Chemical and Physical Properties of the High Melting Glyceride Fractions of Commercial Margarines[1]

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The fat obtained from nine commercial margarines purchased from Canada and the U.S.A. were crystallized from acetone at 15, 10, 5 and 0°C. The high melting triglyceride (HMG) fractions at 15°C contained high levels of palmitic and stearic acids. The 18:1 levels increased as fractionation temperature decreased. Triglyceride analysis revealed that the HMG fractions contained high levels of carbon 54 and 52. The levels of *trans* isomers increased, whereas the *trans* levels in the 18:1 decreased with fractionation temperature. Margarines made from canola oil exhibited β characteristics whereas canola-palm, soybean and corn margarines showed β' crystals. The fractions as crystallized from acetone, showed numerous X-ray short spacings, characteristic of β', β and intermediate forms. Upon heating and cooling, the 15°C fraction showed β' or α and β' characteristics regardless of the polymorphic form present in the original margarines. The differential scanning calorimetry (DSC) melting points of these fractions varied from 53 to 50°C. The difference between the β and β' margarines could be related to the 16:0 and carbon 54 content of the 15°C fraction. In the β tending margarines the 16:0 content was below 11%, in the β' tending margarines above 17%. The carbon 54 content in the 15°C fraction of the β tending margarines was close to 70% and that of the β' tending margarines around 50%. The triglyceride C54 in the 15°C fraction is β tending and therefore should be kept as low as possible. In canola margarines this can be achieved by incorporation of palm oil, preferably in a slightly hydrogenated form.

KEY WORDS: Fatty acids, fractionation, high melting glycerides, margarine, physical properties, polymorphism.

Margarines are manufactured from vegetable oils which are partially hydrogenated. In some cases liquid oil is also incorporated. During the hydrogenation process the double bonds of the fatty acids travel across the fatty acid chain resulting in positional and *trans* isomers (1–3). Formation of *trans* isomers influences the chemical and physical characteristics of the final product because *trans* isomers have higher melting points and greater stability than the *cis* fatty acids (4).

When a fat is cooled the high melting glycerides (HMG) crystallize first. It has been established that the HMG consists of saturated and unsaturated fatty acids. The former are present mainly as palmitic and stearic acid, whereas the latter exist mostly as *trans* isomers (5,6). The HMG can be separated from the original fat by selective cooling procedures or by solvent crystallization (7). Most of the earlier work reported in the literature on the HMG was done with milkfat. Palmer and Wiese (8) were the first to report on the isolation of HMG from milk fat globules at room temperature using ethanol. Since then several researchers have reported on the fatty acid composition of the HMG extracted from milk fat (9–12). Chen and deMan (13) separated milk fat into seven fractions using acetone as the solvent and classified them on the basis of chain length and degree of unsaturation as high, medium and low melting fractions. Persmark *et al.* (14) fractionated palm oil into nine fractions using acetone. Four fractions were investigated further to gain a better understanding of the chemical composition and polymorphic behavior. The first fraction contained high levels of palmitic acid and carbon C48 triglycerides. The percentages of these acids and triglycerides decreased with fractionation temperature.

The composition of the HMG of a fat will dictate the polymorphic form in which the solids will crystallize and their future behavior on storage. Learning more about the composition and physical characteristics of the HMG may help in understanding the crystallization behavior of margarines. Canola margarines tend to crystallize in the β polymorphic form, while soya and corn margarines crystallize in the β' form. It is known that incorporation of palm oil into canola margarines delays or prevents the formation of β crystals (15). This study was undertaken to characterize the fatty acid and triglyceride composition of the HMG fractions of a variety of stick margarines in order to get a better understanding of the reasons for their differences in polymorphic behavior.

MATERIALS AND METHODS

Nine margarines were purchased from supermarkets in Canada and the U.S.A. The margarines were melted in an oven, the oil phase was obtained by removing the aqueous layer, and this was followed by filtration and drying under vacuum.

The HMG were obtained as follows. The fat was melted in the oven and was dissolved in acetone in a ratio of one part by weight of fat to twenty parts by volume of solvent. The solution was left overnight in a water bath to crystallize at 15°C, and was filtered through a 0.45 μm Magna Nylon 66 filter paper (Honeoye Falls, NY) which was supported on a fritted glass vacuum holder. After removal of the fat crystals the filtrate was left overnight to crystallize at 10°C. The fat crystals were filtered and the filtrate was left to crystallize at 5°C. The same procedure was repeated at 0°C. The fat in the filtrate of 0°C crystallization was called the residue. The solvent was removed from the crystals under vacuum. The yield of each fraction was recorded.

Solid fat content (SFC) of the separated fat was measured by pulsed nuclear magnetic resonance (pNMR)

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using a Bruker PC/20 series NMR Analyzer (Minispec) (Bruker Spectrospin, Burlington, Ontario, Canada) according to AOCS method Cd 16–81, with tempering at 25°C instead of 26.7°C (16). Measurements were made at 10 and 21°C.

Fatty acid composition was determined by transesterification and analysis of the methyl esters by gas liquid chromatography (GLC) using a Shimadzu GC-8A gas chromatograph (Shimadzu Scientific Instruments, Columbia, MD) with a two meter, 4 mm ID glass column packed with 10% Supelco SP2330 on 100/200 mesh Chromosorb AW (Supelco, Inc., Bellefonte, PA) and operated at 170°C (17).

Analysis of triglycerides by carbon number was carried out according to the procedure described by Shehata *et al.* (18). A 30 cm glass column was packed with 3% OV-1 on 80/100 Supelcoport (Supelco). Chromatography conditions were detector (FID) and injector at 400°C, and oven programmed from 270°C to 355°C at 5°C/min.

Isolated *trans* fatty acids were determined by the infra-red spectrophotometric method (AOCS Cd 14-61) using a Beckman model 4230 infra-red spectrophotometer (Beckman Instruments, Fullerton, CA).

The polymorphic forms in the original samples and their fractions were established by X-ray diffraction using a Model FR 552 camera (Enraf Nonius, Delft, The Netherlands) which was operated at 23°C. The instrument was fitted with a fine focus copper X-ray tube. The sample holders were flat stainless steel plates 1 mm thick with a rectangular hole. The samples were contained in this space with adhesive tape. The X-ray film was scanned with a Zeineh soft laser scanning densitometer model SLR-504 XL (Biomed Instruments, Fullerton, CA). Short spacings on the X-ray film were measured with a Guinier viewer (Enraf Nonius).

The dropping point of the fats was determined with a Mettler FP3 automatic dropping point apparatus, using the procedure described by Mertens and deMan (19).

Differential scanning calorimetry (DSC) was used to determine the melting and crystallization behavior of the original fat and the fractions. Approximately 8–10 mg of fat was weighed in DSC pans. The pans were placed in closed aluminum dishes and left in a 70°C oven for 15 min. The fat was crystallized by placing the dishes in a freezing cabinet at −16°C for 1 hr before transferring the pans to the DSC unit for scanning. Heating curves were recorded from 15 to 70°C at a heating rate of 5°C/min. For the fractions collected at 15 and 10°C, cooling curves were recorded from 70 to 10°C. The fractions collected at 5 and 0°C were cooled from 70 to −10°C, using dry ice as a coolant. The cooling rates used were 5°C/min. In the original sample the melting curve was wide and rounded. Tangents were drawn and the point of intersection was considered as the melting temperature. Temperature of crystallization was taken as the temperature at the start of the exothermic deflection of the curve.

RESULTS AND DISCUSSION

The ingredients of the margarines as they were listed on the label and their country of origin are given in Table 1. These margarines have been previously analyzed by Postmus *et al.* (20) and deMan *et al.* (21) for the chemical, physical and textural characteristics. Canadian margarines are manufactured mainly from canola oil. The fatty acid profile of the original products is displayed in Figure 1 and the 16:0 content of the margarines is shown in Table 2. Canola margarines can be distinguished from soybean margarines by their palmitic acid content. Canola contains 4.5% of 16:0 (22), whereas soybean oil contains 10.5% (23). Palm oil, which has a palmitic acid content of 44%, is incorporated into canola margarine formulations to increase the diversity of fatty acid chain lengths and thereby delay or prevent the formation of β crystals (24). Cottonseed oil, which also has a high 16:0 content, used to be incorporated in soybean margarines for the same reasons, but this practice has been discontinued. As can be seen from Table 2, product A contained only canola oil. Its crystal structure was in the β form. Product B, in spite of having palm oil incorporated, reverted to the β form. Processing and storage conditions may have caused the

TABLE 1

Composition of Nine Stick Margarines

Country	Product	Composition (from label)
Canada	A	Hydrogenated vegetable oil (may contain palm oil)
Canada	B	Hydrogenated vegetable oil (may contain palm oil)
Canada	C	Hydrogenated vegetable oil (may contain palm oil)
U.S.	D	Vegetable oil blend (partially hydrogenated soybean and cottonseed oil)
U.S.	E	Vegetable oil blend (partially hydrogenated soybean and cottonseed oil)
U.S.	F	Liquid soy oil, partially hydrogenated soy oil
U.S.	G	Hydrogenated vegetable oil
Canada	H	Partially hydrogenated vegetable oil
Canada	I	Liquid corn oil, hydrogenated corn oil

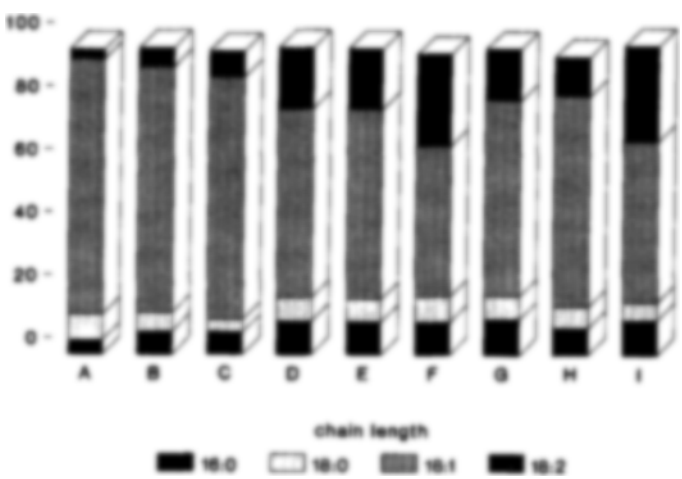

FIG. 1. Fatty acid composition of the fat in the original commercial margarines.

TABLE 2

Palmitic Acid Content of the Fat in the Original Margarines and its 15°C HMG Fraction and the Polymorphic Form in the Original Margarines

Product	16:0 (%)		Polymorphic form
	Original	15°C HMG	
A	4.6	7.9	β
B	7.4	11.2	β
C	7.5	24.6	β'
D	10.7	17.2	β'
E	10.6	18.6	β'
F	10.5	18.0	β'
G	11.5	21.3	β'
H	8.6	16.8	$\beta' + \beta$
I	11.2	18.9	β'

β crystal formation. Yap (15) has demonstrated that palm oil in the unhydrogenated form is less effective in delaying the β transition than hydrogenated palm oil. This is evident in product C, that contained hydrogenated palm oil. The U.S.A. samples all contained only soybean oil and they were in the β' form. Product H was probably a mixture of canola and soybean oil for reasons that will be discussed later. It contained a mixture of β' and β crystals.

The isolated *trans* content is shown in Figure 2. In the same Figure the isolated *trans* content is compared with the *trans* content divided by the 18:1 content in the original margarine. The isolated *trans* content in the original sample varied from 22.4 to 35.2%. It is assumed that the majority of *trans* fatty acids are monoene (18:1). Zalewski and Kummerow (25) found 41–47% *trans* in hard margarines and 18–20% in soft margarines.

The yield of the fractions collected at different temperatures is shown in Table 3. The highest yield was obtained at 15°C. The solid fat content (SFC) of the

TABLE 3

Yield of Fraction (%) Obtained by Crystallization at Various Temperatures

Product	Yield (%)			
	15°C	10°C	5°C	0°C
A	7.7	1.7	7.1	1.2
B	8.7	4.0	6.5	4.8
C	4.0	6.7	7.8	3.5
D	6.4	5.6	5.8	5.4
E	5.9	3.7	1.2	2.0
F	7.4	5.4	5.5	4.3
G	6.0	3.6	4.1	1.7
H	7.4	4.3	2.2	5.7
I	6.3	4.9	6.0	4.1

TABLE 4

Total Yield of the Fractions and the Solid Fat Content of the Margarines as Determined by the AOCS Tempering Method Cd 16-81

Product	Total yield	SFC (%)	
		10°C	21°C
A	17.7	31.3	14.7
B	24.0	33.6	16.7
C	22.0	34.9	16.6
D	23.2	26.6	15.1
E	12.8	31.6	14.2
F	22.6	25.3	16.5
G	15.4	30.6	17.8
H	19.6	29.8	15.4
I	21.3	27.7	14.8

margarine fats at 10 and 21°C and the total yield of the four fractions of the commercial margarines are tabulated in Table 4. When the total yield of the fractions is compared with that of the SFC of the fat it appears that the total fractionated solids are likely to be solids at around

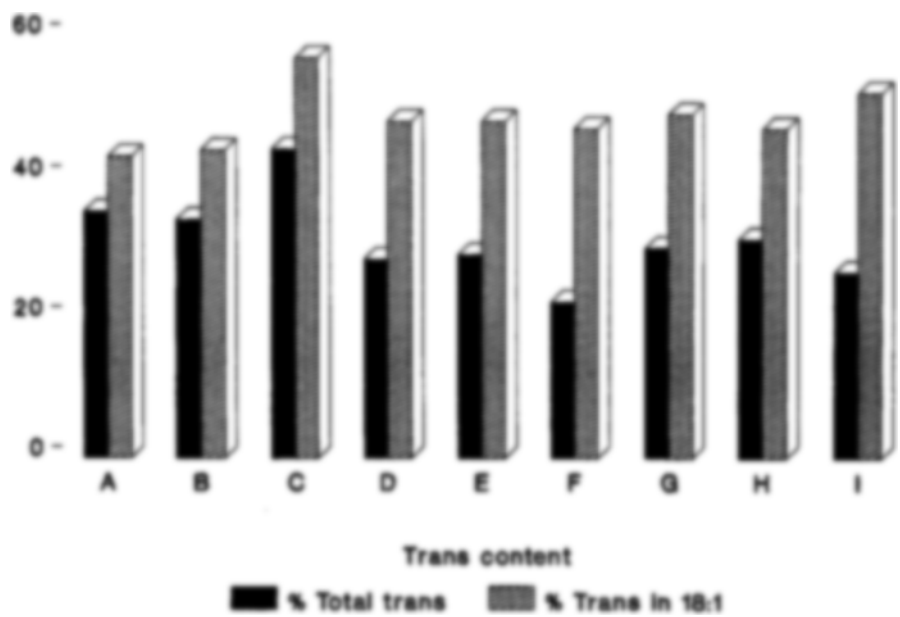

FIG. 2. *trans* Content of the fat in the original commercial margarines.

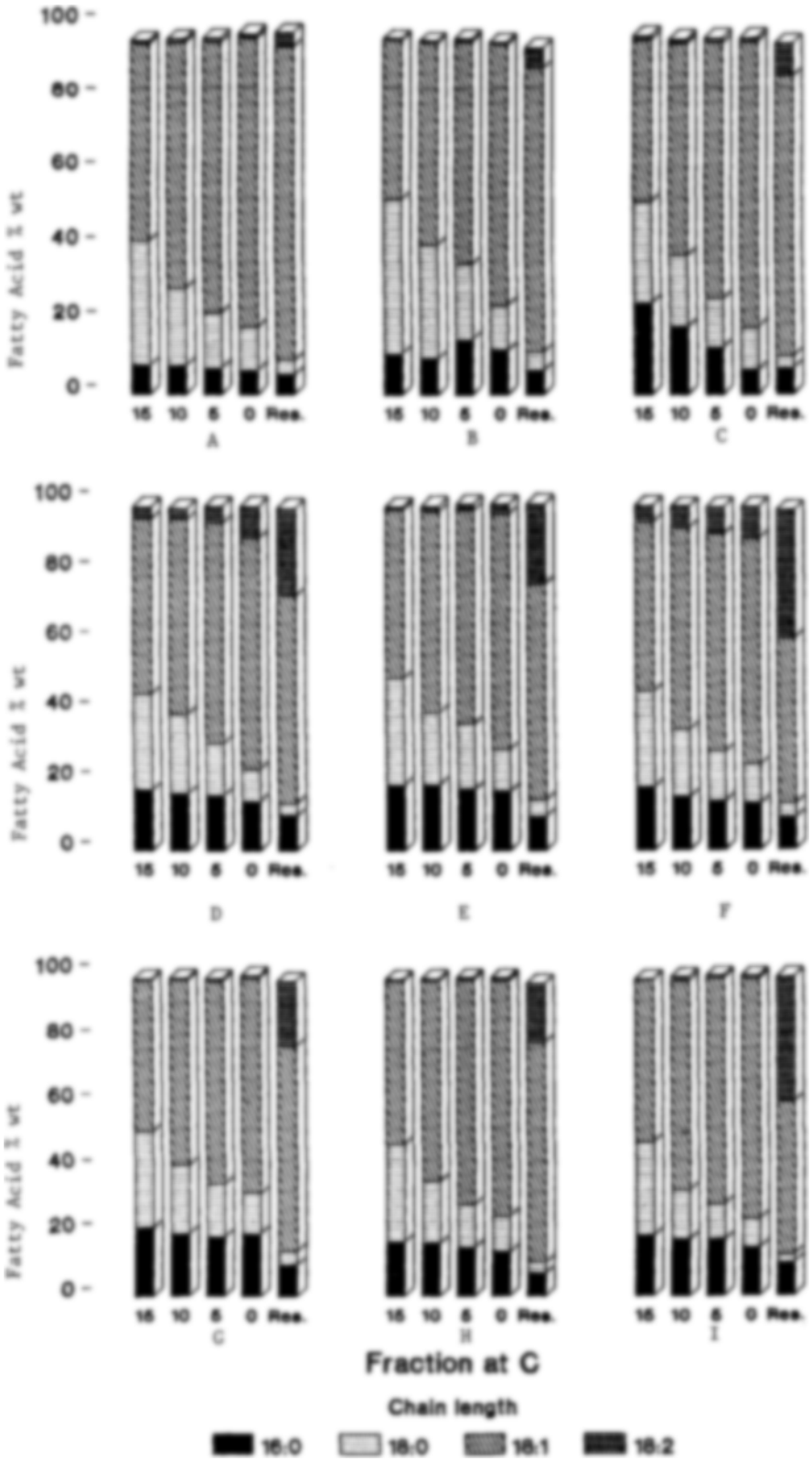

FIG. 3. Fatty acid composition of the HMG fractions crystallized at 15, 10, 5 and 0°C, and the residue.

21°C (products E and G) or between 10 and 21°C (the remainder of the samples) in the fat.

The fatty acid composition of the various fractions obtained by acetone crystallization is shown in Figure 3. Fractions crystallized at 15°C had the highest level of 16:0 and 18:0 which decreased with fractionation temperature. The unsaturated fatty acid (18:1) followed the opposite trend, i.e., as fractionation temperature de-

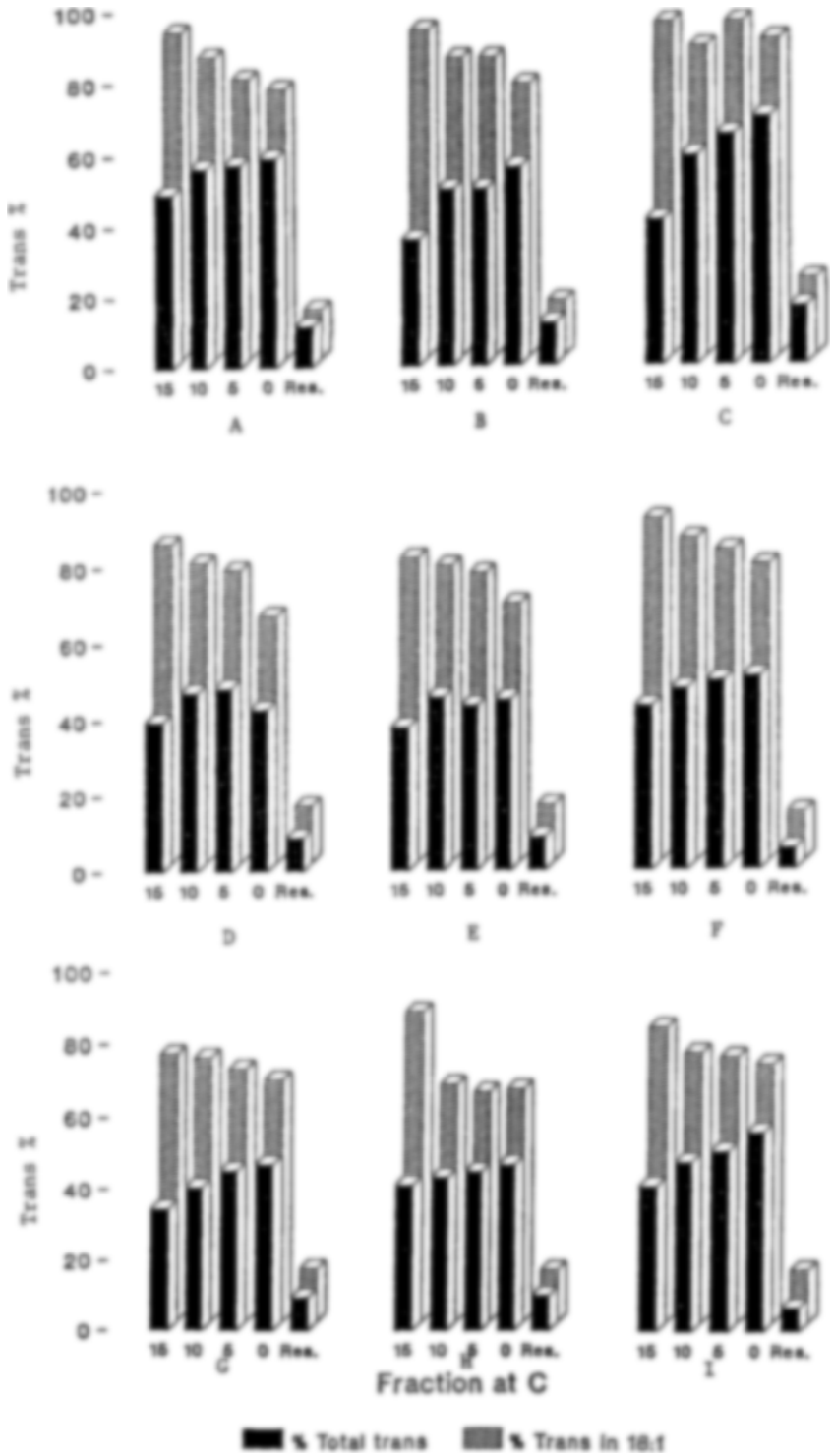

FIG. 4. ***trans*** **Content of the HMG fractions crystallized at 15, 10, 5 and 0°C, and the residue.**

creased the 18:1 content increased. The 16:0 content of the 15°C HMG of the soybean and corn margarines was much higher than that of the canola margarine A that contained no palm oil (Table 2). Therefore, the diversity of fatty acid chain lengths in the solids of the hydrogenated soybean oil is greater than that of canola oil. Addition of palm oil to hydrogenated canola oil contributes to the diversity of fatty acid chain lengths, as can be seen in the fractions of margarines B and C where the 16:0 content is higher (Table 2). The label of product C indicated that it contained hydrogenated palm oil and this could explain the higher content of 16:0 in the 15°C fraction. There was not much difference in fatty acid composition between the various soybean margarines and their fractions.

The total *trans* contents in almost all of the 15°C

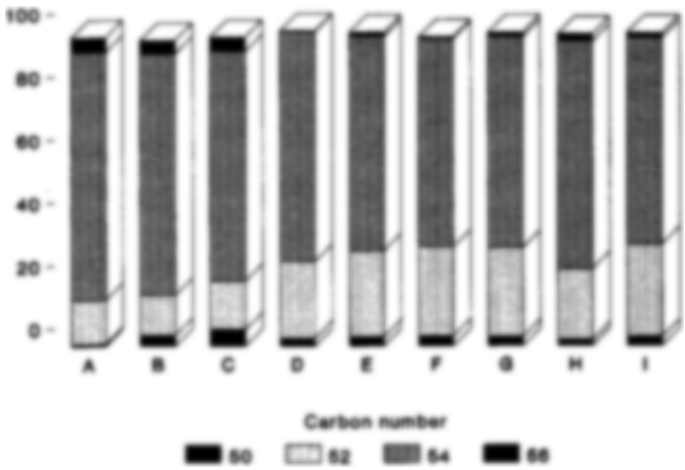

FIG. 5. Triglyceride composition of the fat in the original commercial margarines.

fractions were lower than those in the 10°C fractions (Fig. 4). This is due to the lower content of 18:1 in the 15°C fraction. The levels of *trans* isomers increased as fractionation temperature decreased. When the *trans* content is subtracted from the 18:1 content in each fraction, only a small amount of 18:1 is left, especially in the 15°C fraction. What is left of the 18:1 content is supposed to be in the *cis* form. However, the *cis* bond is not necessarily in the same position as it was in the original oil, and could have moved anywhere along the fatty acid chain. The *trans* content and the *trans* content calculated as percentage of 18:1 content of the fractions is presented in Figure 4. This percentage decreased with fractionation temperature.

The triglyceride composition of the original margarines as specified by carbon number is displayed in Figure 5, and those of the solids fractions and residue in Figure 6. The triglycerides composition in the higher melting solid fractions (I ig. 6) is more diverse than that in the original samples (Fig. 5). Since the oils consisted mainly of 16 and 18 carbon fatty acids it can be concluded that the triglyceride C48 in the solids (Fig. 6) consists mainly of tripalmitin which is derived from palm oil. Addition of palm oil increased the C50 triglycerides, especially in product C. The C50 triglycerides in the 15°C HMFs in both canola and soybean products consists of PSP or PEP (P, palmitic; S, stearic; and E, elaidic) with very small amounts of POP (O, oleic). PSP has been shown to be β' tending (26,27) and PEP a mixture of β' and β (28). The palmitic acid in both canola and soybean products is located in positions 1 and 3 (29,30). The C52 triglyceride in the 15°C HMF consists mainly of PS(E)S(E) or S(E)S(E)P. The triglycerides tend to exhibit β' and β characteristics of equal intensities (26). The soybean and corn margarines contained high levels of C52 triglycerides. These products were also lower in C54 triglycerides than canola margarines. The C54 triglycerides in the 15°C HMF consist mainly of S(E)S(E)S(E), which are β tending.

The triglyceride composition of the HMG fractions obtained at 15°C is tabulated in Table 5. Addition of palm oil increased the C48 and C50 triglycerides in products B and C. The fractions of soybean and corn margarines contained more of C50 and C52 triglycerides than the canola margarines. The fractions of Canadian margarines (A and B) contained higher levels of C54 triglycerides than soybean and corn margarines. Product H, which contained 8.6% palmitic acid (Table 2) contained no C48 triglycerides (Table 5), and therefore no palm oil. This leads to the conclusion that it was made of a mixture of canola and soybean oil. In all of the fractions the levels of C52 triglycerides decreased and C54 increased as fractionation temperature decreased (Fig. 6). The high levels of C54 triglycerides in the lower temperature fractions is due to an increase in the 18:1 content.

Table 6 lists the short spacings and their visually estimated intensities of the crystals of the original products A and F, the 15°C HMG obtained from acetone and the latter fraction after heating and rapid cooling. A typical scan of the X-ray film of the 15°C HMG is shown in Figure 7a. All of the acetone fractions exhibited numerous short spacings corresponding to the major polymorphic forms as well as several intermediate forms. Crystallization from acetone results in crystals of a complex nature. According to Moran (31) the intermediate short spacings may be due to the superimposition of the double chain length over an existing triple chain length structure. The significance of the additional spacings besides the typical ones for β and β' cannot be explained at the present time.

The fractions obtained at different temperatures were melted and cooled at room temperature and analyzed by X-ray diffraction. None of these heat treated fractions showed the presence of intermediate spacings that were observed in the crystals obtained by acetone crystallization. Most of the fractions collected at 15°C exhibited a diffuse band between 4.4 and 4.0 Å along with a strong line at 3.8 Å (Fig. 7b and Table 6). The presence of the diffuse band was probably caused by a mixture of α and β' forms. The diffuse band disappeared upon tempering at 40°C for 1 hr and cooling to room temperature (Fig. 7c). The X-ray diffraction patterns showed short spacings at 4.34, 4.21, 4.03 and 3.82 Å, respectively, which is characteristic of the β' form.

Dropping point of the fat was measured with a Mettler FP 3 apparatus. The determination of dropping point constitutes one of the several arbitrary methods to determine melting point of a fat. The dropping point and the melting temperature obtained by DSC for the

TABLE 5

Triglyceride Composition (%) of HMG Fractions Obtained at 15°C from Commercial Margarine Fats

	Carbon number				
Product	48	50	52	54	56
A	—	2.2	19.8	69.2	5.6
B	3.1	3.1	15.5	68.9	6.0
C	7.3	12.8	20.2	51.1	5.6
D	—	7.6	38.3	50.9	2.0
E	—	8.5	39.6	48.2	2.4
F	—	5.0	33.5	59.2	1.4
G	—	9.8	41.3	44.9	2.6
H	—	6.5	37.6	52.3	2.3
I	—	7.6	42.3	46.6	2.4

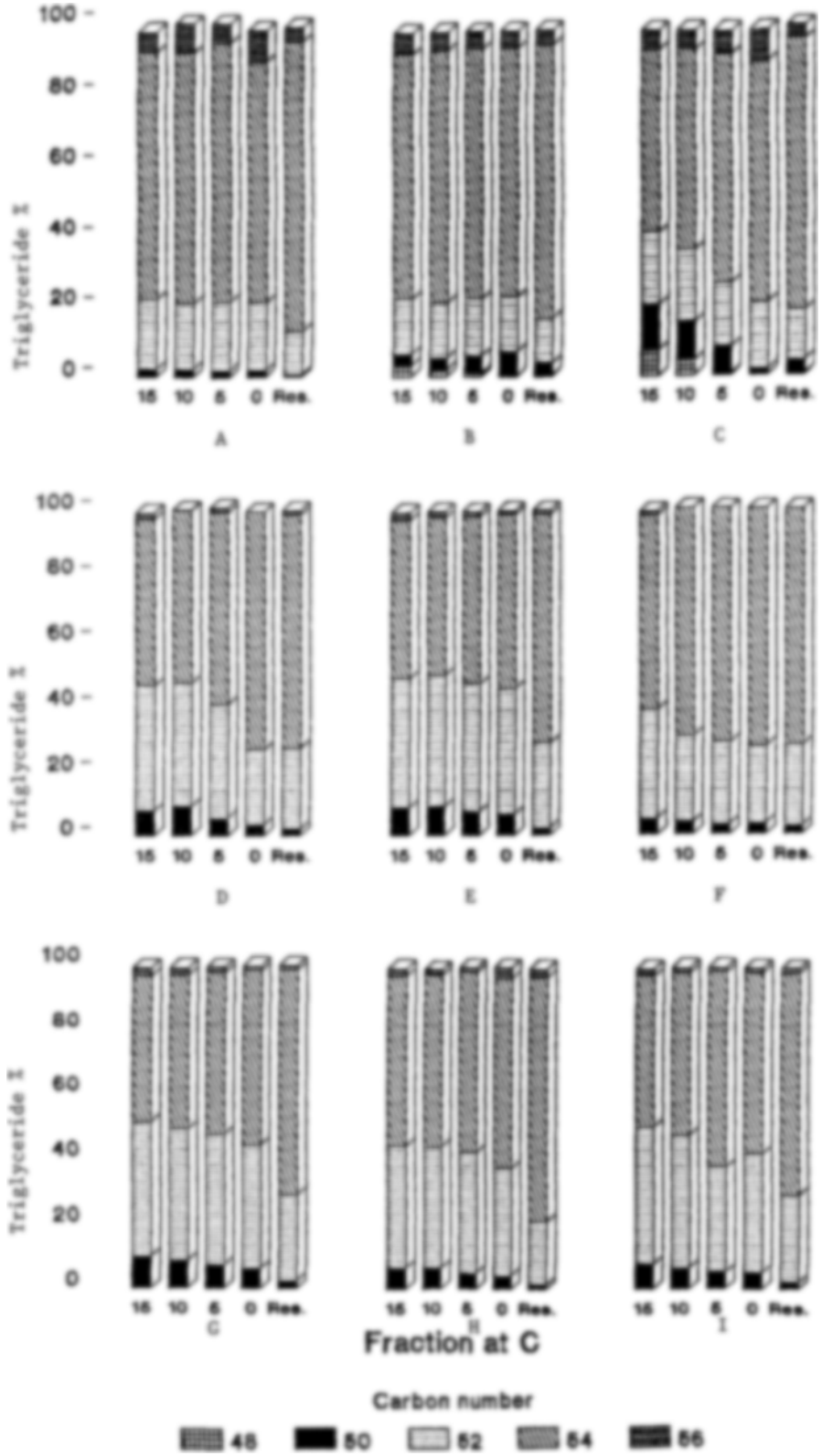

FIG. 6. Triglyceride composition of the HMG fractions crystallized at 15, 10, 5 and 0°C, and the residue.

original fats are tabulated in Table 7. The melting temperature of the original fat as determined by the Mettler dropping point was higher than that of the melting temperature obtained by DSC. The DSC melting peaks for the original fat samples were wide and rounded (Fig. 8a). The broad melting peak suggests that the fat has a wide melting range. The peak temperatures of the DSC-melting diagrams of the original samples, as

TABLE 6

Short Spacings (Å) of Original Fat and HMG (15°C) Obtained from Margarines A and F

Product	Shorting spacing (Å)[a]	Polymorphic
A (original fat)	4.57 S, 4.52 M, 4.43 W, 3.89 S, 3.77 W	β
A (HMG 15°C crystallized from acetone)	5.34 W, 5.25 W, 4.57 VS 4.40 W, 3.89 VS, 3.78 S, 3.66 M	$\beta' + \beta$
A (HMG 15 after heating to 70°C and cooling)	4.38–4.10 (d) S, 3.87 S	$\alpha + \beta'$
F (original fat)	4.40 VW, 4.20 S, 3.79 M	β'
F (HMG 15°C) crystallized from acetone	5.35 W, 5.24 VW, 4.59 VS, 4.53 S, 4.46 M, 4.37 M, 4.23 VS, 4.07 M, 3.90 VS 3.83 VS, 3.77 VS, 3.65 S	$\beta' + \beta$
F (HMG 15 after heating to 70°C and cooling)	4.30–4.20 (d) M, 3.84 M	$\alpha + \beta'$

[a]Typical short spacings for α, 4.15; β', 4.2, 3.8; β, 4.6; S, strong; M, medium; V, very; W, weak intensities; and d, diffuse.

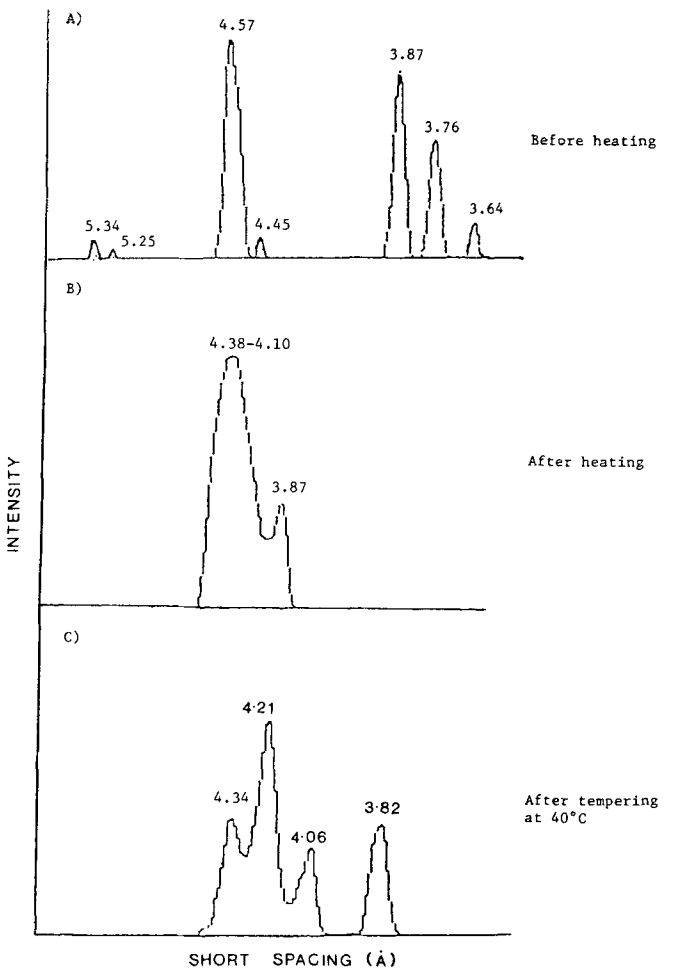

FIG. 7. Typical laser densitometer scans of X-ray film data of the HMG fraction of margarine H (acetone, 15°C). A, Solids crystallized from acetone (15°C); B, solids heated at 70°C and cooled at 0°C; and C, as in B, but tempered at 40°C and cooled at room temperature.

determined by drawing of the tangents to the slope of the broad melting peak (Fig. 8a) can give some indication of this melting range. In contrast, the fractions of these samples obtained at different temperatures showed a sharp endothermic peak (Fig. 8b). The peak temperatures are displayed in Table 7. The melting temperature decreased with fractionation temperature. This is due to the decrease in the levels of saturated fatty acids and *trans* isomers. In some cases an exothermic peak was observed for the HMG fractions collected at 15°C (Fig. 8b). The exothermic peak signifies a polymorphic transition. The exothermic peak disappeared when the sample was tempered at 40°C for 1 hr (Fig. 8c). The crystallization temperatures for the original sample and their fractions are given in Table 8. Crystallization temperature decreased with fractionation temperature.

The polymorphic forms of the fractions directly obtained from acetone are far more complex than those of the original margarines. The short spacings of these fractions cannot be used to predict the polymorphic behavior of the final product. Neither can the polymorphic forms of the heated and cooled fractions be used to predict the polymorphic behavior of the final product because these fractions occurred in the α and β' forms, but not in the β form.

The high melting fractions contained much higher levels of saturated fatty acids (16:0 and 18:0) and *trans* isomers than that of the original product or residue. The diversity of the fatty acid chain lengths is much greater in the solids than in the original product. In the 15°C HMG of the β tending margarines the 16:0 content was less than 12%, while that of the β' tending margarines was over 17% (Table 2). The C54 triglyceride content in the 15°C HMG of the β' tending margarines was about 50% (product F excluded), whereas that of the β tending margarines was 70%. The C54 triglycerides in the 15°C HMG are β tending.

In the formulations of stick margarines, especially canola-palm mixtures, predictability of polymorphic stability could be obtained by analysis of the triglyceride composition of the 15°C HMG. If the C54 content is over 50% the potential of β crystal formation is likely.

TABLE 7

Dropping Points of Original Fats and Temperature of the DSC Melting Peaks of the Original Fat and HMG Fractions

Product	Dropping point	Original fat	Temperature of DSC-melting peaks			
			15°C	10°C	5°C	0°C
A	33.7	24.5	54.0	40.0	36.0	30.0
B	34.5	31.5	54.5[a]	44.0	37.0	27.5
C	33.2	29.5	55.5	46.5	39.0	29.5
D	32.6	30.6	53.0	46.5	38.0	30.0
E	32.7	30.5	52.5[a]	46.5[a]	40.0	30.0
F	33.4	26.0	52.5	44.0	36.0	33.5
G	33.8	32.0	55.0[a]	47.5	40.5	38.5
H	34.3	31.0	54.0	46.0[a]	40.0	36.0
I	32.9	32.0	53.0	45.0	35.0	30.0

[a]Melting diagrams show an exothermic peak.

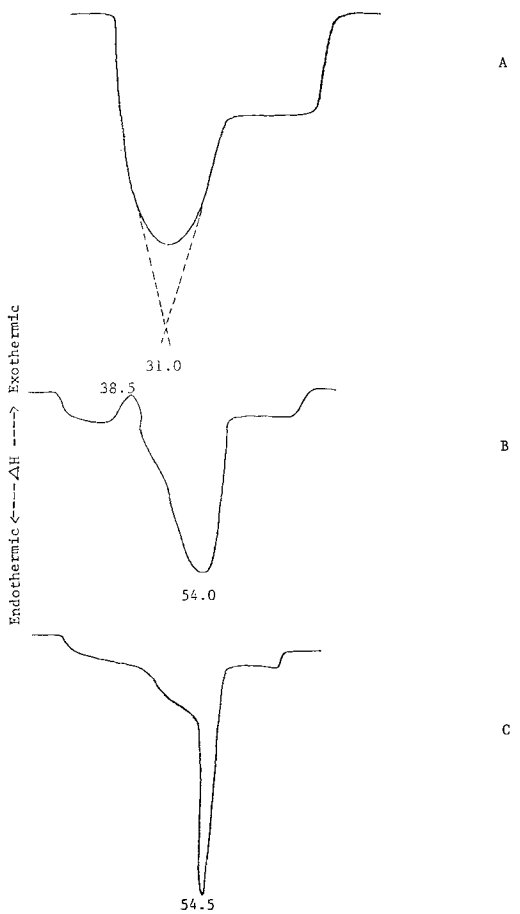

FIG. 8. Typical DSC heating curves (5°C/min) of product H. A, Original fat; B, solid fraction (acetone 15°C) heated to 70°C and cooled at 0°C; and C, as in B after tempering at 40°C.

Increase of palm oil addition, preferably in a slightly hydrogenated form, would then be desirable. This would allow the incorporation of a canola oil hydrogenated to a lesser extent with a higher content of polyunsaturated fatty acids than those that are presently on the market.

TABLE 8

Crystallization Temperatures of Fractions Obtained from Stick Margarines

Product	Original	15°C	10°C	5°C	0°C
A	21.5	37.5	22.0	13.0	10.0
B	20.3	36.5	27.5	20.0	15.0
C	20.5	39.0	29.0	19.0	13.0
D	15.5	26.0	29.0	17.5	15.0
E	16.3	33.0	25.0	19.0	13.5
F	15.3	37.5	25.0	16.0	9.0
G	18.4	26.5	30.0	22.5	18.0
H	16.6	35.0	26.0	20.2	10.1
I	15.7	32.5	24.0	20.0	10.0

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