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Fractionation of Animal Fat Glycerides by Crystallization from Acetone. An Improved Lard Oil[1]

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UNTIL recently the only commercial method for obtaining lard, grease, and tallow oils consisted in graining and pressing the tempered fat. Lard oil, for example, was produced by a process in which the lard was first slowly chilled for three to six days to a temperature of approximately 10°C. The chilled lard was then placed in bags and pressed slowly to express the oil from the crystals. The slow chilling was necessary to obtain the kind of crystals from which the lard oil could be obtained by pressing.

Most of the literature on lard oil and similar oils consists of patent literature. The patents pertaining to lard oil issued within the last 15 years are chiefly concerned with various modifications of low-temperature crystallization of the fats from organic solvents. In 1934 Parkhurst and Voorhees (6) received a U. S. patent for destearinizing fatty oils. Their process for removing stearin and other relatively high melting substances from fatty oils comprised diluting the oil under pressure with a liquefied, but normally gaseous, hydrocarbon. The temperature of the solution was then lowered by allowing some of the hydrocarbon to evaporate, causing the stearins to crystallize from solution. Sufficient solvent was retained in the liquid state to dissolve the liquid fats. Gee (3) obtained a patent in 1948 for a continuous process for fractional separation of fatty oil substances from chilled fat solutions of various polar and nonpolar solvents. Muckerheide (5) likewise was granted a patent for a continuous process, in which he emphasized the use of a polar solvent in which the solubility of water is limited. Isopropyl acetate, ethyl acetate, and methyl isobutyl ketone are such solvents. The inventor reported that the fat solvent properties of such solvents are not appreciably altered by dilution with water.

An interesting modification of the usual solvent crystallization technique for separating mixtures of glycerides or of fatty acids has been disclosed by Spannuth (8). This inventor brings the mixed glycerides or fatty acids to a temperature which is above the melting point of the mixture but below the melting point of a component fraction. He then introduces this mixture into the solvent, which has been cooled to a temperature at which the higher melting fraction is insoluble. It appears that lower proportions of solvent may be successfully used by this technique.

Work has been under way for some time at the Eastern Regional Research Laboratory on the systematic low-temperature crystallization of animal fats (7). It was found that the fractionation of animal fats by crystallization from acetone at 0°C. gives a crystalline fraction consisting principally of trisaturated and disaturated glycerides. The filtrate fraction consists of monosaturated and triunsaturated glycerides. The properties of the crystalline fraction are similar to those of the commercial stearins; the properties of the filtrate fraction are similar to those of lard, grease, and tallow oils. The present paper is an extension of previous work to substantiate general observations and provide more detailed information on yields and properties of the oils. The effect of different degrees of hydrogenation of lard, grease, and tallow oils on the yields, stability, and properties of the oils is of especial interest. The chemical composition of the glyceride fractions has been determined by spectrophotometric analysis and iodine values. For comparison, information on chemical and physical properties of commercial lard oils has been obtained.

Experimental

The lard used was a good grade of prime steam lard. The grease was a commercial grade known as white grease. The inedible tallow, composed chiefly of beef fats, was obtained from a packing house. The edible tallow was also a commercial product. Grease and inedible tallow were treated with carbon at 150-200°C. in the absence of air before they were fractionated or hydrogenated. Fats without carbon treatment contained impurities which seemed to decrease the activity of the nickel hydrogenation catalyst; the carbon-treated samples hydrogenated much more readily. Hydrogenations were carried out at 150°C. with 0.1% nickel catalyst based on the weight of fat. The hydrogenations reported in Table III were performed in all-glass apparatus at atmospheric pressure in batches of about 1 liter of fat; hydrogenations reported in Tables IV and V were performed in a stainless steel laboratory hydrogenator at three-atmospheres gage pressure. All crystallizations were made from acetone solutions that had stood at least overnight at 0°C. The last trace of solvent was removed under reduced pressure at 100°C. while oxygen-free nitrogen was bubbled through the sample.

The analytical and physical constants were determined by standard methods. The content of polyunsaturated acids of each fraction was determined spectrophotometrically; the constants determined for natural acids were employed (1, 2). The oleic acid content was calculated from the difference between total unsaturation as determined by iodine number and that due to polyunsaturated components.

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[1] Report of a study certain phases of which were made under the Research and Marketing Act of 1946.

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Results

Table I shows the effect of different concentrations of lard in acetone at 0°C. on the yields of lard oils and stearins and on some of their properties. It is perhaps surprising that the properties of fractions from the 40 to 1 dilution of acetone (40 ml. acetone to 1 gram fat) are so similar to those from the 10-1 dilution. When the filtrate of the 7 to 1 dilution is compared with the 10 to 1 dilution, it is evident that the two filtrates are similar. From a practical viewpoint, of course, the lower the dilution that will accomplish the desired fractionation, the better. When the still lower dilution of 5 to 1 was tried however, the resulting precipitate, particularly with unaltered lard, was too soft and mushy for convenient filtering in the laboratory. Consequently the acetone dilution of 7 ml. to 1 gram of fat was used in the remainder of the crystallizations reported in this paper even though a more concentrated solution, such as 5 to 1, worked satisfactorily for hydrogenated lards.

TABLE I

Effect of Concentration of Lard in Acetone at 0°C. on Yields of Lard Oils and Stearins and on Some of Their Properties

	Oils from lard[a]			Stearins from lard[a]		
	1	2	3	1	2	3
Ml. acetone per gram fat	40-1	10-1	7-1	50-1	10-1	7-1
% Yield	75	73	71	24	27	29
Iodine No	77.4	79.4	79.7	32.8	33.8	34.3
Titer, °C	32.5	31.4	31.6	48.9	48.3	48.4
Pour Point, °F	33	29	27			

[a] Iodine No. of lard, 66.5.

TABLE II

Properties of Lard and Grease Oils and Stearins Obtained by Crystallization from Acetone (Dilution 7 Ml. to 1 Gram Fat) at 0°C. and of Commercial Lard Oils

	Lard[a]		Grease[b]		Commercial lard oils		
	Oil	Stearin	Oil	Stearin	1	2	3
% Yield	71	29	62	38	....	....	....
Iodine No	79.7	34.3	78.6	42.3	82.8	75.0	77.3
Pour Point A.S.T.M. °F	33	....	25	....	35	35	40
Titer, °C	31.6	48.4	31.8	....	33.0	32.3	33.5

[a] Iodine No., 66.5.
[b] Iodine No., 64.9.

In Table II a comparison is made between some of the properties of lard and grease oils prepared by low-temperature crystallization and those of commercial oils. The yields of lard and grease oils shown are 71 and 62%, respectively. It has been reported (9) that the yield for the graining and pressing process is about 55% lard oil and 45% stearin; yields of lard oil up to 75% by crystallization methods (4) have been reported. The iodine values for the lard and grease oils are 79.7 and 78.6. These fall within the range of the analyses of three commercial lard oils, which have an iodine range of 75.0 to 82.8. The lard and grease oils have pour points of 33 and 25 as compared with 35 and 40 for the commercial oils. The titers of 31.6 and 31.8 are near those of the commercial oils, which range from 32.3 to 33.5°F.

Table III shows the effect of partial hydrogenation of grease on the yields and properties of grease oils and stearins. White grease having an iodine number of 64.7 was hydrogenated to an iodine value of 60.6. The oils obtained from these two greases had iodine numbers of 78.6 and 74.1, respectively. Both samples have acceptable pour points and titers. Fatty acid analysis of the samples shows a drop in polyunsaturation with hydrogenation. However the percentage of monoethenoic acid increased with hydrogenation, going from 46.8 to 47.7% for the unfractioned samples and from 56 to 60% for the oils.

It will be noted that the arachidonic and linoleic acids have been markedly reduced in amounts with continued hydrogenation. In contrast however the monoethenoic acid continued to increase to 52.2 and 66.4% for the unfractionated sample and oil, respectively. This is fortunate since the oleic acid glyceride components are the most important in the production of lard and grease oils.

In this experiment hydrogenation of the grease was continued until the iodine number had dropped to 50.9. This proved to be somewhat lower than might be desired from a practical standpoint for the yield of oil was only 54%. However the pour point and titer of the oil were similar to those of the other oils.

Table IV is similar to Table III except that it applies to tallow instead of grease. Inspection of the two tables shows that the polyunsaturated acid content (sum of percentages of linoleic, linolenic, and arachidonic acids) of the tallow is much less than that of the grease; namely, 2.3% compared with 11.9%. A study of the effect of hydrogenation shows that it is possible to hydrogenate the grease much more than the tallow before adversely affecting the pour points of the oils subsequently obtained from them. For example, when grease, iodine number 64.7, was hydrogenated to iodine number 50.9, the oil obtained from the product had a titer and pour point of only about one unit higher in each case than those obtained from the oil of the original grease. The polyunsaturated acid content of the grease was lowered from 11.9% to 2.4% by the hydrogenation. In contrast, when tallow, iodine number 39.9, was hydrogenated to iodine number 38.1, the oil obtained from the product had a pour

TABLE III

Effect of Partial Hydrogenation of Grease on Yields and Properties of Grease Oils and Stearins

	Grease[a]	Hydrogenated Grease			Oils from Grease	Oils from hydrogenated grease			Stearins from grease	Stearins from hydrogenated grease		
		1	2	3		1	2	3		1	2	3
Iodine No	64.7	60.6	58.4	50.9	78.6	74.1	72.2	64.3	42.8	35.8	37.4	32.0
% Yield	....	....	....	....	62	65	57	54	38	34	43	45
Pour Point A.S.T.M. °F	....	....	....	....	29	30	30	30	....	....	....	....
Titer, °C	....	....	....	....	31.8	31.3	31.0	32.7	....	....	....	....
Linoleic	10.8	8.3	5.4	2.1	13.3	9.8	7.0	2.1	7.2	4.2	2.9	0.5
Linolenic	0.8	0.9	0.4	0.3	1.2	0.8	0.4	0.3	0.9	0.4	0.3	0.1
Arachidonic	46.8	0.1	0.0	0.0	0.3	0.1	0.0	0.0	0.2	0.0	0.0	0.0
"Oleic"	0.3	47.7	52.2	51.5	56.0	60.0	64.9	66.4	29.5	30.0	34.8	34.3

[a] Free fatty acids as oleic, 1.5%.

TABLE IV

Effect of Partial Hydrogenation of Tallow on Yields and Properties of Oleo Oil and Stearin

	Edible tallow[a]	Hydrogenated tallow		Oils from tallow	Oils from hydrogenated tallow		Stearin from tallow	Stearins from hydrogenated tallow	
		1	2		1	2		1	2
Iodine No.	39.9	38.1	36.4	62.3	59.2	57.3	28.8	27.1	26.4
% Yields	....	....	....	34.1	32.5	28.8	66.7	68.2	71.3
% F.F.A.	1.10	1.13	1.16	....	....	....	....	....	....
Pour Point	....	....	....	41	61	63	....	....	....
Titer	....	....	....	36.4	37.5	37.7	....	....	....
Linoleic	1.8	0.8	.8	4.2	3.1	2.1	1.4	1.1	0.6
Linolenic	.4	0.2	0.2	0.6	0.4	0.3	0.3	0.2	0
Arachidonic	0.1	0	0	0.3	0.1	0.1	0	0	0
"Oleic"	41.1	40.2	38.3	58.0	58.8	58.4	28.3	27.4	28.2

[a] Free fatty acids as oleic, 1.1%.

point of 61°F. compared to 41°F. for that of the oil from the unhydrogenated tallow. The hydrogenation of the tallow lowered the polyunsaturated content from 2.3% to 1.0%.

Table V contains data on the effect of hydrogenation of grease and tallow on the stability of the oils obtained from them. The effects of antioxidants and antimetallic compounds are also recorded.

TABLE V

Effect of Hydrogenation of Grease and Inedible Tallow on the Stability of the Oils, and Effects of Antioxidants and Antimetallic Compounds

Sample	Iodine No.	Control	P.H.Q.[a] (0.005%) H_3PO_4 (0.01%)	P.G.[b] (0.01%) H_3PO_4 (0.01%)
		A.O.M. hrs.	*A.O.M. hrs.*	*A.O.M. hrs.*
White grease	55.1	¼		
Oil from white grease	71.8	¼	2	2
Hydrogenated white grease	50.1	½		
Oil from hydrogenated white grease	66.0	1¼	63	90
Inedible tallow	47.0	3		
Oil from inedible tallow	62.5	¾	65	90
Hydrogenated inedible tallow	42.1	½		
Oil from hydrogenated inedible tallow	58.3	2½	>100[c]	>100[c]

[a] Phenylhydroquinone.
[b] Propyl gallate.
[c] After 100 hours the sample still had no measurable peroxide.

White grease having an iodine number of 55.1 was hydrogenated until its iodine number was 50.1. The oils prepared from this grease, before and after hydrogenation, showed stabilities of 2 and 63 hours, respectively, when stabilized with a mixture of phenylhydroquinone and phosphoric acid. A mixture of propyl gallate and phosphoric acid increased the stability of the hydrogenated sample to 90 hours.

Antioxidants without phosphoric acid or other metal deactivators were not tested in the series of experiments shown in Table V. Considerable data however were obtained in preliminary runs on comparable samples which demonstrate the importance of metal deactivators used in conjunction with antioxidants in these hydrogenated materials. For example, a sample of "grease oil" from a partially hydrogenated grease (A.O.M. 1 hr.), to which was added 0.05% phenyl hydroquinone, increased in stability to only 22 hours whereas the same oil containing 0.05% phenyl hydroquinone and 0.05% phosphoric acid increased in stability to more than 65 hours without measurable peroxide formation. The oils prepared from tallow before and after hydrogenation did not show such great differences in stabilities when phenyl hydroquinone and phosphoric acid were added. This is probably due partly to the fact that the tallow was less oxidized than the grease and also contains much less polyunsaturated acids. The tallow had no initial peroxide value whereas the white grease had an initial peroxide value of 23 milliequivalents per kilogram of fat.

Summary

Various edible and inedible grades of animal fats, such as lard, grease, tallow, and selectively hydrogenated lard, grease and tallow were separated into "oils" and "stearins" by crystallization from acetone.

The chemical and physical properties as well as the yields of oils and stearins obtained by this method are described.

Antioxidants and metal deactivators are much more effective in stabilizing lard and grease oils produced from partially hydrogenated fats than in stabilizing corresponding products from unhydrogenated fats.

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