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POLYMORPHISM OF EVEN MONOACID TRIGLYCERIDES IN THE PRESENCE OF SORBITAN MONOSTEARATE, STUDIED BY THE DSC.

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ABSTRACT

Fusion heats of two polymorphic forms, ΔH_α and ΔH_β, of triglycerides were measured. They were compared with corresponding measurements in the presence of a sorbitan ester. Results imply different effects of the emulsifier on long and short chains triglycerides with respect to phase transformation.

INTRODUCTION

The thermal behavior of solid triglycerides was extensively investigated, because of the deleterious consequences of polymorphic transformations on product quality.[1,2]

Monoacid triglycerides exhibit at least three polymorphic forms:α, the lowest melting, β', the intermediate melting, and β, the highest melting. Spontaneous monotropic transformation occurs from α to β.

From the literature it is known that incorporation at low percents of sorbitan esters in tristearin, stabilizes the α form and prevents its transformation to the stable β form[3,4]. Since this subject has not been studied systematically, further investigation must be performed in order to elucidate the effect of emulsifier as crystal structure modifier. In the present work the DSC was used in order to investigate the polymorphic behavior of C_{12}-C_{20} saturated monoacid triglycerides in the presence of food emulsifiers.

EXPERIMENTAL

The emulsifier, commercially available from Grindsted Products of Denmark, was added at 10 wt% of the triglycerides. Thermal measurements were carried out on a Mettler Differential Scanning Calorimeter TA3000. Each sample was melted in order to destroy all the nuclei present, rapidly quenched and consequently the crystallized α form was heated up. The temperature range in which each triglyceride is solid depends on the fatty chain length. The polymorphic transformation in C_{12} wil occur at much lower temperatures than in C_{20}. Further, the very unstable α form of C_{12} needs a high rate of heating in order to melt and show an endothermic peak; on the contrary, the relatively stable α form of C_{20} needs a very low rate of heating in order to crystallize into the β form. Hence, each triglyceride was scanned at the appropriate rate (in order

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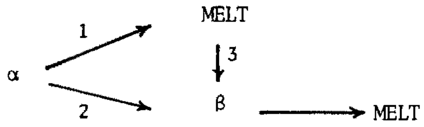
Table I. Calculated values of H_α and H_β for C_{12} and C_{18} in the absence and in the presence of sorbitan monostearate (J/mol).

	LLL			SSS			
	10°C/min	20°C/min	30°C/min	1°C/min	2°C/min	5°C/min	10°C/min
ΔH_α	——	4.4	7.1	79.6	99.8	110.3	117.8
ΔH_β	167.0	161.9	153.3	206.9	196.9	181.9	45.7
LLL + Sorb. monost.				SSS + Sorb. monost.			
ΔH_α	2.0	8.7	12.4	101.7	121.6	109.0	124.9
ΔH_β	157.1	152.9	142.9	163.7	139.9	——	——

As the heating rate increases, a larger α endotherm and a smaller β endotherm are obtained, and at a relatively low heating rate the α endotherm even disappears in C_{12}. These data suggest that during heating, part of the fat melts and recrystallizes into the β form, and part of the fat transforms directly without showing endotherm.



In the first series of experiments, in C_{12} most of the fat chose the path 2 owing to the low energy barrier of transformation. In C_{18} the energy barrier for transformation is evidently much higher, hence the α form passed through the melt before transforming into β (path 1,3).

In these two different situations the emulsifier will cause different effects. In the case of C_{12}, it causes the fat to melt from the α form rather than transform directly to β , while in C_{18} this effect is not possible because the path through the melt is the inherently preferred. On the other side, the C_{18} the β crystallization is delayed by the emulsifier while in C_{12} it is not. The reason seems to be the more difficult arrangement of C_{18} chains into the compact β form than C_{12} and then the steric hindrance of the emulsifier is evident.

to obtain the optimal thermogram for comparing the different triglycerides.)

RESULTS AND DISCUSSION

From the thermogram obtained from each triglyceride the heats of fusion Δ_{α} and ΔH_{β} were computed. In the same experimental conditions, the effect of a solid emulsifier (sorbitan monostearate) on these values, expressed as ΔH^* (the ratio between ΔH with the emulsifier and ΔH of the pure triglyceride) was tested (Fig. 1)

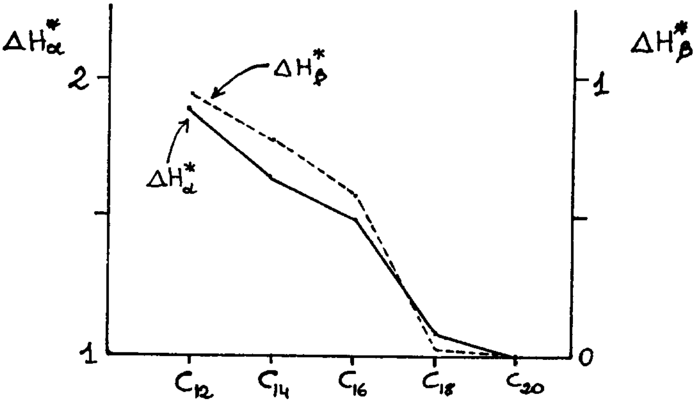


Fig. 1. Values of ΔH^*_{α} and ΔH^*_{β} versus fatty chain length.

The emulsifier effect depends on the chain length of the triglyceride; ΔH^*_{α} is 1 with C_{20} and increases with decreasing chain length; ΔH^*_{β} is 1 with C_{12} and decreases to zero with increasing chain length. Thus, the emulsifier exhibits both an effect on ΔH_{α} which is emphasized in C_{12} and an opposite effect on ΔH_{β} which is emphasized in C_{20}.

In order to check the significance of ΔH changes, an additional series of experiments was carried out, in which C_{12} and C_{18} were scanned at different rates in the presence of the emulsifier. The heats of fusion and crystallization are summarized in Table I.

It is clear that the emulsifier does not inhibit the transformation, but rather acts as a retardant for transformations in which ΔH is high and behaves as impurity accelerating the melting.

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