- 48) H. Lavery, J. Am. Oil Chemists' Soc. 35 (1958) 418
- 49) A. J. Haighton and J. Hannewijk, J. Am. Oil Chemists' Soc., 35 (1958) 457
- 50) M. Loncin, Oleagineux, 13 (1958) 33
- 51) E. S. Lutton, J. Am. Oil Chemists' Soc. 44 (1967) 303
- 52) E. S. Lutton and F. L. Jackson, J. Am. Oil Chemists' Soc. 44 (1967) 357
- 53) M. Goto and E. Asada, Yukagaku, 16 (1967) 402
- 54) R. Perron, A. Mathieu and C. Paquot, Fette Seifen Anstr. 68 (1966) 530
- 55) R. Perron, A. Mathieu and C. Paquot, Bull. Soc. Chim. France, (1962) 2085
- 56) R. Perron, J. Petit and C. Paquot, Rev. Franç. Corps Gras, 8 (1961) 559
- 57) R. Perron, J. Petit and C. Paquot, Rev. Franç. Corps Gras, 9 (1962) 341
- 58) R. Perron, Rev. Franç. Corps Gras, Spec. N $^{\circ}$ (1965) 22
- 59) F. L. Jackson and E. S. Lutton, J. Am. Chem. Soc. 72 (1950) 4519
- 60) E. S. Lutton, F. L. Jackson and O. T. Quimby, J. Am. Chem. Soc. 70 (1948) 2441
- 61) T. Malkin and M. L. Meara, J. Chem. Soc. (1939) 103
- 62) F. R. Hugenberg and E. S. Lutton, J. Chem. Eng. Data, 8 (1963) 606
- 63) E. S. Lutton and F. R. Hugenberg, J. Chem. Eng. Data, 5 (1960) 489
- 64) L. Hartman, Chem. and Ind. (1960) 711
- 65) L. Hartman, J. Chem. Soc. (1957) 3572
- 66) B. M. Craig, W. O. Lundberg and W. F. Geddes, J. Am. Oil Chemists' Soc. 29 (1952) 169
- D. Lefort, R. Perron, A. Pourchez, C. Madelmont and J. Petit, J. of Chromatography, 22 (1966) 266