Technical

Physical and Chemical Characteristics of Butterfat Fractions Obtained by Crystallization from Molten Fat[1]

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ABSTRACT

Both summer and winter butterfats were fractionated using a laboratory procedure which was designed to simulate a commercial fractionation process. The process is based on a slow, controlled cooling of the melted fat, a short stabilization time at the fractionation temperature, and separation of the crystals from the liquid oil by vacuum filtration using a stainless steel perforated disc. Fractionation temperatures of 29, 26, 23 and 19 C for winter butterfat and 29 and 19 C for summer butterfat were used to obtain solid and liquid fractions at each temperature. Three replications at each temperature showed good reproducibility of results. The fractions were characterized by their fatty acid and triglyceride compositions, melting and crystallization behavior, iodine value, peroxide value and melting point.

INTRODUCTION

Among all the naturally occurring fats, butterfat is the most varied in its chemical and physical characteristics. Patton and Jensen (1) listed the presence of 437 different fatty acids in butterfat; they comprised normal, iso and anteiso monobranched and multibranched saturates, *cis*- and *trans*-monoenes, dienes, polyenes, keto, hydroxy and cyclic fatty acids. Because of this great variety of fatty acids, a large number of different triglycerides can be formed; consequently, the melting and crystallization of butterfat occurs over a wide temperature range. The unique character of butterfat, however, can be considered to be a shortcoming when compared to the wide range of specialty vegetable fats and oils which are available to the food-fat industry. One way to overcome this shortcoming is to modify the butterfat by fractionation to produce products which differ markedly from one another in chemical and physical characteristics and which are suitable for use in specific food industries. Proposed food applications for butterfat fractions have included the following: (i) the incorporation of a low-melting fraction into milk powder to improve reconstitutibility (2,3); (ii) the use of low-melting fractions to make normal butter softer (4,5); (iii) the use of high-melting fractions as shortenings for puff pastry and French rolls (6); and (iv) the substitution of cocoa butter in confectionary products by high-melting fractions of butterfat (4).

Fractionation of butterfat can be made either by crystallization of the fat dissolved in an organic solvent such as acetone or alcohol (5,7) or by direct cooling of the melted fat followed by separation of the crystalline matter from the liquid oil by filtration or centrifugation (8-12). Although recrystallization from solvents yields a more distinct separation between crystalline and liquid fractions, the latter method is preferred for food industry applications because of (a) flavor and toxicological problems that may result from solvent residues; (b) the high cost of solvent recovery, and (c) the possibility of destruction of desirable aroma components and vitamins. The main technological problem in the fractionation of butterfat without the use of solvents has been the separation of the crystals from the liquid fraction. The cooling temperature and the rate of crystallization strongly influence the composition, quantity and size of the fat crystals. Several investigators have shown that larger crystals which are obtained by a slow cooling rate and with slow agitation are more easily filtered (8,13,14).

The products which were obtained in experiments involving butterfat fractionation using molten fat have been characterized (9-11). The procedures which were used, however, would be impractical on an industrial scale. This study was undertaken to characterize butterfat fractions which were obtained in the laboratory using a procedure which closely resembles that used in the Tirtiaux industrial fractionation process (S.A. Fractionnement Tirtiaux, Belgium). The Tirtiaux process is based on a slow controlled cooling of the oil, a short stabilization time at the fractionation temperature followed by separation of the crystals on a continuous vacuum filter equipped with a stainless steel perforated belt as the filtration support (12). Characterization of the chemical and physical properties of fractions obtained by this procedure should aid in defining possible uses of these fractions in the food industry.

Both summer and winter butterfats have been fractionated. The results of analyses (fatty acid and triglyceride analyses, thermal examinations by differential scanning calorimetry, melting point, iodine value and peroxide value) of the various fractions are reported in this paper. The thermal oxidative stability of these fractions in comparison to those of selected vegetable oils will be reported in a subsequent publication.

EXPERIMENTAL

Anhydrous Butterfat

Anhydrous butterfat was prepared from fresh butter (Cooperative Agricole de la Cote Sud, Quebec) by melting the butter at 60 C, removing the top oil layer, filtering the oil through glass wool and drying the resulting product over anhydrous sodium sulfate. The oil was then refiltered (vacuum, Whatman 41 paper), flushed with nitrogen and stored at -20 C until it was fractionated.

Fractionation Procedure

Anhydrous butterfat was fractionated according to a standardized batch procedure at 29, 26, 23 and 19 C for winter (January) butterfat and 29 and 19 C for summer (September) butterfat. At temperatures above 29 C, the yields of solid fat were very small; hence, the products were not used in the present study. Below 19 C for winter butterfat and 17 C for summer butterfat, the solid fraction was massive and the liquid fraction could not be separated readily.

The butterfat was heated to 60 C, and 1.5 l was transferred to a Hobart mixer bowl (12 l capacity) equipped with a water jacket. Temperature control of the bowl was accomplished by using a Haake D1 circulating water bath and an EK12 cooling unit. The bowl was preheated to 60 C. The oil was then added, the cooling unit turned on and the

[1] Presented at the AOCS meeting in Philadelphia in May 1985.
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oil cooled slowly to the fractionation temperature with continuous stirring (20 rpm; Hobart flat beater attachment). After 4 hr of total cooling and holding time, the solid crystals were separated from the liquid oil by filtration (14 mesh stainless steel filter; Tirtiaux, Belgium) using vacuum (50-100 mbar below atmospheric pressure). The solid and liquid fractions were weighed and the percentage yield of each fraction was calculated.

Fatty Acid Analyses

The fatty acid composition of each fraction was determined after conversion of the fatty acids into the corresponding methyl esters by a modification of the method of Christopherson and Glass (15). A portion of the anhydrous lipid sample (200 mg) was placed in a vial (7 ml), and petroleum ether (2 ml) was added to dissolve the sample. Sodium methoxide solution (0.1 ml; 2 N $NaOCH_3$ in anhydrous methanol) was added, and the contents of the vial were mixed (1 min) using a vortex mixer. After sedimentation of the sodium glycerolate, a portion of the clear supernatant was dissolved in hexane (1 part supernatant to 100 parts hexane). An aliquot (0.2 µl) of the hexane solution was injected into a fused silica capillary column (30 m × 0.32 mm ID) coated with SP-2340 (Supelco Inc., Canada) (0.2 µm). The column was placed into a Varian 3700 gas chromatograph equipped with a flame ionization detector and a cold on-column injector. The oven temperature was programmed from 50 C to 160 C (5 C/min) after a 1-min hold at 50 C. The carrier gas (helium) flow rate was 1.5 ml/min. The injector temperature was programmed from 70 C to 200 C (100 C/min), and the detector temperature was maintained at 210 C. Correction factors were determined by analysis of a standard mixture of fatty acid methyl esters (Nu Chek Prep, Elysian, Minnesota) having a composition which resembled that of an average butterfat sample.

Triglyceride Analysis

The triglyceride composition was determined by dissolving approximately 15 mg of the anhydrous butterfat or butterfat fraction in 6 ml of hexane and injecting an aliquot (0.2 µl) into a bonded phase fused silica capillary column (DB-5, 0.1 µm; 15 m × 0.32 mm ID; J&W Scientific Inc., Rancho Cordova, California). The same gas chromatograph was used as for fatty acid analyses. The oven temperature was programmed in two stages as follows: first, from 50 C to 240 C at a rate of 25 C/min, and then from 240 C to 350 C at a rate of 3 C/min. The injector temperature was programmed from 70 C to 330 C (100 C/min), and the detector temperature was maintained at 350 C. The carrier gas was helium (1.5 ml/min). Identification of the major groups of triglycerides according to carbon number was made by comparison of retention times to those of standard mixtures of simple triglycerides from C18 to C54 (Nu Chek Prep, Elysian, Minnesota).

Differential Scanning Calorimetry (DSC)

Crystallization and melting curves were recorded using a heat flow differential scanning calorimeter (Mettler TA 3000, Mettler Instrument Ltd., Switzerland), calibrated with indium. A sample (20-30 mg) of fat was placed in an aluminum crucible; the crucible was covered with a pierced lid and sealed. The measuring cell was purged with nitrogen gas (50 ml/min) during the analysis. The samples were treated as follows: (i) heating at 80 C for 10 min to destroy the structure that was associated with the previous thermal history; (ii) crystallization over the temperature range 80 C to -40 C (rate of cooling, 10 C/min, using liquid air); (iii) fusion of the crystals formed by heating over the temperature range -40 C to 80 C (rate of heating, 10 C/min). The relative percentages of liquid fat as a function of temperature were determined by integration of the DSC melting curve of the fat sample using a Mettler TC 10 data processor.

Iodine Value

Iodine values were determined by the Cd 1-25 method of the American Oil Chemists' Society (16). The titrations were performed by the use of a Mettler DL 40 RC Memo Titrator (Mettler Instrument Ltd., Switzerland).

Melting Point

Melting points were determined by the Cc 1-25 method of the American Oil Chemists' Society (16).

Peroxide Value

Peroxide values were determined by the Cd 8-53 method of the American Oil Chemists' Society (16).

Statistical Analyses

Analyses of variance were performed on the mean values (3 replications × 2 duplicates) of the following: major groupings of fatty acids; iodine value data; melting point data, and percentage liquid fraction data. Where significant differences were noted, Duncan's Multiple Range test was used to determine which samples were significantly different. The analyses were performed using the McGill University System for Interactive Computing (MUSIC) and the Statistical Analysis System (SAS).

RESULTS AND DISCUSSION

Yield of Solid Fractions and Percentage of Liquid Oil in the Fractions

Table I shows the results of two experiments (three replications) in which fat obtained from butter produced (a) during the winter months and (b) during the summer months was fractionated. The winter butterfat was fractionated at 29, 26, 23 and 19 C to obtain a solid (S) and liquid (L) fraction at each temperature; summer butterfat was fractionated at 29 and 19 C. The largest variations in yield of solid between replicate runs were observed for the 29 C winter and summer fractions and the 23 C winter fractions. These differences could be related to differences in the amounts of liquid oil in the solid fractions (Table I).

The percentage of liquid oil in the solid and liquid fractions was determined by differential scanning calorimetry (DSC). The values for the solid fractions ranged from 38.2% to 52.3% for the fat from winter butter and from 36.2% to 48.8% for the fat from summer butter (Table I). Results from the corresponding liquid fractions showed that they contained approximately 2-6% of solid contaminants (Table I). These could arise from resolubilization of solid crystals during the filtration step which was conducted at room temperature. Badings et al. (10,11) measured the percentage of liquid oil in solid fractions obtained by stepwise crystallization of melted butterfat. They reported values ranging from 63.4% to 83.8% based on the distribution of carotene between the cake and the filtrate.

Chemical Composition of Fractions

Table II shows that the iodine values varied from 24.70 to 33.07 for the winter fractions and from 29.18 to 37.67 for the summer fractions. This variation was greater than the variation in iodine value of the whole fats from winter and summer butter (30.26 and 35.78, respectively). With the exception of fractions S-19 and S-23 (fat from winter butter), the differences in iodine value between the various

TABLE I

Results of Butterfat Fractionation by Cooling Liquid Fat

Fraction[a]	Fractionation temperature (C)	Replication 1 Yield (%) solid fraction	Replication 1 Composition[b] (% liquid in fraction)	Replication 2 Yield (%) solid fraction	Replication 2 Composition (% liquid in fraction)	Replication 3 Yield (%) solid fraction	Replication 3 Composition (% liquid in fraction)
				Fat from winter butter			
S-29	29	16.2	38.2	22.0	44.4	23.7	49.2
L-29	29	–	95.5	–	97.5	–	97.2
S-26	26	34.3	46.4	37.4	50.9	36.9	50.0
L-26	26	–	96.3	–	96.8	–	96.2
S-23	23	60.0	52.3	55.9	51.9	52.2	50.2
L-23	23	–	97.8	–	98.0	–	97.7
S-19	19	62.6	48.8	60.8	47.8	61.7	47.7
L-19	19	–	95.0	–	95.0	–	93.2
				Fat from summer butter			
S-29	29	16.1	41.6	13.6	36.2	15.0	41.6
L-29	29	–	96.2	–	96.8	–	96.6
S-19	19	53.9	48.8	53.9	48.4	53.4	48.4
L-19	19	–	95.4	–	93.6	–	93.8

[a]Fraction designation indicates physical state (solid, liquid) and fractionation temperature.
[b]The % liquid in fraction was determined by Differential Scanning Calorimetry (DSC).

TABLE II

Iodine Values of Whole Butterfat and Butterfat Fractions

Fraction	Iodine value: Experiment 1 (fat from winter butter)[a]	Iodine value: Experiment 2 (fat from summer butter)[a]
S-29	24.70 ^{h} (±0.95)	29.18 ^{e} (±0.33)
S-26	26.70 ^{g} (±0.38)	–
S-23	27.78 ^{f} (±0.25)	–
S-19	27.94 ^{f} (±0.37)	32.80 ^{d} (±0.18)
Whole butterfat	30.26 ^{e}	35.78 ^{c}
L-29	31.44 ^{d} (±0.06)	36.13 ^{b} (±0.09)
L-26	31.95 ^{c} (±0.05)	–
L-23	32.70 ^{b} (±0.12)	–
L-19	33.07 ^{a} (±0.24)	37.67 ^{a} (±0.02)

[a]Fractionation experiments were performed in triplicate at each temperature; the analysis of each sample was performed in duplicate. Means in each column with different letter superscripts are significantly different at the 5% probability level. The deviation is the average deviation from the mean of three replicate fractions, analyzed in duplicate.

fractions and the whole butterfat from each season were significant ($p<0.05$).

The peroxide values of the whole butterfat and the liquid fractions obtained from this fat were measured to evaluate the effect of the various processing steps (separation of butterfat from butter, storage, re-melting, crystallization and filtration) on the oxidative stability of the fractions. In all instances, the peroxide values were found to be 0.0 meq O_2/kg fat.

The fatty acid compositions of the whole fats (winter and summer) and their corresponding fractions are summarized in Tables III, IV, V and VI. For simplicity of presentation and statistical analyses, the fatty acids (about 40) which were determined have been grouped according to similarities in melting behavior. Unidentified peaks were combined in the "other" category. It is noteworthy to mention that the procedure used for fatty acid composition allowed for the determination of some positional and geometric isomers of unsaturated fatty acids; in particular, elaidic acid and both *cis* and *trans* vaccenic acid were identified.

From the statistical analyses which were performed on the fatty acid data (winter fractions; Tables III and IV), it will be noted that with the short chain saturates, medium chain saturates, long chain saturates and *cis* unsaturates, the 29 and 19 C fractions (with the exception of fraction L-29 vs whole butterfat) are significantly different ($p<0.05$) from each other and from the whole butterfat (Tables III and IV). This was not necessarily true for the 26 and 23 C fractions. In all categories, the S- and L-23 fractions were not significantly different ($p<0.05$) from the S- and L-19 fractions, respectively. Similarly, the L-26 fractions were not significantly different from the L-29 fractions.

It will be noted from the results obtained with the fractions of summer butterfat (Tables V and VI) that the 29 and 19 C fractions were significantly different ($p<0.05$) from each other and from the whole butterfat with respect to short chain saturates, long chain saturates and *cis* unsaturates.

In general, the short chain saturated fatty acids (C4:0 to C10:0) were found in greater amounts in the liquid fractions, and the long chain saturated fatty acids (C16:0 to C20:0) were found in greater amounts in the solid fractions. The *cis* unsaturated fatty acids (C10:1 to C18:3) followed the same trend as the short chain saturated fatty acids. This reflected the similarities in melting behavior of these two groups of fatty acids. As the fractionation temperature decreased, the concentration of short chain saturated fatty acids and *cis* unsaturated fatty acids in the liquid fractions increased. The *trans* C18:1 isomer, however, showed the reverse tendency. The *trans* 18:1 fatty acids, as a proportion of the total octadecenoic acids, were significantly higher ($p<0.05$) in the S-29 fractions and significantly lower ($p<0.05$) in the L-19 fractions compared to the original butterfats. The *trans* 18:1 isomers consisted mainly of the Δ11 isomer (mp 44 C) while the *cis* 18:1 is mainly the Δ9 isomer (mp 11 C). This accounts for the occurrence of a higher proportion of the *trans* 18:1 in the solid than in the liquid fractions.

The present study shows more marked differences in fatty acid composition between fractions obtained by cooling liquid fat than have been previously reported (9,17,18).

TABLE III

Fatty Acid Composition of Winter Butterfat and Solid Butterfat Fractions

Fatty acids	Methyl esters (% by weight)[a]				
	S-29	S-26	S-23	S-19	Whole winter butterfat
Short chain, saturated (C4:0 to C10:0)	10.40^{d}	11.47^{c}	12.08^{b}	12.17^{b}	12.97^{a}
Medium chain, saturated (C12:0 to C15:0)	17.52^{a}	17.27^{a,b}	17.24^{a,b}	17.07^{b,c}	16.86^{c}
Long chain, saturated (C16:0 to C20:0)	47.38^{a}	44.83^{b}	43.53^{c}	42.90^{c}	40.65^{d}
cis, unsaturated (C10:1 to C18:3)	20.43^{d}	21.96^{c}	22.93^{b}	23.18^{b}	24.92^{a}
trans, unsaturated (C18:1)	1.46^{a}	1.43^{a}	1.47^{a}	1.55^{a}	1.55^{a}
Other	2.81^{a}	3.04^{a}	2.74^{a}	3.13^{a}	3.04^{a}
$\frac{\text{trans 18:1}}{\text{Total 18:1}} \times 100$	8.65^{a}	7.97^{a,b}	7.81^{a,b}	8.14^{a,b}	7.58^{b}

[a]Fractionation experiments were performed in triplicate at each temperature; the analysis of each sample was performed in duplicate. Means in each row with different letter superscripts are significantly different at the 5% probability level.

TABLE IV

Fatty Acid Composition of Winter Butterfat and Liquid Butterfat Fractions

Fatty acids	Methyl esters (% by weight)[a]				
	Whole winter butterfat	L-29	L-26	L-23	L-19
Short chain, saturated (C4:0 to C10:0)	12.97^{d}	13.34^{c,d}	13.77^{b,c}	14.29^{a,b}	14.84^{a}
Medium chain, saturated (C12:0 to C15:0)	16.86^{a}	16.49^{b}	16.46^{b}	16.23^{b,c}	16.09^{c}
Long chain, saturated (C16:0 to C20:0)	40.65^{a}	38.89^{b}	38.49^{b}	37.50^{c}	36.69^{d}
cis, unsaturated (C10:1 to C18:3)	24.92^{d}	26.50^{c}	26.89^{b}	27.61^{a}	27.72^{a}
trans, unsaturated (C18:1)	1.55^{a,b}	1.64^{a}	1.30^{b}	1.36^{a,b}	1.40^{a,b}
Other	3.04^{a}	3.12^{a}	3.12^{a}	3.01^{a}	3.25^{a}
$\frac{\text{trans 18:1}}{\text{Total 18:1}} \times 100$	7.58^{a}	7.52^{a}	5.95^{b}	6.05^{b}	6.23^{b}

[a]See Table III.

TABLE V

Fatty Acid Composition of Summer Butterfat and Solid Butterfat Fractions

Fatty acids	Methyl esters (% by weight)[a]		
	S-29	S-19	Whole summer butterfat
Short chain, saturated (C4:0 to C10:0)	9.37^{c}	11.10^{b}	11.82^{a}
Medium chain, saturated (C12:0 to C15:0)	15.88^{a}	15.78^{a}	15.44^{b}
Long chain, saturated (C16:0 to C20:0)	47.04^{a}	41.75^{b}	39.47^{c}
cis, unsaturated (C10:1 to C18:3)	21.14^{c}	24.73^{b}	26.37^{a}
trans, unsaturated (C18:1)	3.13^{a}	3.06^{a}	3.35^{a}
Other	3.44^{a}	3.58^{a}	3.55^{a}
$\frac{\text{trans 18:1}}{\text{Total 18:1}} \times 100$	16.13^{a}	13.76^{b}	14.06^{b}

[a]See Table III.

TABLE VI

Fatty Acid Composition of Summer Butterfat and Liquid Butterfat Fractions

Fatty acids	Methyl esters (% by weight)[a]		
	Whole summer butterfat	L-29	L-19
Short chain, saturated (C4:0 to C10:0)	11.82^{c}	12.95^{b}	13.99^{a}
Medium chain, saturated (C12:0 to C15:0)	15.44^{a}	15.26^{a,b}	15.02^{b}
Long chain, saturated (C16:0 to C20:0)	39.47^{a}	36.98^{b}	35.68^{c}
cis, unsaturated (C10:1 to C18:3)	26.37^{c}	27.81^{b}	29.22^{a}
trans, unsaturated (C18:1)	3.35^{a}	3.15^{a}	2.55^{b}
Other	3.55^{a}	3.84^{a}	3.55^{a}
$\frac{\text{trans 18:1}}{\text{Total 18:1}} \times 100$	14.06^{a}	12.78^{b}	10.10^{c}

[a]See Table III.

The improved crystallization and separation procedures used in the present study permitted a wider range of fractionation temperatures to be used and hence larger differences in chemical composition of fractions compared to those reported previously.

In addition to the fatty acid analyses, the whole butterfat and butterfat fractions from the winter butterfat were analyzed by capillary column gas chromatography (CC-GC) for triglyceride composition. Grob and coworkers (19) noted that fat fractionation can be monitored more sensitively on a triglyceride basis than by classical analysis of fatty acid methyl esters; this is because it is a direct analysis of glyceride species that are being separated. Figure 1 shows typical chromatograms (CC-GC method) which were obtained with winter butterfat and with S-29 and L-19 fractions. The triglyceride compositions according to acyl carbon number, for both solid and liquid, 29 and 19 C winter fractions in comparison to the whole fat, are summarized in Table VII.

It will be noted from Figure 1 that the composite groups of peaks with a carbon number (CN) greater than 42 are more concentrated in the solid fractions; the groups of peaks with a CN less than 42 are more concentrated in the liquid fractions. This reflects the tendency for the higher molecular weight triglycerides to solidify and for the lower molecular weight triglycerides to stay in the liquid fractions. It is also interesting to note the differences that exist within the groups of peaks with the same CN. Although complete identification of all peaks separated on the DB-5 capillary column was not possible, it was determined for the C54 group of peaks that the first peak included the triunsaturated C54 triglycerides and the last peak was the trisaturated, C54 (tristearin) species. The chromatograms (Fig. 1) indicate that the last peak in each group (C44 to C54) having the same CN increased substantially in the solid fractions; the same peak almost disappeared on the chromatograms obtained with liquid fractions. This reflected the tendency for the trisaturated species of each group to concentrate in the solid fractions.

Physical Characteristics

The melting and solidification behavior of an oil or fat as measured (DSC) by the ratio of liquid/solid at different temperatures are of great importance in assessing its use in a particular food application. The percentages of liquid oil in the various fractions as a function of temperature are presented in Tables VIII and IX.

The results of the statistical analyses (with the exception of the liquid fractions at the upper temperatures) showed significant differences ($p<0.05$) in the melting behavior between all fractions obtained in each experiment (Tables VIII and IX). It should be noted that the differences in melting behavior between fractions obtained from the winter butterfat are more pronounced than the differences in fatty acid composition (Tables III and IV). The melting behavior of the S- and L-23 fractions as compared with the S- and L-19 fractions (winter butterfat) were significantly different

TABLE VII

Triglyceride Composition of Winter Butterfat and Butterfat Fractions as Determined by Gas Chromatography

Acyl carbon number	% of Triglyceride (based on peak area/total area of all peaks)				
	S-29[a]	S-19[a]	Whole winter butterfat[b]	L-29[a]	L-19[a]
22	tr[c]	0.06	tr	0.08	0.10
24	tr	0.03	tr	0.08	0.08
26	0.11	0.14	0.16	0.17	0.18
28	0.38	0.57	0.52	0.68	0.79
30	0.82	1.04	1.18	1.25	1.46
32	1.73	2.18	2.32	2.57	2.84
Other	0.22	0.27	0.29	0.30	0.34
34	4.76	5.77	6.58	6.66	7.52
Other	0.95	1.08	1.36	1.31	1.44
36	9.12	10.91	11.35	12.50	14.03
Other	1.29	1.55	1.52	1.71	1.99
38	10.12	12.09	13.67	13.74	15.44
Other	0.41	0.65	0.69	0.71	0.81
40	7.82	9.33	10.17	10.33	11.31
Other	0.23	0.50	0.12	0.50	0.58
42	6.50	7.14	7.29	7.05	6.82
Other	0.28	0.47	0.72	0.46	0.31
44	7.32	6.96	6.58	5.90	5.37
Other	0.95	0.90	0.79	0.63	0.27
46	9.08	7.55	6.60	5.92	5.03
Other	1.45	1.14	0.90	0.95	0.39
48	10.96	8.87	8.12	7.23	6.15
Other	2.86	2.02	2.18	2.24	1.24
50	11.66	9.35	8.40	8.11	6.88
Other	1.84	0.97	0.77	1.12	0.70
52	7.04	6.41	6.12	5.78	5.73
54	2.09	2.07	1.62	2.04	2.20

[a]Fractionation experiments were performed in triplicate at each temperature; the analysis of each sample was performed in duplicate.
[b]The sample was analyzed in duplicate.
[c]Trace.

TABLE VIII

Liquid Oil Content of Winter Butterfat and Butterfat Fractions

Temperature (C)	% Liquid oil in designated fraction[a,b]								
	S-29	S-26	S-23	S-19	Whole winter butterfat	L-29	L-26	L-23	L-19
0.0	9.0^{h}	10.7^{g}	12.1^{f}	12.5^{f}	15.6^{e}	23.3^{d}	24.6^{c}	26.9^{b}	28.1^{a}
5.0	15.2^{i}	17.5^{h}	19.3^{g}	19.7^{f}	24.8^{e}	32.3^{d}	34.2^{c}	37.6^{b}	39.3^{a}
10.0	23.8^{i}	27.7^{h}	29.9^{g}	30.5^{f}	39.3^{e}	47.1^{d}	49.3^{c}	53.9^{b}	57.8^{a}
15.0	31.4^{i}	36.2^{h}	39.3^{g}	40.3^{f}	51.9^{e}	67.0^{d}	71.0^{c}	76.8^{b}	79.3^{a}
20.0	36.6^{i}	44.2^{h}	48.3^{g}	49.0^{f}	64.6^{e}	80.7^{d}	85.3^{c}	93.6^{b}	95.4^{a}
25.0	37.1^{h}	47.4^{g}	54.8^{f}	57.3^{e}	75.8^{d}	89.3^{c}	94.7^{b}	98.2^{a}	98.3^{a}
30.0	46.3^{h}	58.9^{g}	67.4^{f}	70.9^{e}	87.9^{d}	97.7^{c}	98.4^{b}	99.5^{a}	99.5^{a}
35.0	61.6^{i}	74.6^{h}	83.7^{g}	87.2^{f}	97.3^{e}	98.7^{d}	99.1^{c}	100.0^{a}	99.5^{b}
40.0	83.6^{h}	92.5^{g}	96.0^{f}	97.2^{d,e}	98.1^{d}	98.8^{c}	99.4^{b}	100.0^{a}	99.6^{b}
	Melting point of designated fraction (C)[b,c]								
	43.5^{a}	41.5^{b}	39.0^{c}	38.2^{d}	34.6^{e}	29.7^{f}	27.0^{g}	22.9^{h}	20.6^{i}

[a]The % liquid oil at various temperatures was determined by Differential Scanning Calorimetry (DSC).
[b]See Table III, footnote a.
[c]Melting points were determined by AOCS Method Cc 1-25.

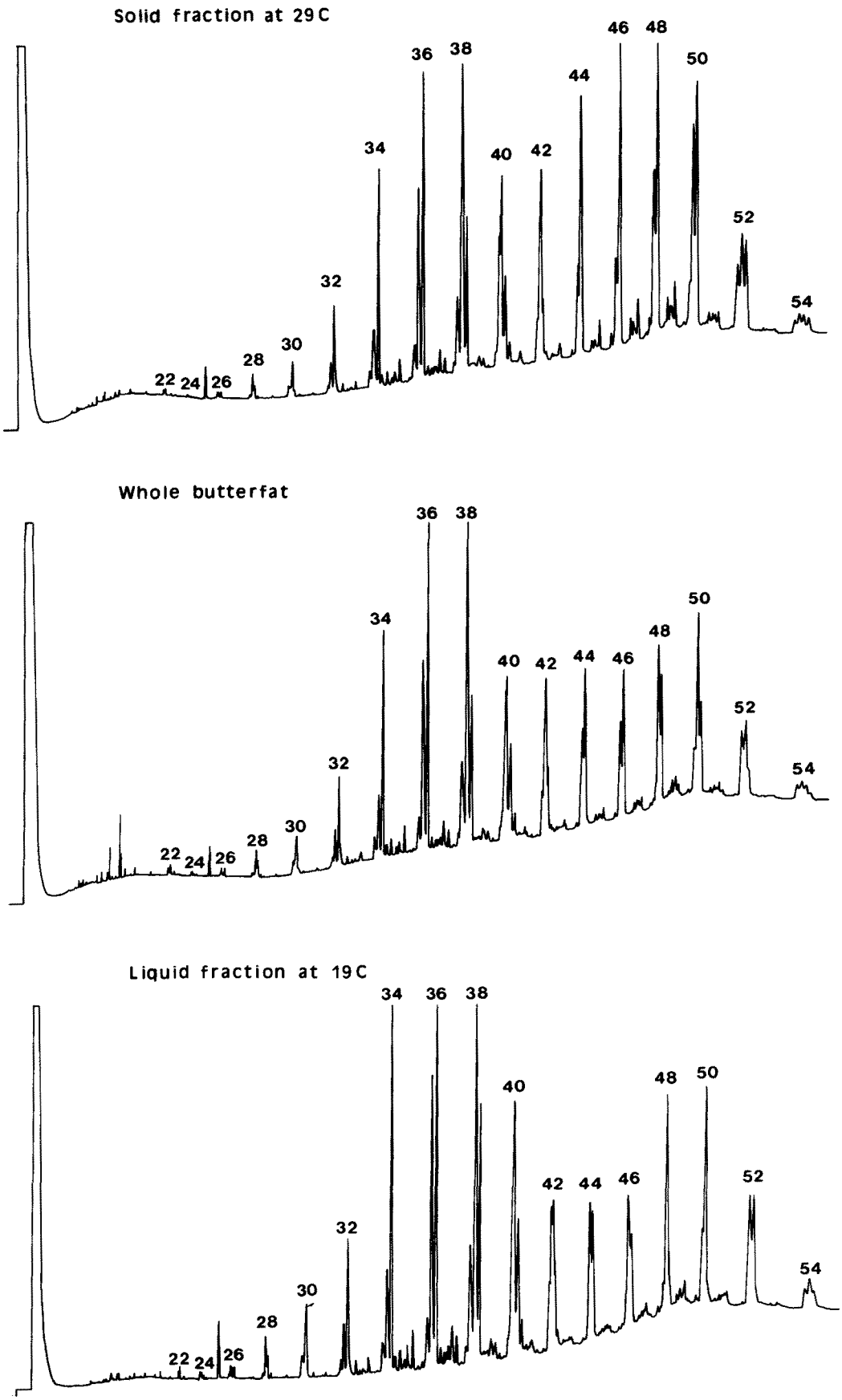

FIG. 1. Typical gas chromatograms of the triglycerides of whole butterfat, a solid fraction at 29 C, and a liquid fraction at 19 C.

TABLE IX

Liquid Oil Content of Summer Butterfat and Butterfat Fractions

Temperature (C)	% Liquid oil in designated fraction[a,b]				
	S-29	S-19	Whole summer butterfat	L-29	L-19
0.0	9.1[e]	14.2[d]	18.2[c]	24.7[b]	29.3[a]
5.0	15.3[e]	22.2[d]	28.9[c]	34.3[b]	40.9[a]
10.0	23.5[e]	33.0[d]	42.8[c]	47.6[b]	56.7[a]
15.0	30.0[e]	43.0[d]	56.6[c]	67.1[b]	78.8[a]
20.0	32.1[e]	49.0[d]	67.4[c]	80.0[b]	96.1[a]
25.0	32.6[e]	56.9[d]	78.6[c]	89.1[b]	99.0[a]
30.0	42.2[e]	70.1[d]	90.2[c]	97.4[b]	100.0[a]
35.0	57.0[d]	85.7[c]	98.0[b]	99.6[a]	100.0[a]
40.0	78.7[b]	96.8[a]	99.9[a]	99.9[a]	100.0[a]
	Melting point of designated fraction (C)[b,c]				
	44.4[a]	38.4[b]	33.4[c]	28.8[d]	19.7[e]

[a]See Table VIII.

[b]See Table III, footnote a.

[c]See Table VIII.

($p<0.05$); the differences in fatty acid composition of the same fractions were not significantly different. The same was true for the L-26 compared with L-29 fractions obtained from the winter butterfat. This would suggest that the arrangement of the fatty acids in the triglycerides has a more marked influence on the physical properties of butterfat fractions than does the fatty acid composition.

Figure 2 shows typical DSC crystallization curves for winter butterfat and the S-29 and L-19 fractions obtained from this fat. Figure 3 shows a comparison of the corresponding melting curves.

The crystallization and melting behavior of the S-29 fraction differed markedly from that of the whole butterfat and the L-19 fraction. The crystallization curves obtained with the S-29 fraction showed a large high temperature peak (at ca. 20 C) which was present only as a small shoulder preceding the low temperature peak in the whole butterfat curve; this was absent in the curve obtained with the L-19 fraction (Fig. 2). Similarly, the melting curve of the S-29 sample had a large peak at 41 C; this was almost absent in the curve obtained with the whole butterfat and did not appear in the L-19 curve. The L-19 melting curve had a large low temperature peak at 17 C, and a portion of the curve indicated there was some melting between -20 C and -5 C. This region of melting was almost absent from the other two curves (Fig. 3).

The present study has shown that butterfat can be fractionated by controlled cooling of melted butterfat, to yield products which differ markedly in their physical and chemical characteristics. These fractions might be incorporated into foods where the melting and crystallization behavior of whole butterfat is not suitable but where the flavor of butterfat is desirable. For example, Tolboe (20) used successfully a high-melting fraction of butterfat which had a melting curve similar to that of the S-29 fractions obtained in the present study, in Danish pastry. The corresponding low-melting fraction was suitable as a cookie fat (20). Further work is under way on the fractionation of the liquid fractions obtained in the present study to obtain additional products that might find some application in the food industry.

ACKNOWLEDGMENT

This work was supported by a research grant from the Dairy Bureau of Canada.

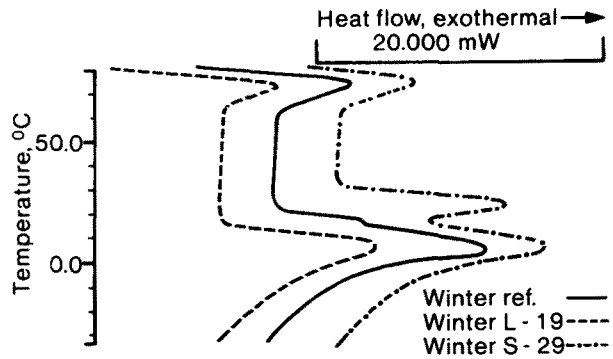

FIG. 2. Typical DSC crystallization diagrams of whole butterfat and butterfat fractions.

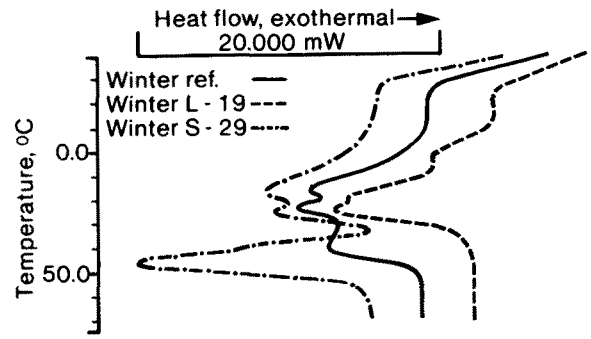

FIG. 3. Typical DSC melting diagrams of whole butterfat and butterfat fractions.

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[Received June 24, 1985]