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POLYMORPHIC TRANSITIONS IN HYDROGENATED CANOLA OIL IN PRESENCE OF SURFACTANTS

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ABSTRACT

The polymorphic transitions of hydrogenated canola oil in the presence of some selected food emulsifiers such as sorbitan monostearate, monodiglycerides, DATAE esters were studied. It has been demonstrated that during the tempering (aging) and heating cycles, the fully hydrogenated canola oil is transformed from its α and β'-forms to the β-form. The presence of 5 wt% surfactant will retard such transition and mostly β' and α-forms will be stabilized. The partially hydrogenated oil (IV=23-69) shows the existence of different low and high melting point forms. The low melting forms will transform into high melting forms at much lower rates of transition in the presence of those emulsifiers than in their absence.

INTRODUCTION

Low Erucic Acid Rapeseed oil (LEAR or Lobra) known as Canola oil is now used in several countries in Europe, America and Japan. Hydrogenated Canola oil as used for margarine and other food applications has been known to appear in more than one polymorphic form. The Canola oil is rich in C_{18} fatty acids and after full hydrogenation it seems to consist mainly of tristearin. The polymorphic transition to the most stable polymorph, named β-form, causes "bloom" and "grain" problems in the final product[1,2].

Hernquist has described the composition of hydrogenated Canola oil and found that the addition of 5 wt% of rac.-1.2 dipalmitoyl glycerol, known to

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crystalize in the β'-form with orthorhrombic chain packing, delayed the β'-β transition[3].

Deman has studied several surfactants and found that the most effective compound in delaying the transition to the β-polymorphic form was sorbitan tristearate[4].

We have studied in detail the effect of various food emulsifiers on the polymorphic transitions of pure tristearin, tripalmitin and their mixtures[5]. We have also described the incorporation of suitable solid surfactants into the crystal lattice to form a "button syndrome" and to delay the transition into the β-form.

When tristearin was mixed with tripalmitin (10 wt% or more) and melted together, the β'-form (orthrombic packing) was stabilized. The addition of surfactant (5-10 wt%) in the presence of the tristearin and the tripalmitin retarded the appearance of the β-form. Alfa and β'-forms were predominantly present after prolonged aging.

The purpose of this work is to study carefully the effect of the presence of impurities (such as hydrogenated palm oil derivatives) and surfactants on the polymorphic transitions of hydrogenated Canola oil at various stages of hydrogenation.

EXPERIMENTAL

1. **Hydrogenation**: Two types of hydrogenations were carried out on salad Canola deodorized oil (from the Canola council in Canada). The first being the potassium formate technique[6] of hydrogenation without the use of hydrogen, gas pressure and temperature, and the second technique being high pressure non-selective hydrogenation in the presence of a catalyst.

The potassium formate technique was carried out as follows: 10, 6, 2 M of potassium formate aqueous solution were stirred in an open vessel with 0.6 wt% of palladium on carbon (10 wt% Pd/C). Canola oil was added at 1:1 w/w ratio to the formate solution and allowed to react for 5-1000 mins. Samples were withdrawn, extracted and washed with $CHCl_3$ and analyzed by GLC, NMR, FTIR and by wet methods to determine internal product distribution, percent of trans isomers, iodine value (IV) and acid value (AV).

The catalytic high pressure hydrogenation was carried out using Canola oil and 0.6 wt% of Pd/C catalyst for 5-300 mins. at 4 atms. of hydrogen pressure. Samples were withdrawn, extracted and washed in a similar way.

2. **Thermal treatment**: Each sample was characterized by the above analytical techniques. The samples were melted to 80°C in the DSC (Mettler TA 3000) and aged at this temperature for 2 mins., cooled at 50°C/min to 0°C and tempered at this temperature for an additional 5 mins. and reheated at the various heating rates (0.2°-20°C/min) to 80°C. This protocol has been named the "screen heating cycle".

The "aging cycle" consists of a similar cooling profile as above, aging the samples in the DSC at 25°C for 10-1000 mins. and reheating them until they melt.

3. **Technique and materials**: The DSC (Mettler TA3000) and X-rays (Philips PW 1050/70) of the samples were recorded. The H_{α}, $H_{\beta'}$ and H_{β} were calculated and evaluated. Emulsifiers such as SMS (sorbitan mono-stearate - Adomim Chemicals, Israel), SSL (sodium steroyl lactylate - Adomim chemicals, Israel), MDG (42% alpha monoglyceride stearate - Henkel), MG-90% (α-monoglyceride - Grindstead, Denmark), DATAE (diacetyltartaric acid ester of monoglyceride stearate - Gronau, Germany), were used in 5 wt% without any further treatment.

RESULTS

The hydrogenation process is described in Fig. 1 from which one can see the decrease in the IV canola with time for each concentration of potassium formate. The highest yield and conversion was obtained with 10M formate after 1000 mins. (over 96%). In table 1 the physical and chemical characteristics of the samples used for this study are described: Similar iodine values were obtained in each technique. Surprisingly the percentages of the trans isomers in the product were identical in most cases. We could not find any significant correlation between the percentage of the trans isomers and the technique of hydrogenation.

The SFI of each sample were quite different, i.e., the internal product distribution of the fats is quite different in the two systems. It seems that the potassium formate hydrogenation led to the formation of the higher SFI.

DSC measurements of Canola fully hydrogenated fat (IV=4.5) at different

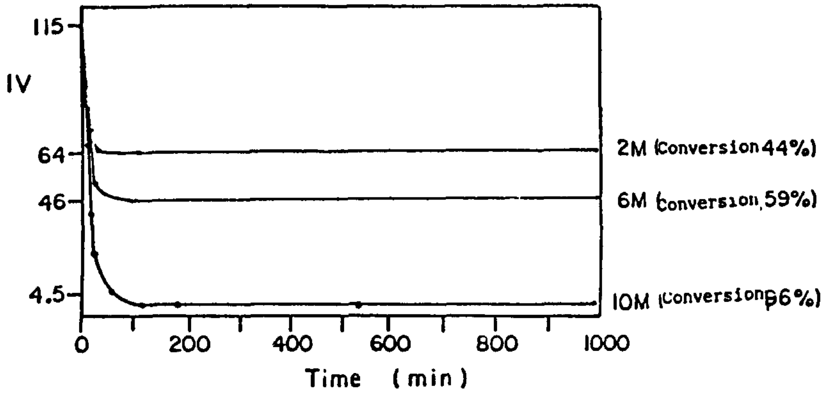

Fig. 1: Decrease of IV with time in the potassium formate hydrogenation technique in 2,6 and 10M of KCOOH aqueous solutions, 1:1 w/w ratio of canola oil and 0.6 wt% of paladium or carbon (10 wt% Pd/C).

TABLE 1: Iodine values of the samples used in this study prepared by potassium formate technique and by pressure technique.

Canola oil (IV=115)

IV of sample prepared by potassium formate technique	IV of sample prepared by pressure technique
101	104
81	77
54	53
39	34
26.5	29
4.5	0

heating rates, Fig. 2, in the screening cycle, shows that for low heating rates only the ß-form was detected. At higher heating rates the ß'-form was also seen and at very high heating rates the melting of the α-form was the only form detected.

This behaviour is characteristic of mixtures of tristearin (SSS) with tripalmitin (PPP) which stabilized the ß'-form (Fig. 3).

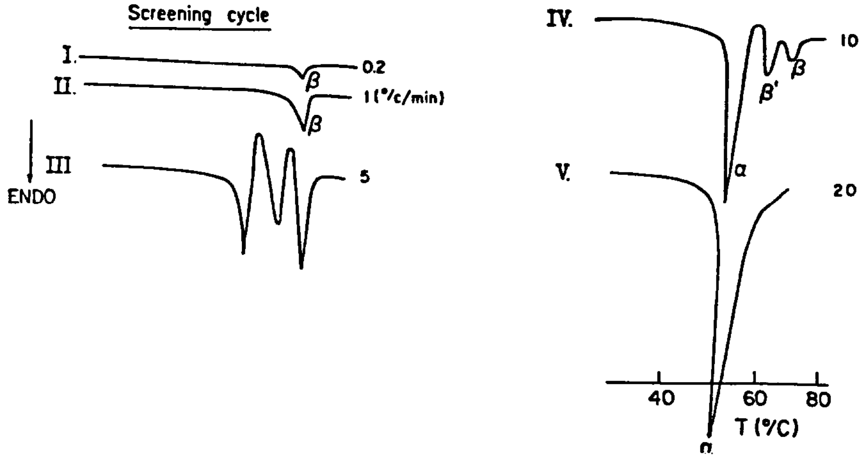

Fig. 2: Polymorphic transitions of canola hydrogenated fat (IV 4.5) at various heating rates without emulsifier: I. 0.2°/min, II. 1.0°/min, III. 5°/min, IV. 10°/min, V. 20°/min.

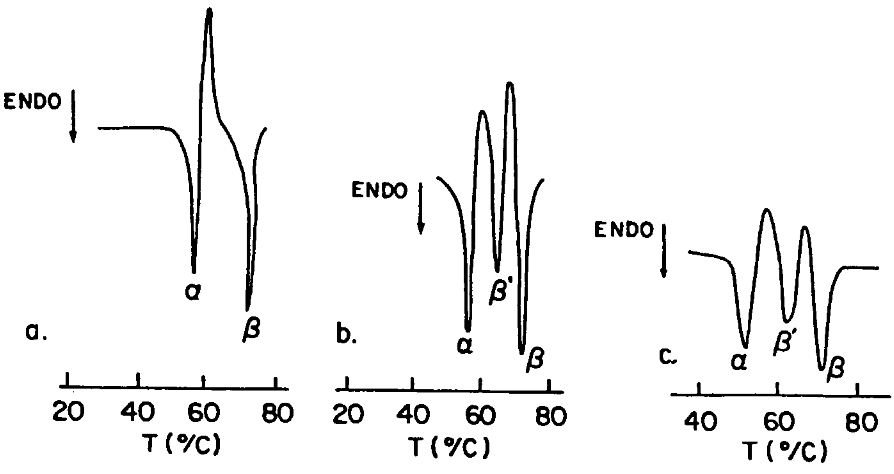

Fig. 3: Polymorphic transitions in the "screen heating cycle" at the heating rate of 5°/min in a. Tristearin, b. Tristearin and tripalmitin (90:10) and c. Canola oil fully hydrogenated.

The aging process shows, in a similar way, the existence of both α, β' and β-forms after short aging. Slow transition of the β' to the more stable β-form (Fig. 4) was measured.

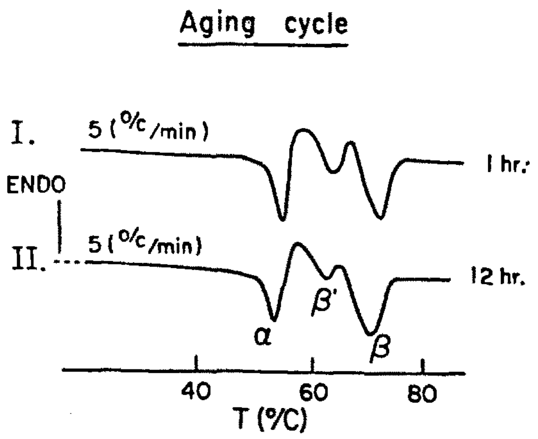

Fig. 4: Polymorphic transitions of canola hydrogenated fat (IV 4.5) during various tempering (aging) without emulsifier: I. 1 hr., II. 12 hr.

Addition of 5 wt% of sorbitan monostearate (SMS) to the hydrogenated fat prior to its melting (Fig. 5,6) causes a significant retardation effect of the β'-β transition. It can be seen that at a heating rate of 5°C only the melting α-form was recorded in the presence of sorbitan monostearate while α, together with β' and β-forms, were seen in its absence. A similar delaying effect was detected at any given heating rate. In a similar way the retardation effect is seen for the aging cycle. Only the α-form is detected in the presence of the emulsifier.

Hydrogenated fat with IV of 26.5 and 54 behaved in a similar way. In the absence of emulsifier, "low and high melting forms" were detected, while in the presence of the sorbitan mono-stearate, "low melting forms" were mostly recorded. The reason that the peaks are small (small H values) is, possibly, due to the fact that at the elevated temperatures the "liquid fats" dissolve part of the "solid fats" and the thermal events of melting or crystallization can hardly be detected. In addition, one must realize that the presence of fats such as SOS (1,3-distearo-oleate), SOO (1,2-dioleo stearate), PSO (Palmito stearo oleate) or PSS (1,2-distearo palmitate) at high iodine values, lead to the formation of other polymorphs such as γ, sub α, pseudo β'_1, β_2 and β, melting at different lower temperatures. We have therefore named these forms

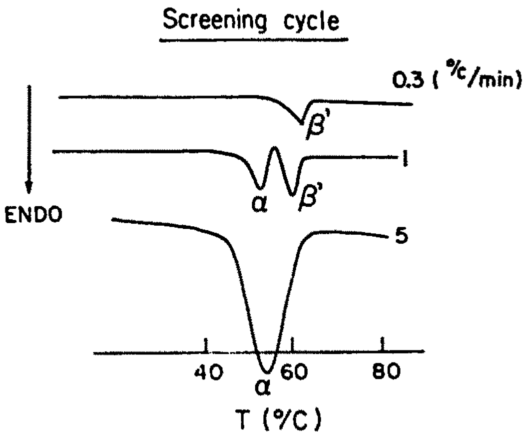

Fig. 5: Polymorphic transitions of canola hydrogenated fat (IV 4.5) at various heating rates with 5 wt% of SMS: I. 0.3°/min, II. 1.0°min, III. 5°/min.

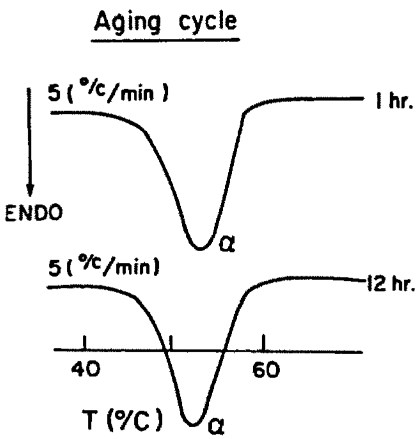

Fig. 6: Polymorphic transitions of canola hydrogenated fat (IV 4.5) during tempering (aging) with 5 wt% of SMS: I. 1 hr., II. 12 hrs.

low, medium and high melting forms. Nevertheless, the effect of the surfactant is quite similar and the crystallization of the high melting form is retarded in "screen process" and the low-high solid-solid transformation is delayed in the aging process (see Fig. 7).

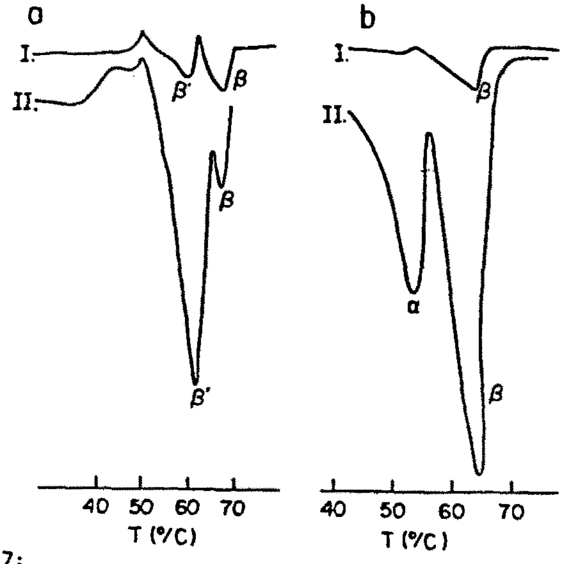

Fig. 7:

(a) Hydrogenated canola oil (IV 26.5) in the "screen heating cycle" in rate of heating of 5°/min:
I. without emulsifier. II. with 5 wt% SMS.
(b) Hydrogenated canola oil (IV 26.5) aged for 1 hr in the aging cycle:
I. without emulsifier. II. with 5 wt% SMS.

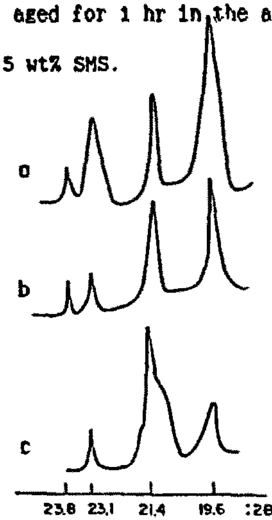

Fig. 8:

X-ray diffraction of canola hydrogenated to IV 34 during tempering for 16 days:
(a) without emulsifier
(b) 5 wt% DATAE
(c) 5 wt% SMS.

The results from the X-ray analysis on the aging process in the presence of SMS, SSL, MDG, MG, DATAE are described in Fig. 8. One can see that SMS is the most effective surfactant. It is a solid α-tending emulsifier with orthrombic packing, incorporated easily into the fat lattice and retards to the maximum the transition of the low melting form into the high melting form.

The other emulsifiers had only a minor retardation effect.

The following order of efficacy was found:

$$0 < SSL = MG = DATAE < MDG < SMS$$

This order applies to any given IV of the fat.

CONCLUSIONS

It has been concluded that full hydrogenated Canola oil does not differ significantly from SSS:PPP (90:10) mixture. The β form together with the β'-form are stabilized during the tempering process and slow transformation to the β-form occurs. Addition of 5 wt% of selected solid emulsifiers such as SMS or STS will retard the formation of the β-form during heating process on the tempering (aging) process. At elevated iodine values the medium melting form is more dominant and the retardation effect is less pronounced. Therefore, it is recommended that the manufacturers of hydrogenated Canola oil (margarine or other products) will mix into their products 5 wt% sorbitan monostearate and, if possible, add "structural impurity" such as tripalmitin. The effect of 1,2 diglyceride will be further studied in our next work.

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