*Thermochimica Acta*, 53 (1982) 183–194
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

# MEASUREMENTS OF ENTHALPIES AND ENTROPIES OF UNSTABLE CRYSTALLINE FORMS OF SATURATED EVEN MONOACID TRIGLYCERIDES

MICHEL OLLIVON and ROGER PERRON

*Organisation Moléculaire et Macromoléculaire, C.N.R.S. BP 28, Thiais 94320 (France)*

(Received 19 August 1981)

## ABSTRACT

The enthalpies and entropies of fusion of unstable $\alpha$ and $\beta'$ forms of saturated even monoacid triglycerides are determined by direct and indirect calorimetric methods. The choice of these two methods is discussed. The enthalpies and entropies are compared to those of the stable $\beta$ form, conventionally measured by calorimetry. Linear laws of the type $y=an+b$ are deduced for each form in order to relate these data to $n$, the carbon number of acyl chains. The significance of the $a$ and $b$ parameters is discussed. A comparison with the corresponding hydrocarbon parameters provides an explanation of the abnormal polymorphism of these glycerides.

## INTRODUCTION

Triglycerides are the major constituents of natural fats and oils, and thus play an important role in biology, in food and chemical industries. These compounds show a particularly complex polymorphism, monotropic in character, which has been extensively studied. They consequently show a parallel complex thermal behaviour for solid–solid or solid–liquid transitions. In this respect, previous research dealt with the description of the polymorphic varieties [1–3]. Concerning calorimetric measurements, which are essential for monotropism and an understanding of the relative stabilities, the stable $\beta$ forms were generally studied. Study of the unstable $\alpha$ and $\beta'$ forms has been limited, due first to a lack of compound purity, and then to the difficulty of controlling the structure before and after the experiment.

Only a few old and indirect determinations of melting enthalpies of the unstable species are found in the literature, one for the $\beta'$ form of tristearin, calculated from melting dilation data [4] by Bailey [5], and three for the $\alpha$ forms of trimyristin, tripalmitin and tristearin [6]. A linear law of the type

$$\Delta H_f = an + b$$

is already known for the stable form.

In this paper, three different methods for the measurement of the enthalpies and entropies of the unstable forms of saturated even monoacid triglycerides are tested, compared and discussed. From the data obtained, equations which relate the enthalpy and entropy of melting to the length of the hydrocarbon acyl chain constituting the glyceridic structure are deduced.

## *Polymorphism of monoacid triglycerides*

The essential features which characterize the complex polymorphism of monoacid triglycerides are outlined below. According to Lutton [7] and Larsson [8], three main crystalline forms are generally accepted in order to describe the polymorphism. In order of increasing stabilities, these forms are designated as: $\alpha$, $\beta'$, $\beta$. In the $\alpha$ form, the parallel hydrocarbon chains are normal to the basal plane and arranged according to a statistic bi-dimensional centred hexagonal structure where chains are able to rotate around their longitudinal axes. In the most stable $\beta$ form, parallel chains are tilted to the basal plane, and arranged according to a triclinic subcell structure. The main crystalline cell is also triclinic. Zig-zag plans of chains are parallel. $\beta'$ forms are also characterized by parallel and tilted chains, but in an orthorhombic subcell structure where zig-zag plans of chains are perpendicular. Moreover, an additional low melting sub $\alpha$ form was found which is only a modified orthorhombic variety of the $\alpha$ form. Transitions between the three main crystalline forms are of monotropic type, and classically depicted as

$$\begin{tikzcd}
\text{sub}\ \alpha \arrow[r, shift left] & \alpha \arrow[l, shift left] \arrow[r] \arrow[rr, bend right] & \beta' \arrow[r] & \beta \arrow[r] & \text{liquid} \arrow[lll, bend right] \arrow[ll, bend right] \arrow[l, bend right]
\end{tikzcd}$$

## *Abbreviations*

The following abbreviations are used.

Acyl chains: C = $C_{10}$; L = $C_{12}$; M = $C_{14}$; P = $C_{16}$; S = $C_{18}$; A = $C_{20}$; B = $C_{22}$.

| | |
|---|---|
| $n$ | Carbon number of acyl chain $\times 3$ |
| $T_\alpha$, $\Delta H_{f\alpha}$, $\Delta S_{f\alpha}$ | Temperature, enthalpy, and entropy of fusion of $\alpha$ |
| $T_{\beta'}$, $\Delta H_{f\beta'}$, $\Delta H_{f\beta'}$ | Temperature, enthalpy, and entropy of fusion of $\beta'$ |
| $T_\beta$, $\Delta H_{f\beta}$, $\Delta H_{f\beta}$ | Temperature, enthalpy, and entropy of fusion of $\beta$ |
| $C_{pl}$ | Specific heat of the liquid |
| $C_{p\beta}$ | Specific heat of the $\beta$ form |
| $\Delta H_T$ | Enthalpy of the transition $\beta' \rightarrow \beta$ |

## MATERIALS AND METHODS

Tricaprin, trimyristin, tripalmitin, and tristearin were synthesized and purified in our laboratory as described previously [9]. Trilaurin and triarachidin were purchased from Larodan Lipids (Stockholm) and tribehenin from Applied Science Lab. (Penn). All compounds were 99% pure as verified by thin layer chromatography and direct high temperature glass capillary gas chromatography [10]. Differential scanning calorimetry (DSC) confirmed the purity of the $\beta$ form crystals.

A modified Thermanalyse flux calorimeter was used for heating rates of 1 deg $\min^{-1}$ and less, and a Perkin-Elmer DSC-1B model was used for other rates (2–64 deg $\min^{-1}$). Taking into account relatively important heats of transition of triglycerides only about 2 mg samples were used and run against air reference in open aluminium pans. Energies were measured by graphical planimetry or weighting of recording paper.

Specific heats were determined with a flux calorimeter, according to the method described by Barberi and Senevat [11]. Evaluation of specific heats was amended by taking into account the total area of the calorimeter response rather than only the area considered in the original method.

Enthalpies of fusion were measured by using lauric and palmitic acids as reference materials. These acids were purified by successive crystallizations in acetone until respective purities of 99.95% ($C_{14} = 0.05\%$) and 99.86% ($C_{18} = 0.14\%$), controlled by glass capillary gas liquid chromatography of the methyl esters, were obtained. The enthalpies of fusion of these two acids were accurrately determined with a Calvet calorimeter by the Centre de Recherche de Microcalorimetrie et de Thermochimie (C.N.R.S., Marseille). The values given are 8.53 ($C_{12}$) and 12.64 kcal $\text{mole}^{-1}$ ($C_{16}$). It is assumed that the fatty acids chosen have specific heats and thermal conductivities close to those of the triglycerides studied. Standardizations were carried out with these two reference acids for each heating rate.

Energies of fusion of the stable forms were measured directly on solvent crystallized samples. On the contrary, those of the metastable forms cannot be determined under the usual conditions of thermal analysis. In fact, liquids resulting from melting are unstable and transform more or less rapidly into thermodynamically more stable species. The recrystallization exotherm and melting endotherm overlap in this case, and the resulting curve cannot be discriminated. Figure 1 shows the usual type of

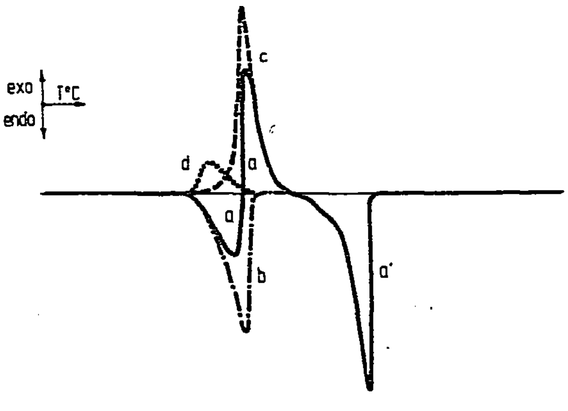


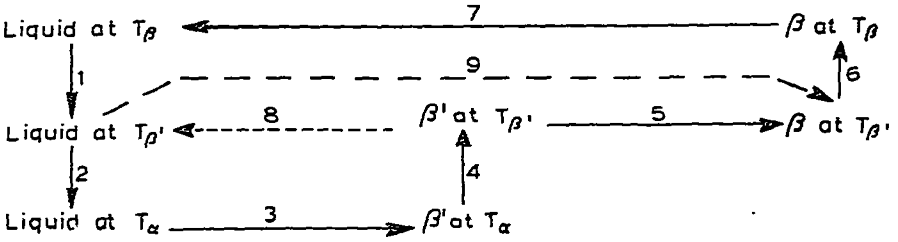
Fig. 1. (a) DSC resultant curve of a $\beta'$ fusion and a $\beta$ crystallization ($\beta'$ SSS sample of 2.1 mg at 2°C $\min^{-1}$); (a') corresponding $\beta$ fusion; (b) theoretical $\beta'$ fusion curve; (c) theoretical $\beta$ crystallization curve; (d) resultant at 0.2°C $\min^{-1}$.

curve obtained. Three different methods were used in order to determine the energies of fusion of the $\alpha$ and $\beta'$ unstable forms.

In the first. heats of dissolution in a solvent of unstable forms were measured and compared with that of the stable variety, all other things being equal. For good accuracy, these heats must be evolved rapidly, and so samples of 10–20 mg were dissolved in 500 $\mu$l of carbon tetrachloride. The heat of transition of the considered unstable form was then obtained as the difference of the heats of dissolution of the stable and unstable forms at room temperature, corrected for the heat capacities required to heat the system up to the melting temperature of the unstable form. These corrections are relatively important, and the accuracy of dissolution measurements is poor (S.D. $>5\%$); thus the method was not considered further.

In the second method, the energy of fusion was directly measured by avoiding, when possible, recrystallization of the more stable form, that is to say, nucleation or growth of crystals of this form. Undesirable nucleation of the stable form is suppressed by the use of unfavourable conditions for its crystallization. On the other hand, the growth of the eventual stable form nuclei is hindered if the unstable melt is submitted only for a very short time to temperatures at which it can occur. Consequently, very high heating rates have to be applied. This second method was used in order to determine all the $\Delta H_{f\alpha}$. For $\Delta H_{f\beta'}$ rather low values were obtained, especially for the low members of the series of compounds examined. In fact, the more pure the triglycerides, the more difficult it is to get the $\beta'$ form alone. In order to avoid formation of the stable $\beta$ form, the shorter the hydrocarbon chains the more rapidly it is necessary to crystallize $\beta'$, but without remaining any residual liquid, which inevitably should transform into the $\beta$ form via the $\alpha$ form. Inevitably, this rapid crystallization gives crystals containing many defects which, unfortunately, contribute to decrease the enthalpy of fusion.

The third method was an indirect one, in which thermal analysis describes steps 1–7 of the cycle



For short triglycerides, recordings of steps 8 and 9 strongly overlap, as mentioned previously, to give step 5. Measurement of energies of steps 1, 5, 6 and 7 allows evaluation of step 8

$$\Delta H_{f\beta'} = \Delta H_{T} + \int_{T_{\beta'}}^{T_{\beta}} C_{p\beta}(T)\,dT + \Delta H_{f\beta} + \int_{T_{\beta}}^{T_{\beta'}} C_{pl}(T)\,dT$$

step: 8 5 6 7 1

$$= \Delta H_{T} + \Delta H_{f\beta} + \int_{T_{\beta}}^{T_{\beta'}} [C_{pl}(T) - C_{p\beta}(T)]\,dT \qquad (1)$$

Transformation enthalpy (step 5) and melting enthalpy (step 7) are easily obtained by recording the corresponding peaks at heating rates low enough to allow the complete $\beta'$ to $\beta$ transformation. Steps 5 and 7 being measured from the same recording it is interesting to note that the measure of $\Delta H_{f\beta'}$ is independent of $\Delta H_{f\beta}$ if the assumption is made that the structure which melts at $T_\beta$ is the same as that which crystallizes at $T_{\beta'}$. So, step 5 being the resultant of steps 8 and 9 (dotted lines on the thermal cycle), the variations of crystallization enthalpy due to defects in the $\beta$ structure are exactly compensated by the variations of melting enthalpy.

Since the influence of the last term of eqn. (1) on the sum is small, we have determined the specific heats of the $\beta$ form and liquid only for PPP. For that we have supposed that specific heats are on the one hand, independent of temperature in the $T_{\beta'}$–$T_\beta$ interval, and on the other, that $C_p$ values of homologues are roughly equal to $C_p$ of PPP. Then we have

$$\Delta H_f\beta' \simeq \Delta H_T + \Delta H_f\beta + \Delta C_p(T_\beta - T_{\beta'}) \tag{2}$$

$C_p$ values so obtained, reported as a function of temperature in Fig. 2, have been extrapolated to an average temperature between $T_{\beta'}$ and $T_\beta$. For the liquid and $\beta$ forms, values of 0.51 and 0.485 cal g$^{-1}$ deg$^{-1}$, respectively, are found, and therefore a $\Delta C_p \simeq 0.025$ cal g$^{-1}$ deg$^{-1}$. For LLL to PPP triglycerides, the sum of steps 1 and 6 is about 0.2 kcal mole$^{-1}$.

Eventual formation of $\beta$ crystals with $\beta'$ may contribute to a decrease of $\Delta H_T$ and then to an increase of $\Delta H_{f\beta'}$. This may result in excessive $\Delta H_{f\beta'}$ values. Consequently, values of $\Delta H_{f\beta'}$ for the low members obtained according to the two methods are slightly different, the real value being almost certainly located between the experimental ones.

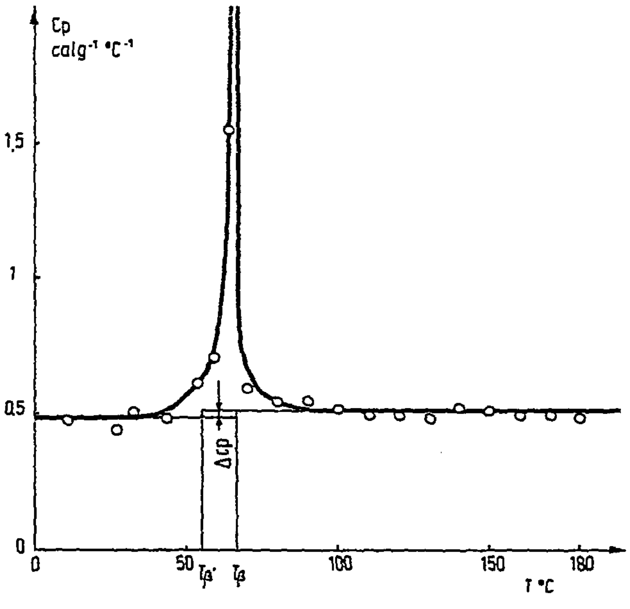


Fig. 2. Specific heat of PPP as a function of temperature.

TABLE I

Temperatures, enthalpies and entropies of fusion of the triglycerides studied

| Carbon No | Triglyceride | $\alpha$ | | | $\beta'$ | | | $\beta$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $T_\alpha$ (°C) | $\Delta H_{f\alpha}$ (kcal mole$^{-1}$) | $\Delta S_{f\alpha}$ (cal mole$^{-1}$ deg$^{-1}$) | $T_{\beta'}$ (°C) | $\Delta H_{f\beta'}$ [a] (kcal mole$^{-1}$) | $\Delta H_{f\beta'}$ [b] (kcal mole$^{-1}$) | $T_\beta$ (°C) | $\Delta H_{f\beta}$ (kcal mole$^{-1}$) | $\Delta S_{f\beta}$ (cal mole$^{-1}$ deg$^{-1}$) |
| 30 | CCC | −9.6 | | | 18.0 | | | 32.2 | 22.3 | 73.0 |
| 36 | LLL | 14.2 | 14.4 | 50.1 | 34.0 | 18.4 | 20.4 | 46.4 | 27.3 | 85.4 |
| 42 | MMM | 31.9 | 18.8<br>(25.0) [c] | 61.6 | 46.5 | 22.3 | 25.7 | 57.6 | 32.3 | 97.7 |
| 48 | PPP | 45.2 | 22.3<br>(30.2) [c]<br>(25.3) [f] | 70.1 | 56.1 | 31.2 | 31.6 | 66.3 | 39.0 | 114.9 |
| 54 | SSS | 55.1 | 26.1<br>(34.7) [c]<br>(29.3) [f] | 79.5 | 63.5 | 34.1<br>(38) [d] | (36.0) [c] | 73.1 | 45.0 | 130.0 |
| 60 | AAA | 62.3 | 29.8 | 88.9 | 69.2 | 38.3 | | 78.3 | 49.6 | 141.2 |
| 66 | BBB | 67.4 | 33.5 | 98.4 | 73.3 | 38.5 | | 82.3 | 54.7 | 153.9 |

[a] Direct determinations.

[b] Indirect determinations.

[c] Ref. 6; [d] ref. 5; [e] ref. 9; [f] refs. 18, 19.

## RESULTS

Results given by the two methods are reported in Table 1 and Fig. 3. Experimental conditions are specified in Table 2. Melting temperatures from Lutton [14] and corresponding entropies are also detailed in Table 1.

It is well known that many physical properties of lipids, enthalpy of fusion is one of them, vary linearly with the carbon number of acyl chains, and particularly when it is $> 10$. In this respect, for the melting enthalpies of $\alpha$ and $\beta$ of saturated even monoacid triglycerides we have deduced

$$\Delta H_{f\alpha} = 0.616n - 7.20 \text{ kcal mole}^{-1} \tag{3}$$

with a correlation coefficient $r = 0.9998$ (for triglycerides MMM to BBB). For triglycerides CCC to BBB we found

$$\Delta H_{f\beta} = 0.920n - 5.56 \text{ kcal mole}^{-1} \ (r = 0.998) \tag{4}$$

Convergence temperatures for $n \rightarrow \infty$ given by

$$T_{\infty} = \lim \left[ \frac{d(\Delta H_f)}{d(\Delta S_f)} \right]_{n \rightarrow \infty}$$

are found to be equal at 127°C for $\alpha$ and $\beta$ forms.

Good correlations obtained for $\alpha$ forms are probably due to the fact that the crystalline structure of these forms results mainly of statistical $CH_2$ Van der Waals interactions between neighbouring chains and therefore the corresponding $\Delta H_{f\alpha}$ values are independent of external conditions applied. In this structure the number of defects is large, but is approximately constant. This is not the case for $\beta'$ and $\beta$ forms, which are crystalline varieties with thermodynamically stable arrangements. There is a large variation of defect number and consequently of the $\Delta H_f$.

In this respect, saturated monoacid triglycerides such as those studied give enthalpies which differ only by a few kcal mole$^{-1}$ according to the conditions of crystallization (lowering of enthalpies of about 5%). On the contrary, for 1-stearo-2,3

TABLE 2

Heating rates (°C min$^{-1}$) used for enthalpy measurements

| Carbon No. | Triglyceride | $\alpha$ | | $\beta'$ | | $\beta$ |
|---|---|---|---|---|---|---|
| | | Fus. | Cryst. | Direct | Indirect | |
| 30 | CCC | | | | | 0.5, 8 |
| 36 | LLL | | 32, 64 | 64 | 8 | 0.5, 8 |
| 42 | MMM | | 16, 32 | 32 and 64 | 2 | 0.5, 8 |
| 48 | PPP | 16 | 16 | 32 | 0.5 | 0.5, 8 |
| 54 | SSS | 8, 16 | 8, 16 | 8 and 16 | 0.2 | 0.5, 8 |
| 60 | AAA | 8 | 8 | 2 | | 0.5, 8 |
| 66 | BBB | 8 | 8 | 1 | | 0.5, 8 |

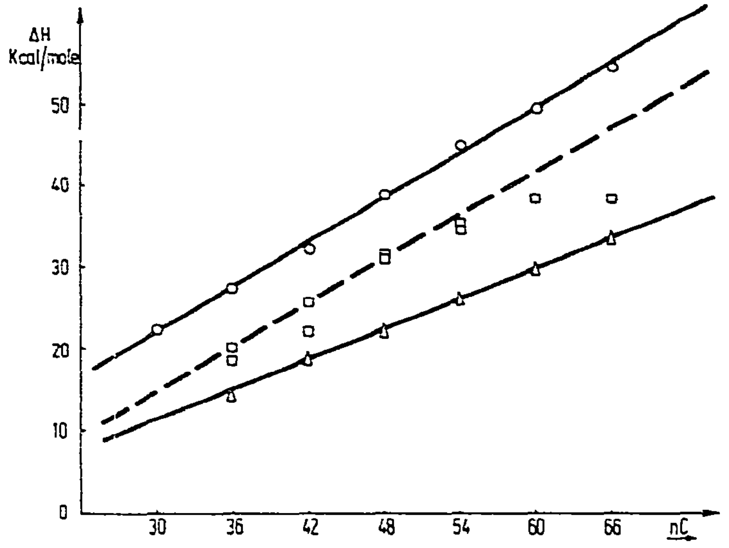


Fig. 3. Enthalpies of fusion of saturated even monoacid triglycerides as a function of carbon number. Δ, $\alpha$; □, $\beta'$; O, $\beta$.

-dipalmitin (SPP) a difference as large as about 10% of the $\Delta H_f$ value is found: 38.3 kcal mole$^{-1}$ for a slow crystallization in hexane against 34.7 kcal mole$^{-1}$ for a sudden crystallization in acetone. Such variations, already reported [12b] for SSS, are accompanied by a $T_f$ lowering of more than 2°C, and are attributed to a great number of defects resulting from the sudden crystallization. Extreme $\Delta H_f$ lowerings of asymmetric triglycerides like SPP are probably increased by a possible solid state demixing of $\beta$ form enantiomers.

For $\beta'$, it seems that enthalpies of fusion do not vary linearly with the carbon number of hydrocarbon chains beyond PPP (Fig. 3). Values found for higher terms (SSS to BBB, and perhaps PPP) are lower than the expected values obtained by extrapolation of lower terms $\Delta H_f$. These differences are probably due to the presence of two $\beta'$ forms as already reported [15]. Enthalpies of higher members would be the weighted average values of the $\Delta H_f$ of the two forms, weights being the proportions of each form.

It is probable that the variations of $\Delta H_f$ are also linear with $n$ for the two $\beta'$ varieties. This particular point will be discussed later [13]. However, an approximate equation can already be deduced from the $\beta'$ indirect enthalpies of LLL to PPP

$$\Delta H_{f\beta'} = 0.93n - 13.3 \text{ kcal mole}^{-1}$$

The 95% reliability limits of the $a$ coefficient are 0.83 and 1.03 kcal mole$^{-1}$ per $CH_2$ group.

Finally, the two methods used appear to be complementary. However, it seems better to use the direct method, even for very high heating rates, as the indirect method comprises the sum of several determinations.

## DISCUSSION

Measured enthalpies for $\alpha$ varieties are significantly lower than those reported by Charbonnet and Singleton [6], already criticized by Bailey [5] and noted in parentheses in Table 1. On the contrary, extrapolations of $C_p$ given by this author led to 0.53 and 0.45–0.50 cal $g^{-1}$ $deg^{-1}$ for the liquid and the solid in good agreement with the values of 0.51 and 0.485 cal $g^{-1}$ $deg^{-1}$ found in this work. Agreement is also rather good with more recent data reported for crystallization enthalpies of PPP and SSS, making the assumption that they are approximately equal to fusion enthalpies.

The $\Delta H_{f\beta'}$ of SSS calculated by Bailey (38 kcal $mole^{-1}$) [5] according to

$$\Delta H_f(\text{cal g}^{-1}) = \Delta V(\text{ml g}^{-1}) \times 306.9 + 3.23$$

which relates $\Delta H_f$ and changes of specific volume on melting for triglycerides, is not very different from that obtained here. It is interesting to note that in this relation no assumption is made on the crystalline variety of which the enthalpy of fusion is calculated.

Numerous enthalpy and entropy values are found in the literature for the $\beta$ form of triglycerides. They are collected in a recent paper of Timms [16]. Elimination of the lowest data, and an error in copying of enthalpies according to Hampson and Rothbart [17], led Timms to propose the following equation

$$\Delta H_{f\beta} = 1.023n - 7.79 \text{ kcal mole}^{-1}$$

where the $a$ constant 1.023 is too high. It is to be noted that by linear regression of the best values of Hampson, weighted by their standard deviations, it is found

$$\Delta H_{f\beta} = 0.89n - 2.88 \text{ kcal mole}^{-1}$$

By eliminating values clearly too high, particularly that given by Hagemann for BBB, and adding the two values recently reported by Lovegren and Gray [18,19] for PPP and SSS, we have obtained

$$\Delta H_{f\beta} = 0.969n - 6.26 \text{ kcal mole}^{-1}$$

against, by adding our own results

$$\Delta H_{f\beta} = 0.950n - 5.71 \text{ kcal mole}^{-1}$$

It is of interest to specify more precisely the significance of the $a$ and $b$ coefficients. In fact, for each crystalline form $a$ represents a difference of enthalpy per $CH_2$, between solid and liquid.

The linearity of $\Delta H_f$ as a function of $n$ found experimentally requires that the influence of end groups (polar and methyl groups) either decreases linearly all along the chain in the liquid state as well as in the solid state, or more probably acts only up to a limited number of carbon atoms, perhaps 10 C. Beyond this point, the $a$ constant only depends on both the solid enthalpy and then on the crystalline subcell, and the liquid enthalpy, hence of liquid structure.

The number of possible crystalline subcells is limited and their structures are well known [8], and we can assume that their corresponding enthalpies per $CH_2$ are to be independent of the series of compounds considered. This is not the case of liquids, for which enthalpies vary with the organization order, which depends on the type of end groups. In this respect, it is interesting to compare the literature data for the three corresponding subcells of hydrocarbons, which are the most studied compounds, with our own values.

For the hexagonal arrangement of hydrocarbon chains, the linear regression on the Broadhurst data [20], from $C_9$ to $C_{36}$, gives $a = 0.607$ kcal mole$^{-1}$ $CH_2$. This value is close to that found in this work (0.616).

For the 0⊥ subcell of hydrocarbons, Flory and Vrij [21], on the basis of literature values, have adopted a 0.950 kcal mole $CH_2$ which does not differ strongly from that of the $a$ value of polymethylene found and compared by Billmeyer [22]: $a = 0.922$ kcal mole$^{-1}$ $CH_2$. In fact, these values are close to that proposed by us: $a \simeq 0.93$ for $\beta'$ forms.

Finally, we have calculated for the T// arrangement of hydrocarbons by linear regression from $C_{10}$ to $C_{20}$ reported data [20] a value of 0.99 slightly different from our value $a = 0.92$ kcal mole$^{-1}$ $CH_2$, for $\beta$ forms of triglycerides.

For a given subcell a relatively small difference is observed between the $a$ parameters of hydrocarbons and triglycerides; this probably being due to the low polarity of triglycerides not quite different to those of hydrocarbons. The influence of liquid structure on $a$ parameters seems rather reduced in this case. Nevertheless, this structure of the liquid due to interactions between polar groups can explain slight variations of this parameter for more polar long chain compounds.

Kitaigorodsky [23] has related the thermal stability to the compactness of molecular structures. It appears that the most compact structure seems to be the most stable. The theory was applied to the comparison of orthorhombic and triclinic subcells of hydrocarbons. It resulted that the 0⊥ subcell seems slightly more stable than the T//. In order to compare the stabilities of these two more compact subcells with that of the hexagonal arrangement, we have calculated the $CH_2$ molar volumes in each case. Starting from the average increase in chain length of crystalline long chain compounds per carbon atom given by Skau [24] and from other structural data of the literature (noted between parentheses), we found for hydrocarbons:

| | |
|---|---|
| 23.57 Å$^3$ for 0⊥ subcell | [20] |
| 23.78 Å$^3$ for T// subcell | [20] |
| 26.6 Å$^3$ for hexagonal subcell | [8] |
| 28.2 Å$^3$ for liquid polyethylene | [21] (70°C extrapolation) |

This classification is sensibly that recently reported by Hageman [25], but one can see that it is different from the classification observed with the polymorphic varieties of triglycerides, for which the most stable form is $\beta$(T// subcell) and not the $\beta'$ form (0⊥). An explanation of this discrepancy may be formed by comparing the $b$ terms.

The $b$ term cannot be considered as an absolute measure of the aptitude to crystallize in a given variety. In fact, contrary to the accepted assumptions [5,16], the structure of the first hydrocarbon chain carbons may be maintained in the liquid state [8,26]. These structures would not depend on the chain length and would increase the negative $b$ term by a lack of contribution by these carbons to energies of fusion.

Nevertheless, if the structure of the melted different crystalline varieties of a same compound are assumed to be identical, their relative $b$ parameters can be compared. The high value of the $b$ term of the triglyceride $\beta'$ form ($\simeq$ 13.3 kcal mole$^{-1}$) with regard to that of the $\beta$ form (5.5 kcal mole$^{-1}$) permits the assumption that the end group structure induced by the $0\perp$ chain crystallization is less compact, and hence less stable than that induced by T//.

## CONCLUSION

Three methods were tested and compared in order to determine enthalpies and entropies of fusion of unstable $\alpha$ and $\beta'$ forms of saturated even monoacid triglycerides. Direct and indirect calorimetric methods were adopted. They allowed the determination of $\Delta H_f$ of the unstable forms from LLL to BBB and moreover the $\Delta H_f$ of stable forms from LLL to BBB. From the values obtained, linear laws relating the thermodynamic quantities to the carbon number of acyl chains were deduced. The relation established for the $\beta$ forms has been compared to the relations previously published in the literature, while enthalpies of fusion of the unstable forms were compared to one another.

The significance of the various $a$ parameters has been discussed in terms of structure of the melt which is mainly conditioned by the nature of the end groups. Moreover, these parameters have been compared with the $a$ parameter of the corresponding subcells of hydrocarbons. It was found that the stability order differs from that of triglycerides, the $0\perp$ subcell being slightly more stable than T// for hydrocarbons while this is not true for triglycerides. The reason for this might be established by considering the contribution of the $b$ term, which reflects the aptitude to the formation of a given crystalline variety, all other things being equal.

## REFERENCES

1 E.S. Lutton, J. Am. Chem. Soc., 67 (1945) 524.
2 K. Larsson, Acta Chem. Scand., 20 (1966) 2255.
3 C.W. Hoerr and F.R. Paulicka, J. Am. Oil Chem. Soc., 45 (1968) 793.
4 A.E. Bailey and W.S. Singleton, Oil Soap, 22 (1945) 265.
5 A.E. Bailey, Melting and Solidification of fats, Interscience, London, 1950, Chap. III.
6 G.H. Charbonnet and W.S. Singleton, J. Am. Oil Chem. Soc., 24 (1947) 140.
7 E.S. Lutton, J. Am. Oil Chem. Soc., 49 (1972) 1.
8 K. Larsson, Fette, Seifen, Anstrichm., 74 (1972) 136.
9 M. Ollivon and R. Perron, Chem. Phys. Lipids, 25 (1979) 395.
10 M. Ollivon and H. Chaveron, 13th Int. Symp. Chromatogr., Cannes, 30 June–4 July 1980.

11 P. Barberi and J.T. Senevat, Journées de Calorimétrie et d'Analyse Thermique, Rennes, 9 et 10 mai 1974 Abstr. 4–19.
12 D. Chapman, The Structure of Lipids,Methuen, London, 1965, (a) p. 273; (b) p. 267.
13 M. Ollivon and R. Perron, to be published.
14 E.S. Lutton and A.J. Fehl, Lipids, 5 (1971) 90.
15 J.W. Hagemann and W.H. Tallent, J. Am. Oil Chem. Soc., 49 (1972) 118.
16 R.E. Timms, Chem. Phys. Lipids, 21 (1978) 113.
17 J.W. Hampson and H.L. Rothbart, J. Am. Oil Chem. Soc., 46 (1969) 143.
18 N.V. Lovegren and M.S. Gray, J. Am. Oil Chem. Soc., 55 (1978) 310.
19 M.S. Gray and N.V. Lovegren, J. Am. Oil Chem. Soc., 55 (1978) 601.
20 M.G. Broadhurst, J. Res. Natl. Bur. Stand., Sect. A, (1962) 241.
21 P.J. Flory and A. Vrij, J. Am. Chem. Soc., 85 (1963) 3548.
22 F.W. Billmeyer, Jr., J. Appl. Phys., 28 (1957) 1114.
23 A.I. Kitaigorodsky, Molecular Crystals and Molecules, Academic Press, New York, 1973, p. 48.
24 E.L. Skau, J. Am. Oil Chem. Soc., 50 (1973) 245.
25 J.W. Hagemann and J.A. Rothfus, J. Am. Oil Chem. Soc., 56 (1979) 1008.
26 P.T. Callaghan, Chem. Phys. Lipids, 19 (1977) 56.