Polymorphic Stability of Hydrogenated Palm Oleins in Dilutions with Unhydrogenated Liquid Oils

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Palm oil was hydrogenated under selective and nonselective conditions. Some of the hydrogenated samples were chosen for their physical characteristics and were diluted with 70% sunflower oil. A commercial hydrogenated palm olein (H-olein) was diluted up to 80% with canola oil. The diluted mixtures were evaluated for their polymorphic β' stability by a temperature-cycling procedure between 4 and 20°C. All of the mixtures were stable in the β' form. The dropping point and solid fat content of the mixtures were compared with those of commercial soft and stick margarines. Soft margarines can be prepared from mixtures of 20% H-olein and 80% unhydrogenated oil, and stick margarines from 40% H-olein and 60% liquid oil. If canola oil is the liquid oil, the saturated content in the soft formulation is 13% and that of a stick formulation 17%.

KEY WORDS: β' stability, canola oil, hydrogenated palm oil, hydrogenated palm olein, palm oil, palm stearin, physical properties, polymorphism, sunflower oil.

Palm oil can be fractionated into a solid palm stearin and a liquid palm olein by dry, detergent or solvent processes (1). The fractionation process is not a clear-cut separation as far as iodine value (IV) and melting point are concerned. The degree of fractionation depends on the kind of equipment used (1). Means of physical and chemical characteristics of the various fractions have been published by Rossell *et al.* (2). A so-called super olein is obtained when a standard olein is fractionated again to yield a palm mid fraction (PMF) and a double-fractionated olein (DfPOo). PMF is a component of true cocoa butter equivalents (3). Recently, new plants have been put into operation for the production of super oleins in one single dry fractionation step. Standard olein is being imported from Malaysia in large quantities and fractionated in the country where it is consumed (4). Palm olein is widely used as a frying oil in tropical and subtropical climates. It is easier to transport than palm oil in temperate climates because of its lower solids content. Yap *et al.* (5) reported on the chemical and physical properties of palm olein hydrogenated at 175°C and 15 psi. This study is concerned with palm olein hydrogenated under different conditions. Commercially available products were also evaluated.

MATERIALS AND METHODS

Refined, bleached and deodorized palm olein and a commercially hydrogenated palm olein were obtained from Lam Soon (M) Bhd, Kuala Lumpur, Malaysia. Sunflower oil and canola oils were bought from a local supermarket.

Hydrogenation was carried out in a Parr pressure reaction apparatus with a 2-L vessel and a charge of 1 kg of oil. Nickel catalyst Nyosel 325 (Harshaw/Filtrol Partnership, Cleveland, OH) was used at a level of 0.2% by weight of oil. The dry reduced catalyst contained 22% nickel. The reaction temperature and pressure were 200°C and 8 psi (48 KPa) for selective and 160°C and 48 psi (303 KPa) for nonselective hydrogenation (6). The rate of agitation was 680 rpm. Samples were taken at 5-min intervals. The reaction was stopped at 35 min.

IVs were determined by the AOCS Method Cd 1-25 (7). Fatty acid composition was determined as described by Shehata *et al.* (8), and dropping points as described by Mertens and deMan (9).

Solid fat content (SFC) determinations followed the AOCS cooling and tempering procedures of Method Cd 10-57. The tempering step was at 25°C instead of 26.7°C. A Bruker PC/20 pulsed nuclear magnetic resonance (NMR) analyzer (Minispec) was used (Milton, Canada).

To study the polymorphic behavior of hydrogenated palm olein in liquid oils, the following procedure was carried out. Approximately 3 g of the melted sample was transferred to a small tube (6 × 1 cm). The mixtures were heated at 70°C for 2 h, then crystallized in ice and water and left overnight in the refrigerator. A temperature-cycling procedure was then applied, consisting of tempering at 20°C for 2 d followed by storage at 5°C for 3 d (cycle 1). The next step was tempering at 20°C for 10 d and 5°C for 10 d (cycle 2), followed by tempering at 20°C for 1 d and 5°C for 1 d (cycle 3) and finally at 20°C for 2 d and 5°C for 1 d (cycle 4).

The polymorphic forms of the fat crystals were established by X-ray diffraction (10). Differential scanning calorimetry (DSC) was used to determine crystallization behavior (10).

RESULTS AND DISCUSSION

The crystallization curves of palm oil and palm olein in Figure 1 illustrate how a higher-melting crystalline fraction has been removed from palm oil.

IVs and rate of hydrogenation, based on time zero under selective and nonselective conditions, of palm olein are shown in Table 1. Nonselective hydrogenation proceeded at a much faster rate than selective hydrogenation as was expected (6). The change in fatty acid composition and *trans* content are shown in Figure 2 for selective and in Figure 3 for nonselective conditions. The maximum *trans* content was 27.3% at 20 min under selective and 20% at 15 min under nonselective conditions. The commercial product contained 35.6% *trans*. Palmitic acid (16:0) content is not recorded in Figures 2 and 3 because its content does not change during hydrogenation. Palmitic acid content of palm olein was 38.6% while that of the Malaysian hydrogenated olein was 31.9%. Changes in D.P. (dropping point) are also shown in Table 1. Figures 4 and 5 represent the changes in SFC at the various temperatures for selective and nonselective conditions, respectively. Selective hydrogenation resulted in higher levels of SFC at the same IV than nonselective hydrogenation, which

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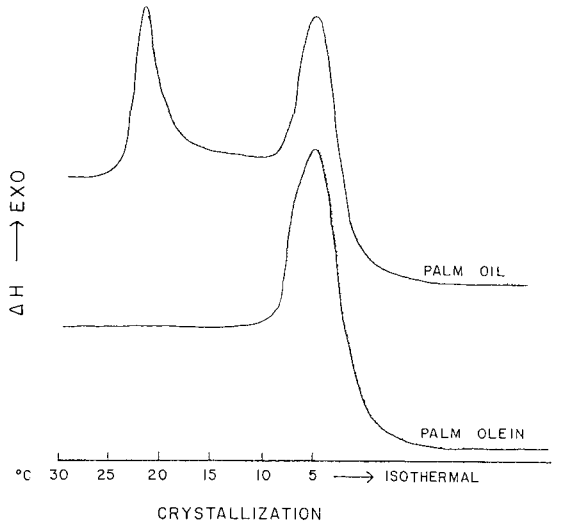

FIG. 1. Differential scanning calorimetry-crystallization curves of palm oil and palm olein.

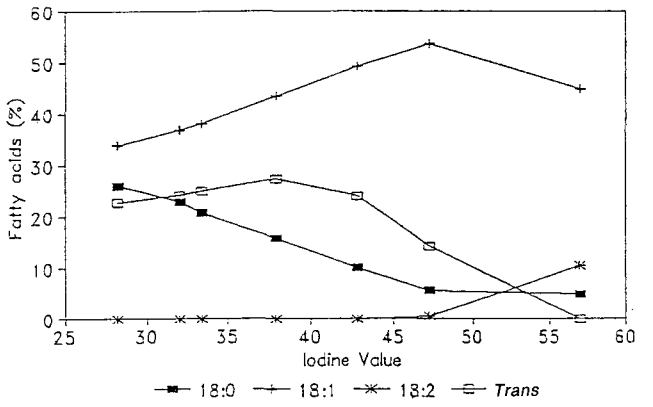

FIG. 2. Change in fatty acid composition during selective hydrogenation of palm olein.

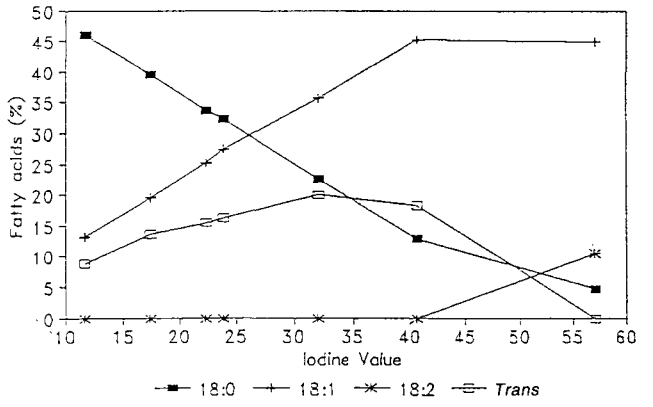

FIG. 3. Change in fatty acid composition during nonselective hydrogenation of palm olein.

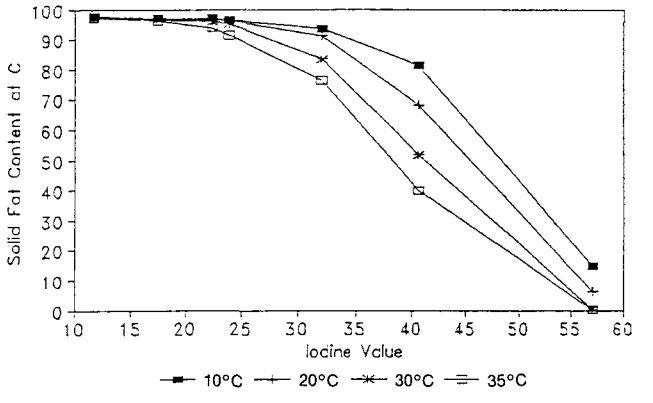

FIG. 4. Change in solid fat content at 10, 20, 30 and 35°C during selective hydrogenation of palm olein.

TABLE 1

Iodine Value (IV), Rate of Hydrogenation (IV/min) and Dropping Point (D.P.) Under Selective and Nonselective Conditions of Palm Olein

Hydrogenation time (min)	Selective			Nonselective		
	IV	IV/min	D.P. (°C)	IV	IV/min	D.P. (°C)
0	57.0		21.2	57.0		21.2
10	47.2	−.99	39.5	40.6	−1.64	47.1
15	42.8	−.95	46.3	32.0	−1.66	52.3
20	37.9	−.95	49.8	23.9	−1.66	54.4
25	33.4	−.95	51.8	22.5	−1.50	55.9
30	32.0	−.83	52.6	17.4	−1.32	57.0
35	28.2	−.82	53.8	11.7	−1.30	58.8

is the result of the elevated *trans* content in selective hydrogenation.

The laboratory-hydrogenated palm oleins were diluted with sunflower oil at a ratio of 30% hydrogenated palm olein and 70% sunflower oil. Based on the results of their SFC and D.P., six samples were chosen in the polymorphic stability study. The commercially hydrogenated palm olein was diluted with several levels of canola oil, of which three levels are reported because their SFC and D.P. are within the ranges of commercial soft and stick margarines (Table 3). Table 2 presents the characteristics of the hydrogenated and the diluted samples. Range and means of SFC and D.P. of commercial soft and stick margarines analyzed in our laboratory are shown in Table 3. After the fourth temperature cycle, all of the dilutions of hydrogenation palm oleins were still in the β' form, even the dilution of the commercially hydrogenated palm olein that contained 80% liquid oil (Table 2). For comparative purposes, dilutions of palm oil, hydrogenated palm oil and palm stearin are also included in Table 2. Hydrogenated palm oil (H-palm) is not as stable in dilution as H-palm olein. A small dilution of unhydrogenated palm oil (only 20% of liquid oil) showed some β crystallinity after the first cycle. Yet, palm oil in a mixture of hydrogenated canola oil can delay the formation of β crystals of the β-prone hydrogenated canola (10,11). Palm stearin was the least β'-stable.

The 20:80 and 40:60 dilutions of the commercially hydrogenated palm olein had SFCs and D.P.s similar to

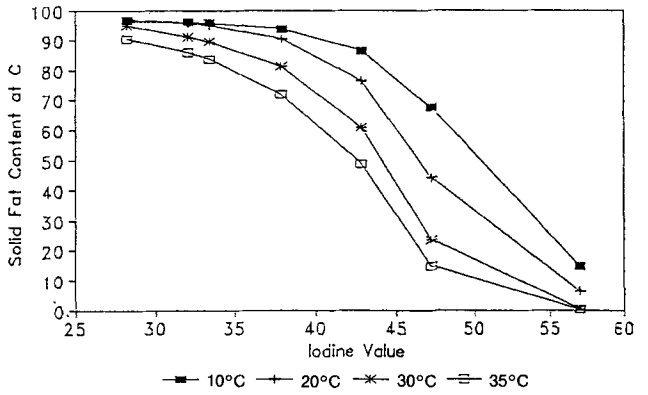

FIG. 5. Change in solid fat content at 10, 20, 30 and 35°C during nonselective hydrogenation of palm olein.

TABLE 2

Characteristics of Selected Hydrogenated Palm Olein Samples and Palm Products and the Same in Dilution with Liquid Oils[a]

Sample and ratio of sample in liquid oil	D.P. (°C)	SFC at 10°C (%)	Polymorphic form after number cycle	
H-Olein[b]				
SH[c]	39.5	67.4		
30:70	26.5	13.5	β′	4
SH IV 42.8	46.3	86.6		
30:70	36.5	20.0	β′	4
NSH[d] IV 40.6	47.1	81.3		
30:70	38.1	18.6	β′	4
SH IV 37.9	49.8	93.7		
30:70	41.4	23.7	β′	4
SH IV 32.0	52.6	95.9		
30:70	44.0	25.5	β′	4
NSH IV 32.2	52.3	93.5		
30:70	43.9	23.2	β′	4
Commercial H-Olein[e]	41.7	85.6		
40:60	35.8	26.4	β′	4
30:70	33.0	19.6	β′	4
20:80	30.2	12.8	β′	4
H-Palm Oil	42.1	69.9		
30:70	36.5	13.6	β′	4
25:75	34.9	12.9	β′ = β	4
Palm Oil	39.8	47.7		
80:20	38.6	31.7	β′ >> β	1
60:40	37.3	19.4	β > β′	1
Palm stearin	53.8	68.4		
60:40	50.3	35.7	β	1

[a]D.P., dropping point; SFC, solid fat content; IV, iodine value.
[b]Diluted with sunflower oil.
[c]Selectively hydrogenated.
[d]Nonselectively hydrogenated.
[e]Diluted with canola oil.

TABLE 3

Range and Mean of Solid Fat Content (SFC) at 10°C and Dropping Point (D.P.) of Commercial Soft and Stick Margarines (N = number of samples)

	Soft (N = 27)	Stick (N = 32)
SFC at 10°C		
Range	7.1-18.8	23.0-38.1
Mean	13.7	30.2
D.P.		
Range	27.3-34.2	31.5-35.8
Mean	31.3	33.4

those usually found respectively in soft and stick margarines (Table 3).

The advantage of hydrogenated palm olein is that a large amount of liquid oil can be incorporated in the soft formulation and that the mixture remains in the β′ form. Large amounts of liquid oil mean that the polyunsaturated fatty acids are preserved, and also that the process is cheaper because only a small amount of oil needs to be processed beyond refining.

The laboratory hydrogenation conditions used in this study did not produce large amounts of *trans* fatty acid and, as a result, the SFC curves were not as steep as that of the commercial Malaysian hydrogenated olein, which contained 85.6% solids at 10°C and which had a D.P. of 41.7°C. A sulfur-poisoned catalyst may be needed to obtain a desired SFC at 10°C of approximate 86% with a D.P. of about 42°C. A super olein, which is more unsaturated, may also produce more *trans* fatty acid and consequently produce a steep SFC curve.

For a soft margarine formulation with canola oil as the liquid oil, the total saturated content would be approximately 13%, and for a stick margarine formulation 17%. If a high content of polyunsaturated fatty acids is desirable, it is best to use sunflower oil as the liquid oil.

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