Polymorphic Stability of Some Shortenings as Influenced by the Fatty Acid and Glyceride Composition of the Solid Phase

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A number of North American vegetable and animal fat shortenings, which had been analyzed previously for their physical and textural characteristics, were analyzed also for their chemical composition. The fatty acid and triglyceride composition of the solids were calculated by analyzing the composition of the original product and the liquid phase, and by determination of the solid fat content (SFC) of the fat. The solids were also isolated by isopropanol (IP) separation, and the high melting glycerides (HMG) by acetone crystallization at 15°C. There was not much difference in total saturates and *trans* content between vegetable and animal fat shortenings. Changing formulations from soy-palm to soy-cottonseed does not change the total saturates plus *trans* content. The solids of the vegetable shortenings in the β form contained about 20% of 16:0, those in the β′ form 30% or more. The animal fat shortenings were mainly in the β form, their solids contained 30% or more of 16:0. C54 triglyceride content of the solids of β vegetable shortenings (calculated and IP-separated) was >45%, that of all animal fats was <25%. Solids of animal fat shortenings contain high levels of C52. The C54 triglycerides are β-tending and should be kept low in vegetable shortening. In the HMG the C54 should not exceed 30%. This can only be achieved by incorporation of a β′ hard fat, preferably palm hard fat. Animal fat, especially lard, crystallizes in the β form because the palmitic acid in the glyceride molecule is located in the 2-position, whereas those of vegetable fats are in the 1- and 3-position.

KEY WORDS: Animal fat, cottonseed oil, fatty acid, palm oil, polymorphism, shortening, solids, triglyceride.

In a previous paper by deMan *et al.* (1) the physical and textural characteristics of a number of North American vegetable and animal shortenings were reported. X-ray diffraction analysis showed that the fat crystals of most of the vegetable shortenings were in the beta prime (β′) form, whereas those of the animal fat shortenings were in the beta (β) form. In the USA, soybean oil is mainly used in vegetable shortening formulations. A fully hydrogenated β′ hard fat is added, which is usually made from palm oil, in order to extend the plastic range and to stabilize the β′ polymorphic form of the fat crystals (2,3). Addition of palm hard fat is usually at the level of 10 to 12% (2). Because of the bad publicity palm oil has received in the USA, companies have been forced to replace palm hard fat with cottonseed hard fat. DeMan *et al.* (4) have studied a variety of hard fats and found that palm hard fat was the most β′-stable.

In Canada, canola oil is the major oil and is therefore incorporated into shortening formulations, but only to a certain level (5). Canola oil, when hydrogenated, is a β-tending fat, more so than hydrogenated soybean oil. Therefore, soybean oil at present is not usually substituted entirely with canola oil in shortening formulations.

Mattel and Norris (6) have pointed out that, when the higher melting fraction of a fat is comprised of glycerides that are stable in the β′ form, the entire fat will crystallize in the β′ form. However, it is difficult to separate the higher-melting fraction and the solids from the liquid phase. Van der Hoek (7) separated the solid fat from vegetable margarines by a pressure filtration method. Postmus *et al.* (8) obtained the oil in the liquid phase of margarines by inserting chromatography paper strips into the product and letting the oil rise. D'Souza *et al.* (9) separated the high-melting glycerides (HMG) of a series of stick margarines by means of acetone fractionation at 15°C. Polymorphic stability could be predicted by triglyceride analyses. When the C54 content was over 50%, the potential of β crystal formation was high. Chawla and deMan (10) separated the solid and liquid components of a fat by means of isobutanol.

This study was undertaken to examine the predictability of crystal stability of a series of shortenings. Since nutritional studies (11,12) have shown that *trans* fatty are undesirable, the shortenings were also analyzed for their *trans* content.

MATERIALS AND METHODS

Samples were the same as those reported by deMan *et al.* (1), who analyzed the shortenings for physical and textural characteristics. Two additional shortenings were purchased in the USA in 1991, they were labelled to contain hydrogenated soybean and cottonseed oils (Table 1, No. 4 and No. 5). The liquid oil in the shortening was separated from the solids by inserting Whatman No. 1 chromatography paper strips into the product and letting the oil rise (8). The oil was extracted from the filter paper with hexane.

The HMG were crystallized from an acetone solution of the fat at 15°C (5 g of fat in 100 mL of acetone), which was filtered through a 0.60-μm Magna Nylon filter paper (Magna, Honeoye Falls, NY) (9).

The solid fat in the shortening was separated by suspending 2 g of shortening in 12 mL of isopropanol by means of a glass pestle tissue grinder. The suspension was transferred to a 50-mL stoppered tube. The tissue grinder was rinsed with 3 × 5 mL of isopropanol, which was added to the first suspension. The final suspension was well agitated before filtering as outlined above.

Fatty acid composition, isolated *trans* fatty acids and triglyceride analyses were determined as outlined by D'Souza *et al.* (9).

RESULTS AND DISCUSSION

Composition of the major fatty acids of the original shortenings and the liquid phases are presented in Table 1. Because the palmitic acid (16:0) content of soybean and canola oil does not change during hydrogenation (the 16:1

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TABLE 1

Composition of the Major Fatty Acids (%) of the Original Shortenings (orig) and Their Liquid Phases (liq)

Sample	16:0		18:0		18:1		18:2		*Trans*	Saturates + *trans*
	Orig	Liq	Orig	Liq	Orig	Liq	Orig	Liq	Orig	Orig
Vegetable (USA)										
1. Soy-palm	16.1	10.8	10.9	5.1	43.7	48.2	26.3	32.4	16.0	43.0
2. Soy-palm	14.0	10.9	10.9	5.4	46.9	48.9	25.9	31.3	19.4	44.3
3. Soy-palm	16.0	11.1	11.2	6.0	42.8	47.2	26.7	31.6	13.4	40.6
4. Soy-cottonseed	13.6	10.3	7.1	5.5	45.6	46.7	30.2	33.8	20.3	41.0
5. Soy-cottonseed	13.2	10.5	11.5	3.6	42.2	46.1	30.0	35.7	21.0	45.7
6. Canola-soy-palm	11.1	5.6	10.5	4.8	66.2	75.6	8.2	10.0	20.1	41.7
7. Canola-soy-palm	11.3	5.9	10.8	5.0	64.5	73.4	9.5	11.5	18.5	40.6
8. Canola-palm	7.5	3.6	13.1	4.8	70.3	81.4	5.1	6.5	37.3	57.9
9. Soy	11.0	8.8	14.0	5.3	44.5	47.9	25.5	32.6	18.2	43.2
10. Palm-vegetable	30.3	23.0	6.7	4.7	52.2	57.9	8.5	10.9	16.6	53.6
11. Palm-palm kernel	36.4[a]	29.8[b]	6.7	4.1	32.0	35.3	7.1	8.2	9.3	69.5
Animal										
12. Lard, USA	24.6	21.2	15.8	6.7	42.9	51.4	9.9	12.3	.9	41.3
13. Lard, Can	24.0	20.9	14.8	7.1	41.9	49.1	11.6	13.8	2.0	40.8
14. Lard, Can	24.8	22.3	14.8	7.6	42.3	48.8	9.6	11.3	1.7	41.3
15. Tallow-lard, Can	25.5	20.4	19.3	12.4	39.8	48.7	5.3	7.2	3.4	48.2
16. Tallow-lard, Can	25.2	20.7	20.2	12.5	39.2	48.8	5.7	7.8	3.0	48.4
17. Meat-veg, USA	20.9	18.0	16.4	8.7	44.5	52.0	10.0	12.9	6.0	43.3
18. Meat-veg, USA	22.6	19.3	17.1	8.3	42.5	51.1	9.8	12.6	4.3	44.0
19. Veg-tallow, Can	17.7	13.5	19.7	7.8	43.2	54.9	9.9	12.9	1.6	39.0
Pure oils and fats										
Tallow	24.5		19.1		45.2		2.7			
Soybean oil	10.6		4.1		22.7		54.7			
Canola oil	4.5		2.0		55.0		26.0			
Cottonseed hard fat	23.0		76.2							
Palm hard oil	42.6		54.3							

[a]Also contains 12.2% of 12:0 and 4.9% of 14:0. [b]Also contains 14.3% of 12:0 and 5.4% of 14:0.

content is very low), the 16:0 content is often used to identify the two oils. Judging from the 16:0 content of the liquid phase of samples 1 to 5 (Table 1), it appears that this phase was mainly derived from soybean oil (the 16:0 content of soybean oil is 10.6% and of canola oil 4.5%). The 16:0 content of the liquid phase of samples 6 and 7 (Table 1) was 5.6 and 5.9, respectively, which indicates that these contain more canola than soybean oil in that phase. In the canola-palm sample (No. 8), the 16:0 content is lower than that of canola oil, which would indicate that some of the palmitic acid ended up in the solids. The percent difference between the 16:0 content in the original samples and that of their liquid phases is more pronounced in the vegetable shortenings (except the soy only) than in the animal fat shortenings.

The 18:0 content in all samples was lower in the liquid phases than in the original samples, indicating that the solids contained most of the stearic acid.

The 18:1 and 18:2 contents in all samples were higher in the liquid phases than in the original samples, indicating that the solids contained less of these fatty acids. The 18:2 content of the liquid phases of samples 1 to 9 was considerably lower than that of either soybean or canola oil, the oils they were drived from (Table 1), because the oils were partially hydrogenated.

The *trans* content of the vegetable shortenings was much higher (exception No. 11) than that of the animal shortenings. But when the total saturates and *trans* content were calculated, the differences between the vegetable and animal shortenings were minor.

Judging from the 16:0 content of sample 2 (Table 1), it probably also contained cottonseed hard fat instead of palm hard fat. The texture of this sample was quite similar to that of soy-cottonseed samples 4 and 5, which were softer than the soy-palm samples 1 and 3, as analyzed by deMan *et al.* (1). Changing a shortening formulation from soy-palm to soy-cottonseed does not decrease the total saturates plus *trans* content.

The polymorphic crystal forms as established previously (1) are presented in Table 2. One symbol (>) signified approx. 10%. It is thought that fatty acid chainlength diversity in the solids promotes β' crystallinity (13). For this reason, the 16:0 content in the solids was calculated from the 16:0 contents of the original samples and of the liquid phases (Table 1) and the solid fat content at 20°C as determined by pulsed nuclear magnetic resonance (pNMR) of the fat according to the AOCS method, with a tempering step at 30°C instead of 26.7°C. This tempering step was found by deMan *et al.* (1) to give a better estimate of the solid fat in shortenings than a tempering step at 26.7°C. The formula is:

$$\%\ 16{:}0 \text{ in solids} = \frac{\%\ 16{:}0 \text{ in original} - \%\ 16{:}0 \text{ in liquid} \dfrac{(100 - \text{SFC})}{100}}{\text{SFC}} \times 100$$

TABLE 2

Calculated 16:0 Content in the Solids and the Solid Fat Content According to the AOCS Method with Tempering at 30°C, and the Polymorphic Form of the Crystal in the Shortening

Sample	Solid fat at 20°C	16:0 Content in solids at 20°C	Polymorphic form
1. Soy-palm	17.8	40.6	β′
2. Soy-palm (cottonseed)	15.8	30.5	β′
3. Soy-palm	17.3	39.5	β′
4. Soy-cottonseed	14.8	32.6	β′
5. Soy-cottonseed	15.1	28.4	β′>>>β
6. Canola-soy-palm	16.5	38.9	β′
7. Canola-soy-palm	16.5	38.6	β′
8. Canola-palm	19.9	23.2	β>>β′
9. Soy only	20.1	19.7	β
10. Palm-vegetable	29.4	47.8	β′
11. Palm-palm kernel	22.6	59.0	β′
12. Lard	26.9	33.8	β
13. Lard	26.2	32.7	β>>>β′
14. Lard	25.3	32.2	β
15. Tallow-lard	27.0	39.3	β>>>>β′
16. Tallow-lard	28.7	36.4	β
17. Meat-vegetable	25.0	29.6	β′>>>β
18. Meat-vegetable	26.9	31.6	β′=β
19. Vegetable-tallow	26.6	29.3	β

TABLE 3

Composition of the Major Fatty Acids of the Isopropanol-extracted Solids from Some Shortenings

Sample	Fatty acid		
	16:0	18:0	18:1
Soy-palm	40.5	37.2	19.6
Soy-canola palm	37.4	37.8	22.6
Canola-palm	20.4	37.7	38.9
Palm-vegetable	50.4	11.9	34.7
Vegetable-tallow	29.9	54.2	9.3
Lard	33.6	36.4	22.4

TABLE 4

Fatty Acid Composition of HMG of Some Shortenings

Sample	Fatty acid		
	16:0	18:0	18:1
Soy-palm	40.7	40.6	15.0
Canola-soy-palm	39.8	42.3	15.9
Soy-cottonseed	30.1	50.8	17.5
Canola-palm	27.6	47.6	21.7
Palm-vegetable	56.5	14.0	26.8
Vegetable-Tallow	30.6	59.2	4.5
Lard	36.4	44.4	14.4
Commercial tallow	33.2	37.3	22.0

The results are shown in Table 2. The 16:0 content is high in samples containing palm oil, except in sample 8. The estimated palm hard fat content in this sample was 7.6%, whereas the soy-palm samples contained at least 12%. The solids of sample 8 were mainly in the β form. The solids of the product containing soy only (No. 9) were completely in the β form, and its 16:0 content was the lowest of all samples. The solids of the soy-cottonseed shortenings contained lower amounts of 16:0 than the soy-palm samples because cottonseed is lower in 16:0 than palm (cottonseed 23% and palm 44%). This may result in a lowering of β′ stability, as shown in sample 5 (Table 2).

The solids of the animal fat shortenings also contained high levels of 16:0, yet their solids were mainly in the β form. The theory of fatty acid chainlength diversity promoting β′ stability holds true for vegetable fats but not for animal fats.

In order to check the calculated 16:0 content of the solids (Table 2), the solids of some samples were isolated by the isopropanol method, and the fatty acid composition was determined. Since shortenings containing the same fats were also similar in fatty acid composition (Table 1), only a few of the samples were selected. Results are shown in Table 3. The 16:0 content obtained by the two methods is quite similar (Table 2 and Table 3). There are still substantial amounts of 18:1 fatty acids present in the isopropanol-separated solids, which in the case of the vegetable shortenings are probably present in the *trans* form.

The HMG were also separated from some of the shortening samples, and the fatty acid composition was determined. Results are shown in Table 4. The tallow sample was not processed and, therefore, the solids were not separated with isopropanol. The 16:0 and 18:0 contents were higher and the 18:1 content was lower in the HMG than in the isopropanol-separated solids. The yields of the HMG were also lower than those of the isopropanol-separated solids. The yield of the latter compared well with the solid content in Table 2 except for the lard sample, whose isopropanol solids were lower than that in Table 2. Some of the lard triglycerides may have dissolved in isopropanol.

D'Souza *et al.* (9) examined the fatty acid chainlength diversity in HMG of vegetable stick margarines and found that for stick margarines to be in the β′ form the 16:0 content of the HMG had to be approximately 20%. Stick margarines are stored at refrigerator temperatures, whereas shortenings are stored at room temperature. There is more stress on the crystal structure at higher temperatures. Therefore, for vegetable shortening the requirement for chainlength diversity in the HMG is increased if the solids must remain in the β′ form. This theory does not hold true for animal fat shortenings.

The original shortenings and their liquid phases were also analyzed for triglyceride composition by carbon number. The triglyceride composition of the solids was then calculated as described in the previous formula. Results are shown in Table 5. The isopropanol-separated solids were also analyzed for triglyceride content. Results are shown in Table 6. There is little difference between the calculated triglyceride compositions and those of the isopropanol solids except for the lard sample. As mentioned previously, the yield of the isopropanol solids from lard was lower than that of the solids in Table 2. The solids of the β-form vegetable shortenings (canola-palm and soy only) contained the highest level of C54 (Table 6).

The triglyceride composition of the HMG of some of the shortenings is displayed in Table 7. The C54 content

TABLE 5

Calculated Composition of the Major Triglycerides in the Solids of the Shortenings

Sample	Carbon number (%)			
	48	50	52	54
Soy-palm	7.7	34.7	39.6	16.1
Soy-palm	7.0	31.6	37.1	24.4
Soy-cottonseed	2.5	22.3	36.9	37.6
Canola-soy-palm	6.1	29.7	34.4	27.3
Canola-soy-palm	6.7	32.5	38.4	24.2
Soy only	2.5	12.1	27.2	46.7
Palm-vegetable	12.0	40.5	30.6	15.1
Palm-palm kernel	24.4[a]	34.0	20.9	5.1
Lard, USA	1.5	16.0	75.3	7.8
Lard, Can	1.7	13.4	77.3	6.5
Lard, Can	3.1	16.7	72.8	4.7
Tallow-lard, Can	9.0	35.3	55.3	9.6
Tallow-lard, Can	7.9	27.8	53.9	13.4
Meat-vegetable, USA	6.2	19.1	53.1	18.9
Meat-vegetable, USA	4.9	19.3	56.7	15.7
Vegetable-tallow, Can	8.5	21.8	43.0	24.1

[a]Includes lower-carbon triglycerides.

TABLE 6

Composition of the Major Triglycerides in the Solids Extracted by Isopropanol of Some Shortenings

Sample	Carbon number (%)			
	48	50	52	54
Soy-palm	7.2	34.5	37.0	19.4
Canola-soy-palm	6.7	32.8	36.3	21.5
Canola-palm	2.7	17.5	29.5	44.3
Soy only	1.9	11.6	25.9	53.9
Palm-vegetable	19.6	42.1	26.8	10.1
Lard	4.6	26.1	61.1	7.6
Meat-vegetable	5.9	20.8	50.0	21.5
Vegetable-tallow	9.3	23.2	44.2	21.1

TABLE 7

Composition of the Major Triglycerides in the HMG of Some Shortenings

Sample	Carbon number (%)			
	48	50	52	54
Soy-palm	8.4	36.5	36.7	16.7
Canola-soy-palm	8.5	37.0	36.9	16.5
Canola-palm	3.8	25.5	33.8	32.3
Palm-vegetable	25.5	41.0	23.5	7.8
Lard	8.4	29.5	47.0	12.9
Vegetable-tallow	9.2	25.7	41.6	20.6
Tallow	14.4	30.6	34.9	17.1

of the HMG is lower than those of the isopropanol solids (Table 6), whereas the C48 level is higher. Because the oils consisted mainly of 16- and 18-carbon fatty acids, the C48 triglycerides consist mainly of tripalmitic acid and the C54 of stearic, elaidic and positional 18:1 *cis-* and *trans-*isomers with higher melting points than the original oleic acid (14). Part of the high level of calculated C48 (24.4%) in Table 5 of the palm-palm kernel sample was derived from palm kernel oil, which contains 12:0 and 14:0 fatty acids (approximately 48 and 16%, respectively), and therefore only part of the C48 consisted of tripalmitin. In the HMG of stick margarines, D'Souza *et al.* (9) showed that a high percentage of the 18:1 fatty acids were in the *trans* form. Tripalmitic and tristearic are β-tending triglycerides. The *trans* fatty acids behave like stearic acid. In vegetable oils 16:0 is mainly located in the 1- or 3-position of the glyceride molecule. C50 consists mainly of PSP (or PEP) and C52 of PSS (or PEE). These triglycerides are more stable in the β' form (15). In vegetable shortenings it is important to keep the C54 low in the HMG, possibly as low as 20%. This can only be achieved by addition of a β' hard fat in sufficient quantity.

Cottonseed hard fat contains approximately 40% of C54 and is less effective than palm hard fat, which contains only 11% of C54, in suppressing polymorphic transition from the β' to the β form.

In our previous paper (1) it was pointed out that the palm-vegetable and the palm-palm kernel shortening (No. 10 and No. 11, Table 1) had a unique texture. The crystal structure as seen under the polarizing microscope was very fine. Upon prolonged storage at room temperature, the crystal structures had not changed in spite of the fact that the HMG of the palm-vegetable sample contained 25% C48 (Table 7), which is a β-tending triglyceride.

According to Christie (13), 17 mol% of the palmitic acid in beef fat is located in the 2-position of the triglyceride molecule, 41% in the 1- and 22% in the 3-position. In pig back fat, 72 mol% is located in the 2-position, 10% in the 1 with trace amounts in the 3-position. Sonntag (16) and Gunstone *et al.* (17) reported on the triglyceride composition of tallow and lard. Tallow contains 17.4% trisaturates, with 7.1% having the palmitic acid in the 2-position. It also contains 40.3% disaturates, 7.5% having the palmitic in the 2-position. The major trisaturates are PPS (3.6%) and PSS (3.2%). The major disaturate is POS (10.5%). Tallow is a β'-tending fat, but its polymorphic crystal structure is not very stable. Addition of some liquid oil to tallow has been found, in our laboratory, to change the crystals into the β form. Into the vegetable-tallow sample (No. 19, Table 1), some beef hard fat was incorporated. Beef hard fat has been found to be β-tending (4). This could explain why the vegetable-tallow sample was in the β form. It would be interesting to find out if a palm hard fat would keep a vegetable-tallow shortening in the β' form. Lard contains approximately 7% trisaturates and 30% disaturates (13). The major trisaturates are PPS and SPS (both 2%). The major disaturates are PPO (7.9%) and SPO (12.8%). All of these triglycerides have 16:0 in the 2-position. The C52 content was high in the calculated solid (75%), the isopropanol solids (61%) and the HMG (47%) (Tables 5–7). SPS and SPO are C52 triglycerides, with β tendencies because the palmitic acid is flanked by higher-carbon fatty acids.

In the development of new vegetable shortening formulations, it may be helpful to analyze the 15°C acetone-crystallized HMG for triglyceride composition. The C54 content should preferably not exceed 25% for a β'-stable product. This recommendation will only hold true for hydrogenated shortenings. When the shortening fat or its

solids are interesterified, part of the palmitic acid will shift to the 2-position of the glyceride molecule and, in this way, will alter the polymorphic β' stability. This has been demonstrated in the animal fat shortenings.

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[Received September 18, 1991; accepted December 31, 1991]