Hydrogenation of Palm Stearine: Changes in Chemical Composition and Thermal Properties

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The progress of hydrogenation of palm stearine using a *trans* promoting catalyst has been followed by monitoring the chemical composition and the thermal properties by NMR and DSC techniques. The results show that hydrogenation occurs in 2 stages. In the first stage, the formation of the triglyceride, PEP from the lower melting PLP, allows an enhanced mixed crystal formation with the high melting PPP. Although this promotes a greater rate of crystallization in the α form and transformation to the β' form in tempering, further transformation to the β form is inhibited. T^m is thereby reduced in the early stages even though both the rate of crystallization and the solid fat content at temperatures <40°C are increased. In the later stages of hydrogenation, the conversion of the triglyceride POO to the higher melting POS increases the proportion of the sample which can crystallize in the high melting fraction to at least 80%. Although this still cannot be transformed into the β crystal form, T^m for the overall sample and the solids content at all temperatures are now greater than those of the original palm stearine sample.

In a previous paper, the chemical composition and thermal properties of a typical palm stearine sample were described and interpreted in terms of the crystalline content (1). In this paper we describe the changes in chemical composition and thermal properties which occur during the commercial hydrogenation of the batch of palm stearine from which that sample was taken.

The hydrogenation of fats and oils is a widely used commercial operation which, purposefully increases the softening point, improves the consistency for use as margarine and other edible fats, and increases the resistance to oxidation. Extensive research over the past few decades has led to an improved understanding of the chemistry of the process such that it is now possible to control the changes required—by selection of the appropriate hydrogenation catalyst and processing conditions. The mechanism of the hydrogenation process and factors affecting selectivity and reaction rates are reviewed by Khieri (2). The hydrogenation process generally leads to an increase in the degree of order in the fatty acid residues in two ways: (i) *cis* double bonds are converted to saturated bonds; (ii) *cis* double bonds are converted to *trans* double bonds by an isomerization process; the *trans* configuration allows the acyl chain to take up an all-*trans* conformation. Both changes lead to higher melting points and the former change facilitates crystallization due to increased chain flexibility. As there are both mono- and diunsaturated fatty acid residues present in all natural fats and oils (the most common in palm stearine being oleic and linoleic esters, respectively), and because hydrogenation is only taken to partial conversion, the order, or lack of it, in which the hydrogenation and isomerization processes occur has an important influence on the thermal properties of the product.

Hydrogenation has not commonly been applied to palm stearine in the past, because the melting point is already high and the consistency can be improved by a carefully chosen combination of blending and transesterification (3). However, economic advantages and the selectivity by choice of catalyst are improving to such an extent that its commercial use is increasing. There is one report in the literature (3) which describes the hydrogenation under conditions of high *trans* selectivity. Under these conditions poly- and monounsaturated acid residues are converted to a high proportion of *trans* monounsaturated acid residues which has the effect of improving the consistency of the product without increasing the melting point.

EXPERIMENTAL

Material. The palm stearine used in this work was a typical sample of that used for the production of margarine and shortenings in Australia.

Hydrogenation. Hydrogenation of the palm stearine sample was performed in the refinery reaction vessel at Meadow Lea Foods. The concentration of the catalyst (Resan 22, a *trans*-promoting catalyst) was 0.11% by weight. Hydrogen addition was controlled by a pressure controller and a fixed orifice plate. The temperature was 150°C and the head pressure was not allowed to exceed 10 psi. These conditions have been shown to be highly selective for polyunsaturated fats.

Samples, taken at 5 min intervals during the reaction, were filtered to remove catalyst and analyzed. They are labelled according to the time of removal, e.g. PS 5 refers to the sample removed after 5 min hydrogenation.

Chemical composition. GC analysis of the fatty acid methyl ester composition after transesterification of the samples, HPLC analysis of the triglycerides and the iodine value in each sample were performed as previously described (1).

Thermal analysis. Shot melting points, solids content as a function of temperature and DSC experiments were performed as previously described (1).

RESULTS AND DISCUSSION

Chemical composition. The fatty acid residue composition at various stages of the hydrogenation process is listed in Table 1 and shown graphically in Figure 1, for the components showing significant change. As expected, there is a decrease in the concentration of oleic ($C_{18:1c}$) and linoleic ($C_{18:2}$) and an increase in the concentration of stearic (C_{18}) and elaidic ($C_{18:1t}$). The marked changes in slope between 15 and 20 min hydrogenation on three of the graphs indicate that the process is reasonably selective. The rates over the approximately linear portions of the graphs before 15 min and after 20 min (Table 2) show

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TABLE 1

Fatty Acid Methyl Ester Compositions of Samples Taken at 5 Min Intervals During the Hydrogenation Reaction of Palm Stearine

	PS[a]	PS5	PS10	PS15	PS20	PS25	PS30	PS35
C_{12}	0.2	0.4	0.3	0.4	0.4	0.4	0.4	0.4
C_{14}	1.2	1.3	1.2	1.3	1.2	1.2	1.2	1.2
C_{16}	51.4	51.5	51.4	51.5	51.4	51.7	51.5	51.3
$C_{16:1}$	0.2	0.1	0.1	0.1	0.1	0.0	0.0	0.0
C_{18}	5.0	5.6	6.2	7.0	8.1	10.3	11.7	13.7
$C_{18:1t}$[b]	0.0	1.0	3.0	4.8	6.9	8.9	10.9	11.9
$C_{18:1c}$[b]	32.7	31.7	31.3	31.1	29.7	25.6	23.5	20.5
$C_{18:2}$	8.3	6.6	4.8	3.0	1.6	1.2	0.2	0.3
$C_{18:3}$	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_{20}	0.1	0.3	0.3	0.4	0.4	0.4	0.4	0.4

[a] PS designates palm stearine and the number following refers to the time hydrogenated.

[b] Elaidic and oleic acid are distinguished by *t* and *c* after $C_{18:1}$, respectively.

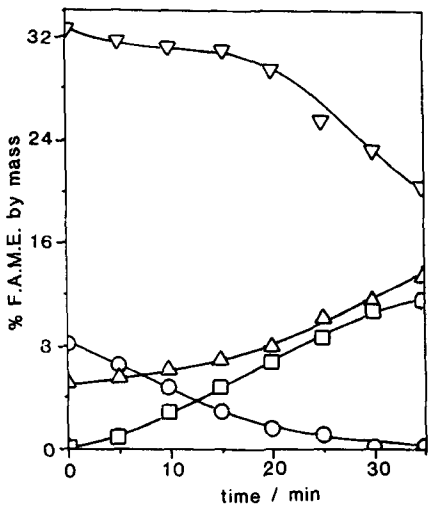

FIG. 1. Effect of hydrogenation time on the C_{18} fatty acid composition of palm stearine. ∇ $C_{18:1c}$ (oleic); ○ $C_{18:2}$ (linoleic); △ C_{18} (stearic); □ $C_{18:1t}$ (elaidic). F.A.M.E.: fatty acid methyl ester.

TABLE 2

Rate of Change of Fatty Acid Residue Concentration During Two Stages of Hydrogenation of Palm Stearine

	Rate of change, % min^{-1}	
Fatty acid	0-15 min	20-35 min
Linoleic	−0.35	−0.09
Oleic	−0.11	−0.61
Elaidic	0.32	0.33
Stearic	0.13	0.37

that linoleic ester is preferentially hydrogenated in the first stage, while oleic ester, which is initially four times the concentration of linoleic, is hydrogenated at a low rate in the first stage and a high rate in the second stage when the concentration of linoleic ester has decreased to one-twentieth that of the oleic ester. The products of the hydrogenation of linoleic ester could be oleic, elaidic or even stearic ester while the products of hydrogenation of oleic ester are stearic and elaidic ester, the latter from isomerization. Assuming that the following reactions do not occur—(i) linoleic → stearic (in one step); (ii) elaidic → stearic; and (iii) elaidic → oleic (i.e., net change is always the reverse reaction)—one can conclude then the rates given in Table 2 show that in the first stage, linoleic ester is converted to elaidic ester at 0.33% min^{-1} and oleic ester at 0.02% min^{-1} while oleic ester is being converted to stearic ester at 0.13% min^{-1} with negligible conversion to elaidic ester. In the second stage the bulk of the reaction is the conversion of oleic ester to stearic ester at 0.37% min^{-1} and to elaidic ester at 0.24% min^{-1}. The fact that the origin of the bulk of the elaidic ester formed during the first stage (>90%) of the hydrogenation process was linoleic ester, while during the second stage (>73%) it was oleic ester, suggests that the isomerization of oleic ester has a very low efficiency during the early stages of the hydrogenation process. This may be due to the conditions prevailing at this stage, i.e., higher gas pressures and lower temperatures, or it may be due to the lack of suitable reaction sites; these being taken up preferentially by the linoleic acid ester units.

It is interesting to note that the total rate of hydrogenation, i.e., the sum of the rates of loss of linoleic and the gain of stearic esters, is identical in the two stages of the process. This is also shown by the observed change in iodine value during hydrogenation (Fig. 2) which is close to linear throughout.

The triglyceride composition as a function of hydrogenation is shown in Table 3. The progress of the components showing major change is illustrated in Figure 3. Although peak resolution was a problem for several triglycerides, some important observations can be made

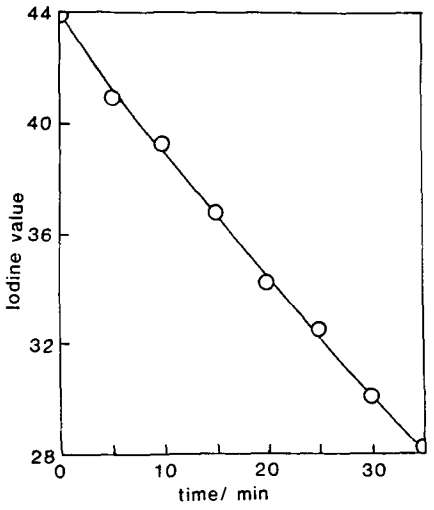

FIG. 2. Effect of hydrogenation time on the iodine value of palm stearine.

TABLE 3

Triglyceride Compositions, Determined by HPLC, of Samples Taken at 5 Min Intervals During the Hydrogenation Reaction of Palm Stearine

Triglyceride[a]	PS	PS5	PS10	PS15	PS20	PS25	PS30	PS35
					mol %			
PLL	3.6	2.3	1.2	0.5	0.0	0.0	0.0	0.0
LOO	1.3	0.8	0.5	0.4	0.2	0.3	0.0	0.0
PLO	7.8	6.0	4.2	2.9	1.4	0.5	0.0	0.0
PLP	12.7	9.4	7.5	4.3	2.7	0.6	0.4	0.0
PEL	0.0	0.0	0.0	1.5	1.4	1.0	0.7	0.1
POO/OOO	19.6	18.1	19.2	17.9	17.1	13.4	51.1[b]	46.8[b]
POP/POE	33.4	33.4	35.9	38.3	39.4	41.1		
PPP/PEP/PEE	13.6	17.7	18.2	19.4	20.6	22.1	22.3	24.3
SOO	1.0	1.6	1.7	1.9	1.9	1.4	1.5	0.0
SOP/SOE	4.3	5.8	6.4	6.7	8.3	9.3	9.5	10.5
SPP/SEP/SEE	2.4	4.0	4.1	4.8	5.8	8.7	11.5	15.7
SOS	0.3	0.4	0.5	0.6	0.3	0.6	0.7	0.5
SSP/SES	0.0	0.5	0.6	0.8	0.7	0.9	2.1	2.1

[a]E, L, O, P and S refer to the fatty acid residues elaidic, linoleic, oleic, palmitic and stearic, respectively; the arrangements of the fatty acids on the triglycerides are not necessarily the ones reported.

[b]Peaks not resolved.

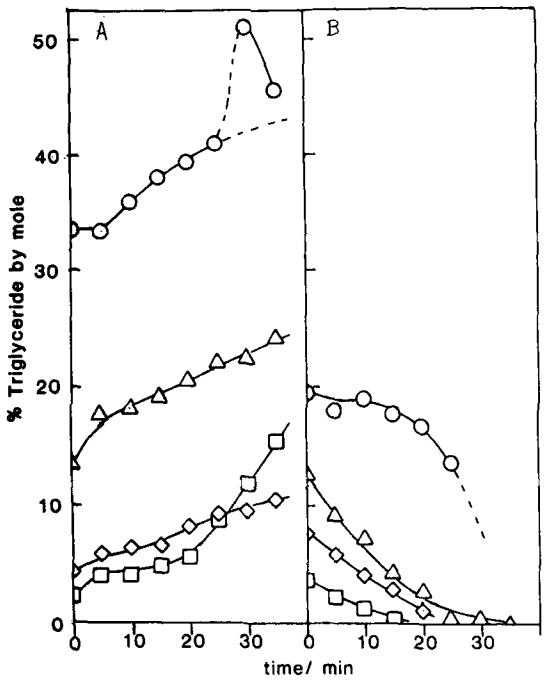

FIG. 3. Effect of hydrogenation time on the triglyceride composition determined by HPLC analysis. (A) ○ POP/POE (includes POO/OOO after 30 and 35 min), △ PPP/PEP/PEE, ◇ POS, □ PPS/PES; (B) □ PLL, ◇ PLO, △ PLP, ○ POO/OOO.

as follows: (i) All triglycerides containing linoleic esters decreased in concentration early in the reaction at a rate roughly proportional to the initial concentration. By 20 min the total linoleic ester concentration from these three triglycerides—PLL, PLO and PLP—had fallen to 15% of the initial value. This is within the experimental error range of the corresponding value for the total linoleic ester concentration determined by GC. (ii) The triglycerides containing stearic esters—SOP/SOE, SPP/SEP/SEE and SSP/SES—all increase in concentration during hydrogenation; it is particularly noticeable that the two latter peaks increase in two approximately linear stages in agreement with the observations made from the fatty acid residue analyses. It should be noted that the increases in the composite peak (SPP/SEP/SEE) are virtually all due to the triglyceride SEP since the precursors of the other two are not present in significant amounts. (iii) The composite peak (PPP/PEP/PEE), which is the only peak associated with E and not with other fatty acid residues involved in the reaction, increases steadily with hydrogenation in a similar manner to that observed for elaidic acid methyl ester in the GC analysis. (iv) Likewise, the composite peak due to the triglycerides, POO/OOO, decreases in two clearly defined stages divided by the 20 min mark. However, it should be noted that the peak was unresolved from that due to the triglycerides, POP/POE, after 25 min. Later points were taken by extrapolation. The average rates of change over the two stages are -0.11% min^{-1} and -0.7% in reasonable agreement with the rates of loss of oleic acid methyl ester in the corresponding periods (Table 2).

The overall pattern of the hydrogenation process based on the composition analyses for the principal triglycerides present in the palm stearine sample is shown in Figure 4.

Melting characteristics. The shot melting point varies with hydrogenation as shown in Figure 5. A decrease in melting point of palm stearine with hydrogenation has previously been reported (3), although for most fats and oils the melting point rises continuously with hydrogenation. Indeed, a prime purpose of commercial hydrogenation is to raise the melting point. Clearly, palm stearine is unusual in this respect. The melting point decreases almost 3°C during the first stage of the process up to a point which corresponds approximately with the point where chemical analysis suggests that linoleic ester hydrogenation changes to oleic ester hydrogenation; thereafter it increases and passes the original melting point after about 30 min hydrogenation.

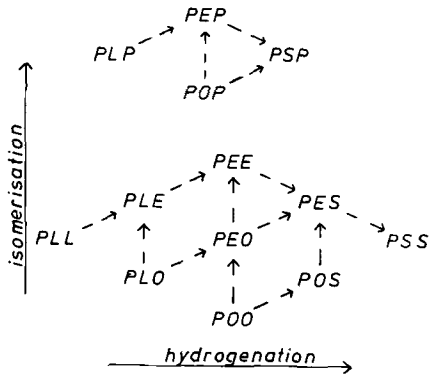

FIG. 4. Probable chemical reactions occurring during the hydrogenation of palm stearine. P = palmitic, L = linoleic, E = elaidic, S = stearic, O = oleic (fatty acid residues in the triglycerides).

This effect is also reflected in the solid fat content of the sample, determined by the NMR technique, at various stages of the hydrogenation. At the lower temperature of 10°, 20° and 30°C, the solids content rises steadily with hydrogenation as expected (Fig. 6). A minimum appears in the curves at 40°, 45° and 50°C after increasing times of hydrogenation. The results are plotted as solid fat content vs temperature at specific stages in the hydrogenation in Figure 7. Before hydrogenation the curve contains an inflection point indicating a two-stage melting process. The second stage becomes undiscernible as the hydrogenation proceeds showing that a change of mechanism, probably a simplification of the melting process, is responsible for the unusual behavior. This simplification is also illustrated by the graphs of the progress of solidification at 0°C after various stages of hydrogenation (Fig. 8). The clear two-stage nature of the

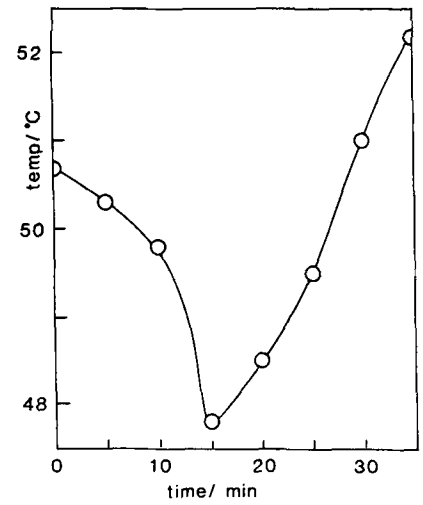

FIG. 5. Effect of hydrogenation time on the shot melting point of palm stearine.

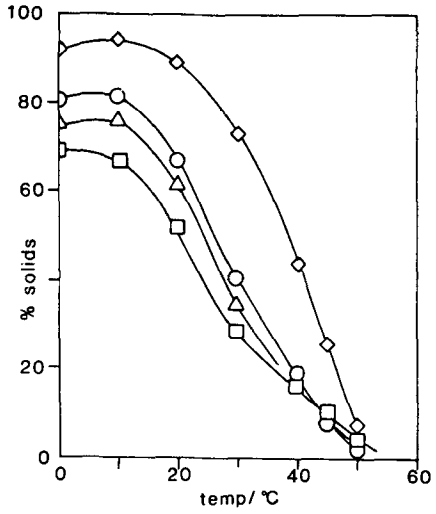

FIG. 7. Effect of temperature on the solid fat content at different hydrogenation times: □ 0 min; △ 10 min; ○ 20 min; ◇ 35 min.

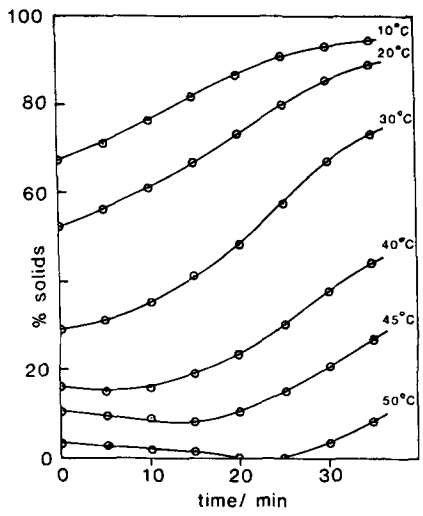

FIG. 6. Effect of hydrogenation time on the solid fat content of palm stearine determined by the NMR method.

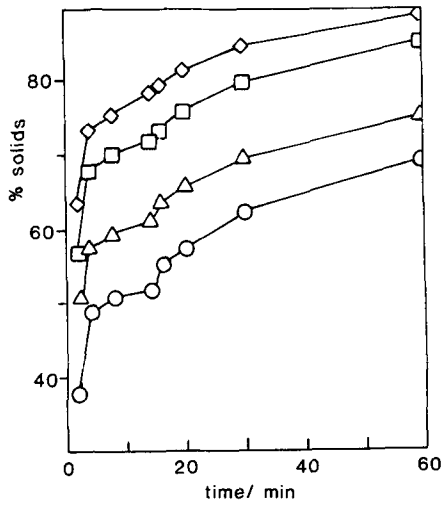

FIG. 8. Effect of hydrogenation time on the solidifcation of palm stearine at 0°C determined by the NMR method. Hydrogenation times: ○ 0 min; △ 15 min; □ 20 min; ◇ 25 min.

solidification evident before hydrogenation has virtually disappeared after 25 min hydrogenation. On the other hand, solidification at 20°C is always a single stage process (Fig. 9) with the rates of solidification and the level of solidification increasing markedly with the progress of hydrogenation.

Thermal analysis by DSC. DSC provides a more detailed analysis of the melting behavior than either the shot melting point or the solids content measurements. At high heating rates, the melting behavior of the sample present at the commencement of the scan can be analyzed, since under these conditions structural rearrangements during the time of the scan are at a minimum. The DSC scans taken at 80° min^{-1} after various stages of hydrogenation are shown in Figure 10. The low melting peak B gradually disappears and is replaced partially by a slightly higher melting peak C (at 21°C), with a much smaller area. In our previous paper (1) we described how peaks B and C could be assigned to the melting of a sub α and a β' crystal form, respectively, on the basis of tempering experiments (1). The increase in molecular ordering accompanying the hydrogenation process will certainly facilitate crystallization in the β' form relative to the less ordered α phases.

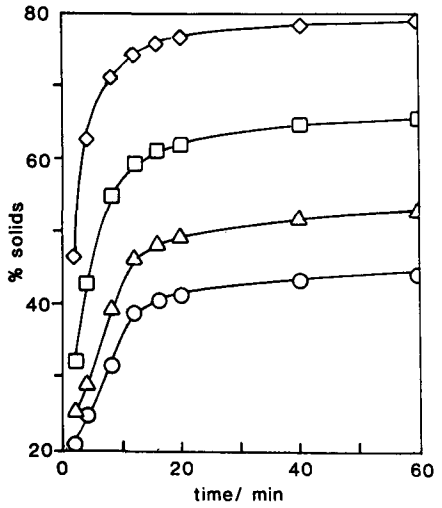

FIG. 9. Effect of hydrogenation time on the solidification of palm stearine at 20°C. Hydrogenation times: ○ 0 min; △ 10 min; □ 20 min; ◇ 30 min.

At the same time, melting peak A grows in size and gradually shifts to higher peak temperatures, i.e. from 39° to 47°C from unhydrogenated to 35 min hydrogenated. After 35 min hydrogenation, peak A dominates the melting curve and shows why only one melting process can be observed by the NMR method of solid content analysis. This is in contrast with the unhydrogenated sample where two almost independent melting curves of almost equal area and with peaks separated by almost 30 degrees are observed by DSC. Peak A is most likely due to the melting of α crystals (1). The shift to higher temperatures is consistent with the higher stearic ester content, and the growth in size shows that many of the triglycerides which melted in the low melting fraction before hydrogenation have been chemically converted to triglycerides compatible with the higher melting fraction.

The effects of hydrogenation on the DSC scans taken at 10° min^{-1} are shown in Figure 11. At lower scan speeds, structural reorganization can occur during the scanning process. The behavior is then closer to that in a normal melting point determination or other thermal treatment involving slow heating processes. Before hydrogenation, extensive crystallization occurs at 37°C and at 50°C, as denoted by the exotherms, X_D and X_E, into the higher melting forms D and E, which have been associated with β' and β crystal forms, respectively (1). Even after 15 min hydrogenation, recrystallization to the highly ordered β structure is completely inhibited. Naguib-Mostafa and deMan (4) found that an increased concentration of *trans* isomers reduced the ease of β

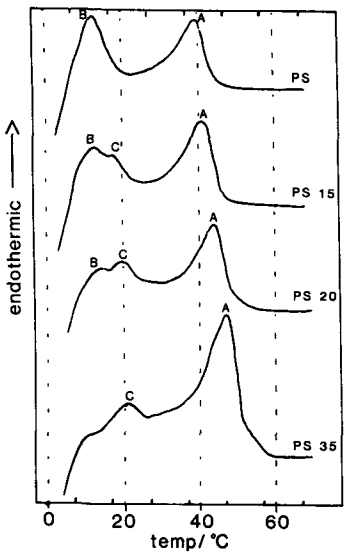

FIG. 10. DSC thermograms of palm stearine after various times of hydrogenation. Heating rate 80° min^{-1}. Prior treatment: cooled at 80° min^{-1} from 70°C to 0°C, 0.1 min at 0°C before scanning. Hydrogenation times in min given on scans.

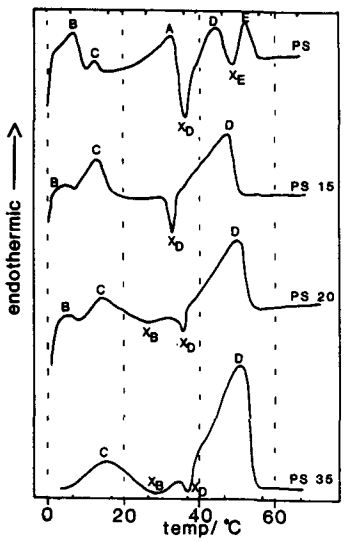

FIG. 11. DSC thermograms of palm stearine after various times of hydrogenation. Heating rate: 10° min^{-1}. See Figure 10 legend for further detail.

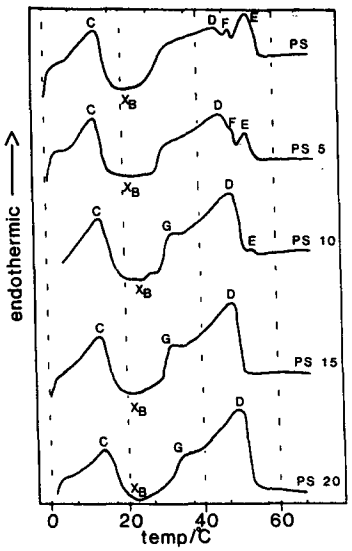

FIG. 12. DSC thermograms of palm stearine after various times of hydrogenation. Influence of tempering for 20 min at 0°C prior to scan at 10° min^{-1}. See Figure 10 legend for prior treatment.

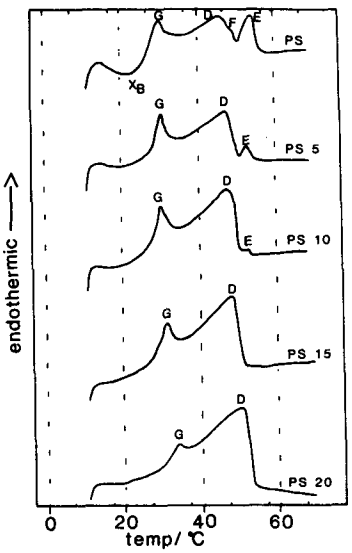

FIG. 13. DSC thermograms of palm stearine after various times of hydrogenation. Influence of tempering for 10 min at 10°C prior to scan at 10° min^{-1}. Prior treatment: cooled at 80° min^{-1} from 70° to 0°C, 10 min at 0°C, 80° min^{-1} to 10°C.

crystal structure formation in hydrogenated canola oil. They suggest that the presence of the *trans* isomers in the mixed crystal structures with saturated fatty acids sterically hinders transformation to the β structure. This inability to transform to the β structure shows why the shot melting point decreases in the early stages of hydrogenation. However, crystallization X_D still proceeds to produce the β′ structure D. In the later stages, i.e. after 15 min, both the peak temperature and the area of peak D increase markedly in favorable comparison with the behavior of the shot melting point.

Tempering experiments at 0°C (Fig. 12) indicate a similar trend. Peak E develops well in the unhydrogenated sample but after 10 min hydrogenation, it is reduced to a minor peak. Other developments are the loss of peak F and the gain of peak G. Peak F was previously assigned (1) to a second high melting β′ structure formed from the higher melting triglycerides released during the transformation of low melting α crystals (peak B) into β′ crystals (peak C). This is entirely consistent with the observed reduction of the low melting fraction with hydrogenation. Peak G, which was assigned to the β form of the lower melting fraction, is also formed at higher tempering temperatures (Fig. 13) where it is seen to gain maximum prominence after short hydrogenation times. After 20 min hydrogenation, it had almost merged into peak D following annealing at 10°C.

Changes in thermal properties during hydrogenation. The hydrogenation of palm stearine proceeds with a high degree of selectivity in two stages. In the first stage the main chemical changes are the conversions of the triglycerides, PLP and PLO, into PEP and PEO, respectively, and in the second stage the main changes are the conversions of POO, POP and PEO into POS, PSP and PES, respectively. One possible explanation of the conversion of two-stage melting prior to hydrogenation into one-stage melting after hydrogenation is that the formation of PEP from the lower melting component PLP allows enhanced mixed crystal formation with the higher melting PPP. This is compatible with the promotion of greater rates of crystallization in the α crystal form and transformation to the β′ crystal form on tempering, and with the inhibition of further transformation to the highly ordered β crystal form. This results in a reduction of the melting point during the first stage of the hydrogenation even though the rate of crystallization and the solid fat content at temperatures lower than 40°C are increased.

The conversion of one of the main contributors to the low melting fraction of palm stearine, POO, to the higher melting POS/PES during the second stage of hydrogenation results in a steady increase in the proportion of the sample which can crystallize in the high melting fraction. After 35 min hydrogenation, DSC shows that greater than 80% of the crystallized material melts in this higher temperature range. Although this cannot be transformed into the β crystal form by tempering, the shot melting point of the overall sample is now greater than that of the original palm stearine sample. Also at this point, the solids content, as measured by NMR, is greater at all temperatures than that of the untreated sample.

The production of margarine requires a fast crystallizing fat with a stable crystalline form over the temperature range of use. The β′ form is preferable to the β crystal form since the grain size of the latter is generally too large for the consistency required in margarine. This work has shown that the hydrogenation of palm stearine is an entirely suitable process for this purpose since the product is stable in the β′ crystal form and has a high rate of crystallization.

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