toxyl groups of the latter kind can also be determined by direct titration with standard base.

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Beef Tallow in Shortening Preparations[1]

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IT IS WELL KNOWN that much edible grade tallow is diverted to inedible channels owing to lack of market in the edible field. It is also known that present meat merchandising practices cause much edible tallow to be lost as kitchen waste. In 1953 the production of edible tallow and oleo stock under Federal inspection was about 114 and 115 million pounds, respectively. In the same year there were about 17.6 million cattle slaughtered under federal inspection. At a conservative estimate of about 35 lbs. of fat available per animal, the total production of edible beef fat should have been over 600 million pounds. There is little doubt that the production of edible beef fat would be substantially increased if more of a market in shortening or margarine products could be created.

Blends of animal and vegetable fats for use as shortening or cooking fats have been on the market for three decades or more, with the principal objective of meeting the demand for low-price shortenings. In more recent years however it has been recognized that animal and vegetable fats are equal nutritionally, that with modern processing technology they should be interchangeable in the manufacture of the highest quality shortenings, and that they should command a comparable price.

Tallow, in general, has a poor plastic range and is too firm at room temperatures to meet the accepted requirements of a shortening. Hence the advantage of its admixture with vegetable oils or soft fats in the manufacture of shortenings appears obvious. The ratio of tallow to vegetable oil can also be adjusted to permit adequate control of extent of hydrogenation, thus facilitating the manufacture of a more uniform product. The application of ester interchange (rearrangement) in the manufacture of shortenings of this type has not been thoroughly investigated although the value of this process in effecting desirable changes in the physical properties of lard appears to be well established (1, 2, 3).

In addition to being too hard, tallow as such generally has an undesirable odor and flavor, and, even after deodorization, tends to develop "reverted" flavors. The limited use of tallow in shortenings has been attributed by some to its tendency to revert.

This paper describes a number of experimental shortenings made with tallow and cottonseed oil in an attempt to obtain a good plastic range and other desirable properties by varying the proportion of tallow and cottonseed oil and introducing some variations in processing treatments.

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Experimental

Materials. The materials used in this study were a typical edible beef tallow rendered in the laboratory from fresh beef fat tissue; a commercial edible grade cottonseed oil that had been refined and bleached; and commercial lard flakes with an iodine value of 4.2.

Hydrogenation. Hydrogenation was carried out in a stainless steel apparatus at 150°C. with 0.1% nickel catalyst and at a gage pressure of 50 lbs.

Rearrangement. The products were rearranged by a catalytic treatment with sodium methylate similar to the method of Vander Wal (2, 4).

Penetration data. Micropenetration data were obtained at 5° intervals from 20 to 35°C. by the procedure of Feuge and Bailey (5). Penetrations exceeding 375 mm./10 at a given temperature were considered as being too soft for a reading.

Dilatometric data. The dilatometers used were the type described by Schroeder (6), and the estimated percentages of solids were calculated according to Fulton *et al.* (7).

Carbonyl Values. The degree of reversion of the shortenings was measured by determining the amount of volatile carbonyl compounds formed by aging the oil under specified conditions, according to the procedure of Chang and Kummerow (8).

Cake Volume Tests. Baking tests were conducted with the experimental shortenings, using a pound-cake formula (2); the cake volume was determined by the seed-displacement method and was expressed as cc./100 g.

Consistency, or C Number. The C numbers of the shortenings were determined according to the method of Harrington *et al.* (9).

Preparation of Shortenings. Ten experimental shortenings were prepared as described below. All

TABLE I

Properties of Experimental Beef Tallow Shortenings and of Commercial Hydrogenated Vegetable Shortenings

Description	Designation	Tallow (T) or HT Content (%)	Micropenetration (mm./10) at: 20°C.	25°C.	30°C.	35°C.	Solids (%) at: 20°C.	25°C.	30°C.	35°C.	40°C.	Consistency No.	Cake Volume cc./100 g.
Hydrogenated mixtures of tallow and cottonseed oil	A	57 T	22	35	108	288	25.2	20.4	17.6	.....	5.8	24.0	226
	B[a]	57 T	25	40	101	221	27.4	23.1	18.9	13.3	6.2	23.0	230
	C	52 T	35	88	198	365	33.4	24.7	18.4	13.0	6.7	19.6	232
	D	45 T	32	57	145	332	26.9	21.6	16.1	10.0	3.7	19.4	218
Mixtures of hydrogenated tallow and cottonseed oil	E	58 HT	29	58	129	355	24.9	19.4	16.2	11.0	6.1	21.6	232
	F	50 HT	32	90	320	TS[b]	18.0	14.1	11.8	8.3	3.9	.....	.....
	G[c]	57.5 HT	30	61	145	320	27.4	21.5	16.9	13.1	7.9	26.4	242
Samples rearranged in presence of glycerine	H	58 HT	30	80	182	TS[b]	23.4	17.8	14.0	9.2	4.0	15.5	175
	I[d]	54.5 HT	27	44	111	190	.....	.....	.....	.....	....	32.2	214
	J	70 HT	48	51	105	TS[b]	26.5	22.3	16.7	12.2	6.2	20.1	202
Commercial sample	HVS		32	80	218	321	23.8	20.8	16.7	12.7	8.0	23.7	229
Avg. of 8 commercial samples			30	90	200	300							

[a] Rearranged before hydrogenation.
[b] Too soft.
[c] Sample F with 15% HT added (85 g. sample F to 15 g. HT).
[d] Sample H with 6% lard flakes added.

samples were deodorized after preparation and were stabilized by the addition of Tenox VI[3] in concentration sufficient to represent 0.01% butyl hydroxy anisole.

The hydrogenated tallow, designated in this paper as HT, is tallow with an iodine value of 40.3, hydrogenated to an iodine value of 34.1, deodorized (3), and treated with carbon.

The hydrogenated vegetable shortening was a commercial product and is designated as HVS.

Hydrogenated Mixtures

Sample A: a mixture of 57% tallow and 43% cottonseed oil, iodine value 71.5, hydrogenated to iodine value 62.8, rearranged, deodorized, and stabilized.

Sample B: same mixture as A, but rearranged first, then hydrogenated to iodine value 62.8, deodorized, and stabilized.

Sample C: a mixture of 52% tallow and 48% cottonseed oil, iodine value 73.6, hydrogenated to iodine value 66.1, rearranged, deodorized, and stabilized.

Sample D: a mixture of 45% tallow and 55% cottonseed oil, iodine value 79.2, hydrogenated to iodine value 65.1, rearranged, deodorized, and stabilized.

Hydrogenated Tallow + Cottonseed Oil

Sample E: a mixture of 58% HT and 42% cottonseed oil rearranged, deodorized, and stabilized.

Sample F: a mixture of 50% HT and 50% cottonseed oil rearranged, deodorized, and stabilized.

Sample G: sample F with 15% HT added (85 g. F to 15 g. HT).

Hydrogenated Tallow + Cottonseed Oil + Glycerine

Sample H: a mixture of 58% HT and 42% cottonseed oil, rearranged in the presence of glycerine (0.43%), deodorized, and stabilized.

Sample I: sample H with 6% lard flakes added.

Sample J: a mixture of 70% HT and 30% cottonseed oil, rearranged in the presence of glycerine (0.43%), deodorized, and stabilized.

Results and Discussion

The properties of these experimental shortenings are shown in Table I. At the end of the table are given for comparison the corresponding data for a typical commercial hydrogenated vegetable shortening (HVS) and also the approximate average penetration data for eight such commercial shortenings. These latter data can be taken as a desirable standard in comparing the penetration values of the experimental shortenings.

The first four experimental samples (A to D inclusive) were made by hydrogenation of a mixture of tallow and cottonseed oil. Compared with the commercial average, samples A and B are somewhat hard at 25 and 30°C. although their consistency numbers and cake volumes agree closely with those of the commercial vegetable shortening. The lower percentage of tallow in samples C and D yielded somewhat softer shortenings which had plasticity ranges similar to that of the standard but were slightly softer at 35°C. The consistency numbers were also lower. The cake volumes were satisfactory.

Samples E to G, inclusive, consisted of hydrogenated tallow and cottonseed oil mixtures. Sample E, with 58% HT (approximately the same saturated acid content as lard), was too hard at 25 and 30°C. and somewhat soft at 35°C., as indicated by the micropenetration data, but its percentage of solids was in good agreement with that of the hydrogenated vegetable shortening. Sample F, with 50% HT, was too soft at temperatures above 25°C., as shown by the penetration data. When 15% more HT was added to improve the plasticity (Sample G), a good plastic range resulted, and an excellent cake volume of 242 cc./100 g. was obtained.

Samples H to J, inclusive, illustrate the effect of glycerine on the rearrangement of fats. Sample H was the same as Sample E except that 0.43% glycerine was present during its rearrangement. The penetration data at 35°C., low percentage of solids, consistency number, and cake volume, all indicate the softness of this shortening. When 6% lard flakes were added to the shortening (Sample I), the cake volume rose from 175 to 214, suggesting that a higher ratio of hydrogenated tallow to cottonseed oil could be used if glycerine were added during rearrangement of the mixture. When the hydrogenated tallow content was raised to 70% however, as in Sample J, a product with a very short plastic range was obtained; it was not only still too soft at 35°C., but it was too hard at the lower temperatures.

Attempts were made to evaluate the experimental

[3] Reference to a commercial product is not intended to be a recommendation of this product by the U. S. Department of Agriculture over others not mentioned.

shortenings from the standpoint of reversion, both organoleptically and by carbonyl index determinations. Since the shortenings were deodorized and stabilized, they were substantially bland in taste and odor. They showed no development of reversion odors or flavors after heating in an oven at 60°C. for six days. Their original carbonyl index values of from 45 to 55 showed no increase after this oven-aging.

To establish whether or not the hydrogenation and stabilization treatments were responsible for protecting these shortenings from reversion, some shortenings in which these treatments were omitted were tested organoleptically and by the determination of carbonyl index values after oven-aging. Samples prepared similarly, but not hydrogenated, had detectable odors of reversion after oven-aging, and their carbonyl index was raised to 66. When the antioxidant was omitted from this type of shortening as well as the hydrogenation, the original carbonyl index value of 50 rose to 117 after oven-aging, and more pronounced reversion could be detected organoleptically. These experiments indicated that slight hydrogenation and the use of antioxidants are effective in stabilizing shortenings containing tallow against reversion.

Summary

Experimental shortenings were prepared from various mixtures of tallow and cottonseed oil. Three series of shortenings were produced by somewhat different procedures: a) mixtures of tallow and cottonseed oil were hydrogenated and then catalytically rearranged; b) mixtures of hydrogenated tallow and cottonseed oil were rearranged; and c) mixtures of hydrogenated tallow and cottonseed oil were rearranged in the presence of 0.43% glycerine.

Certain combinations and treatments of tallow and cottonseed oil produced shortenings which compared reasonably well with standard vegetable shortenings.

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Isomerization During Hydrogenation. III. Linoleic Acid

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IT HAS BEEN WELL ESTABLISHED that, during the hydrogenation of linoleic acid (*cis*-9,*cis*-12-octadecadienoic acid) to a monoene, the product formed is a mixture of isomeric acids (7). It has been shown that the mixture is composed of not only the *cis* and *trans* geometrical isomers but also positional isomers which may be formed by saturation of either of the double bonds in the chain and also by migration of the bonds during the hydrogenation reaction (5).

The data presented in the first report in this series, on octadecenoic acids (3), showed that both geometrical and positional isomerizations occurred at the same time by a half hydrogenation-dehydrogenation reaction.

When the reaction was investigated further by the hydrogenation of a conjugated diene system (*cis*-10, *cis*-12-octadecadienoic acid), it was found that hydrogenation took place with equal ease in the 1,2, 1,4, and 3,4 positions of the diene system (2).

The present extension of the study is concerned with the diene system whose double bonds are separated by a methylene group.

Experimental

Linoleic acid and methyl linoleate were prepared from crude safflower-seed oil by saponification or ester interchange followed by low-temperature crystallization and separation of remaining monounsaturated acids or esters by treatment with urea as described by Swern (11). The acid (and ester) prepared in this way is essentially pure (over 95%) when saponification of the oil is carried out in dilute (below 5%) alcoholic KOH at room temperature for 24 hrs. However, even with the most careful handling, the linoleic acid always contained a small percentage of an isomer with a double bond at the 8 position. This isomer is believed to be present in the original safflower-seed oil since the ester, in which only a catalytic amount of alkali was present during the ester interchange, contained the 8 isomer. Also the isomer was not detected in cottonseed oil treated in the same manner. The acid and ester were prepared by crystallization instead of by bromination-debromination (9) since the debrominated material contained large amounts of positional and geometric isomers and less than 75% of the 9,12-octadecadienoic acid.

Hydrogenations under pressure were carried out in a Parr medium-pressure hydrogenation apparatus. Hydrogenations at atmospheric pressure with poor hydrogen dispersion were performed as described previously (3).

The catalyst was nickel formate reduced in cottonseed oil. No attempt was made to remove saturated material before use.

The percentage of isolated *trans* isomers was determined as described in the first paper of this series (3).

The fatty-acid composition of partially hydrogenated products was determined by A.O.C.S. methods Cd 1-25 and Cd 7-48 (rev. May 1951) after correction of the iodine value for conjugated double bonds as suggested by Feuge *et al.* (7).

Positional isomers were determined by chromatographic separation of the dibasic acids produced by

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