Detection and Estimation of Dipalmito and Distearo Glycerides in Hydrogenated Oils

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Introduction

The glyceride composition of natural fats has been studied at length by Hilditch and co-workers. Much of their work is included in his book—The Chemical Constitution of Natural Fats. Longenecker's paper entitled The Composition and Structural Characteristics of Glycerides in Relation to Classification and Environment is also of interest and has an excellent bibliography. This paper was given at the April, 1941, meeting of the American Chemical Society in St. Louis and appears in the October, 1941, issue of Chemical Reviews.

Apparently the methods developed by these workers have not been applied at all extensively to vegetable shortenings. Available information as to change in glyceride composition during the course of hydrogenation has been obtained incidentally when hydrogenation was applied to the natural fats as one of the steps in determining original composition.

Compound type shortening depends mostly on trisaturated glycerides for its consistency or physical characteristics. These glycerides are normally a mixture of tristearin and mono-palmito-distearin. The consistency of an all-hydrogenated blend is determined largely by its disaturated-mono-unsaturated glycerides. These will be mostly distearo-monounsaturated, palmito-stearo-unsaturated and dipalmito unsaturated. Iso-oleic is also a factor, but for the time being, has not been considered in our work. The amounts and kinds of disaturated glycerides in an all-hydrogenated blend depend upon oil composition and hydrogenation. Variations in these components probably determine the properties of the product, as far as physical characteristics are concerned.

We have developed a crystallization method, using the principles offered by Hilditch which, when applied to hydrogenated oils, will give some information as to the composition of the unsaturated or partially saturated glycerides. This method has been applied to several samples of widely varying oil composition with results which will be discussed later.

Method

The sample is dissolved in four parts by weight of C.P. acetone and then stored in a tightly capped bottle at 0°C. for three days. The precipitate is separated by rapid filtration on a Buchner funnel. The solvent is evaporated from the filtrate and the amount of fat recovered is obtained. Iodine value, thiocyanogen value, and saponification value are determined on this portion.

The precipitate from the first crystallization is dissolved in ten parts of C.P. acetone and crops obtained after twenty-four hours at 15.0°C. and then after twenty-four hours at 0°C. Yields, iodine, thiocyanogen, and saponification values are obtained on the fat in both precipitates and the filtrate from this second crystallization.

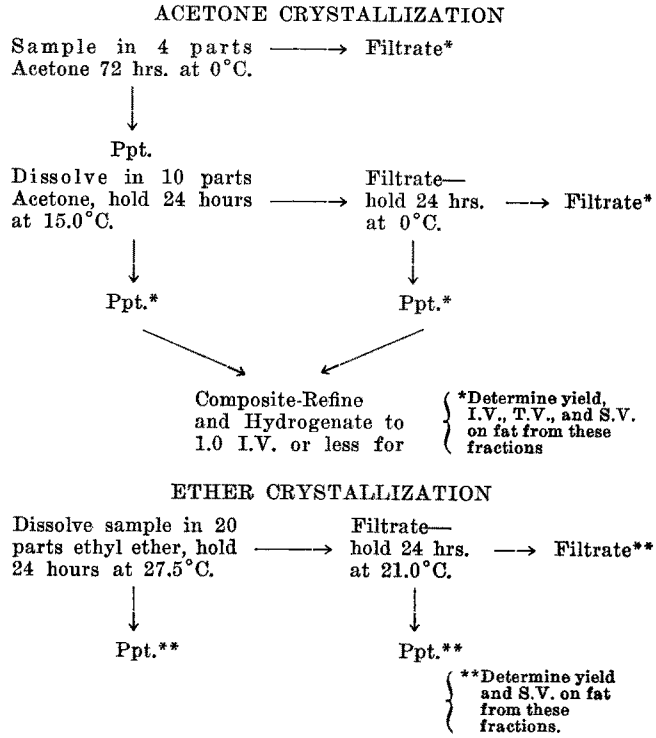
The 15.0°C. and 0°C. precipitates from the second crystallization, which contain most of the disaturated glycerides in the original sample are composited and, after refining, hardened to 1.0 iodine value or less. This stearine is dissolved in twenty parts of ethyl ether and allowed to stand twenty-four hours at 27.5°C. followed by twenty-four hours at 21.0°C. Crops of crystals are separated at both temperatures. Yields and saponification values are obtained on the fat recovered from each precipitate and the filtrate.

The fat from the filtrate contains the di- and tripalmitin. Since any glycerides of shorter chain acids, such as those in coconut oil, are also present in this fraction, it is necessary to determine the palmitic acid content by methyl ester distillation.

A record is kept of the quantities obtained at all points in the procedure. It is desirable for a study of the results to convert all fractions to percentages of the original sample, making the necessary corrections for losses. Olein and linolein in each fraction may be calculated from the iodine and thiocyanogen values.

If a methyl ester distillation for the determination of palmitic acid in the ether filtrate fraction is to be made, an original sample of 500-1000 grams is desirable. If this is omitted, a much smaller amount, possibly 100 to 200 grams, will provide sufficient material from the several separations for analysis.

Crystallization Flow Sheet



Discussion of Results

The olein and linolein figures on the various acetone fractions indicate the degree of separation which has been obtained between saturates and unsaturates. The saponification numbers on the acetone fractions are of little value if coconut oil is present because, while this component appears mostly in the less saturated fractions, it nevertheless influences all the saponification numbers to some extent. On the ether crystallization fractions, the saponification number indicates the disposition of the palmitic acid and in this separation the coconut oil appears only in the most soluble fraction.

There appear to be six points of major interest in the experimental data:

1. There are essentially no trisaturates in hydrogenated shortenings containing no added stearine. The fractions insoluble at 15.0°C. from the second acetone crystallization contain approximately one-third unsaturates or an average of one per glyceride, except in the case of blend No. 4, where the unsaturates are lower by an amount in proportion to the quantity of trisaturates known to be present.

2. The portion insoluble at 27.5°C. in the ether crystallization is an index of the monounsaturated distearine in the original sample. In the blends studied, this component increases in proportion to the amount of soybean oil present (i.e. numbers 1, 2, and 3) and undoubtedly, is derived from the hydrogenation of this oil.

3. The other two ether fractions, after subtraction of the dipalmito glycerides, are composed mainly of glycerides which were palmito-stearo-monounsaturated in the original shortening.

4. The monosaturated-diunsaturated glycerides may have some bearing on the consistency characteristics of a shortening. These appear largely in the filtrate from the second acetone crystallization, but also to some extent in the other fractions. An idea as to the proportions of palmitic and stearic comprising the saturated acids can be gained from saponification number data.

5. The glycerides containing two or three palmito groups are not completely recovered when palm oil is present. Judging from the amount of these components present in palm oil, as indicated by our acetone separation and also the data of Hilditch and co-workers, roughly one-half the amount present in the original sample appeared in the final filtrate from the ether crystallization of blends numbered 2 and 4.

6. More di- and tripalmitin was recovered from hydrogenated cottonseed oil and blend No. 1 than was to be expected. According to the "even distribution" theory of Hilditch and experimental work of Hilditch and Jones (J. Soc. Chem. Ind. 1934, 53, 13T) the amount of these in cottonseed oil is negligible. If the recovery of them in our procedure is assumed to be as poor as for the same components in palm oil, the deviation from the "even distribution" theory is even more pronounced.

This work has been preliminary in nature and the conclusions should be considered as tentative. There are some findings which are not readily understandable, as for instance, the relative recoveries of dipalmito glycerides from cottonseed oil and from palm oil. Variation in the positions at which the palmitic acid groups are attached to the glycerol is an interesting possibility which might account for solubility differences. Another opportunity for further work would be the correlation of glyceride composition with finished product behavior.

TABLE 1

Experimental Data on Various Oils and Blends

Sample	Palm Oil	Hyd. Cotton Oil	Hyd. Blend No. 1	Hyd. Blend No. 2	Hyd. Blend No. 3	Compound Type Blend No. 4
Composition %						
Palm Oil	100.0	.....	.....	20.0	.....	42.0
Cottonseed Oil	.....	100.0	95.0	31.0	31.0	8.0
Soybean Oil	.....	.....	.....	44.0	64.0	50.0*
Coconut Oil	.....	.....	5.0	5.0	5.0	.....
1st Acetone Crystallization						
Fraction soluble at 0°C.—% of original sample	53.0	63.7	65.5	58.0	56.0	63.4
Olein—% in fraction	49.3	64.5	59.2	60.1	67.2	60.2
Linolein—% in fraction	12.3	11.5	12.5	10.6	11.8	17.6
Saponification Number	194.7	190.0	197.2	193.9	194.9	193.8
2nd Acetone Crystallization (Insoluble Portion From 1st Crystallization)						
Fraction insoluble at 15.0°C.—% of original sample	12.0	15.8	13.6	16.5	20.0	14.6
Olein—% in fraction	7.9	42.1	38.2	29.5	30.8	17.1
Linolein—% in fraction	3.1	0.4	0.2	1.2	3.7	2.6
Saponification Number	206.7	197.7	198.5	195.6	193.3	198.2
Fraction insoluble at 0°C.—% of original sample	23.0	10.3	10.7	13.0	14.0	12.2
Olein—% in fraction	30.0	51.4	44.8	47.0	49.7	39.3
Linolein—% in fraction	4.1	1.8	4.3	3.4	5.0	3.2
Saponification Number	203.1	196.6	198.0	195.8	194.0	199.2
Fraction soluble at 0°C.—% of original sample	12.0	10.2	10.2	13.5	10.0	9.8
Olein—% in fraction	.....	56.7	54.9	57.2	62.1	51.8
Linolein—% in fraction	.....	7.3	8.8	9.6	5.2	14.9
Saponification Number	199.5	192.6	197.0	196.7	195.2	195.7
Ether Crystallization (Composite of Insoluble Fractions From 2nd Acetone Crystallization Hydrogenated to 1.0 I. V. or lower)						
Fraction insoluble at 27.5°C.—% of original sample	.....	0.0	0.5	12.1	17.6	7.4
Saponification Number	.....	.....	195.3	191.5	190.8	194.3
Fraction insoluble at 21.0°C.—% of original sample	.....	13.6	13.2	5.4	5.8	10.3
Saponification Number	.....	.....	194.4	193.5	192.4	196.8
Fraction insoluble at 21.0°C.—% of original sample	.....	12.4	10.6	12.0	9.6	9.1
Saponification Number	.....	.....	198.0	198.3	195.5	199.8
% Palmitin in Fraction	.....	42.3	44.8	44.2	34.0	66.6
Di- and Tripalmitin necessarily present—calculated as dipalmitin—% of original sample	.....	3.1	3.7	3.2	0.3	8.8

Tristearine	189.0	Saponification Number
Palmito-distearine	195.5	Saponification Number
Dipalmito stearine	202.0	Saponification Number
Tripalmitin	208.6	Saponification Number

* Includes 4.5% stearine.