

ON THE DETERMINATION OF STEARIC ACID IN FATS.

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THE quantitative determination of the individuals composing the mixture of fatty acids obtainable from any fat or oil is one of the most difficult problems of analytical chemistry and one which is very far from solved at the present time. Apart from the determination of certain constants, such as the iodine absorption, amount of potassium hydroxide consumed, etc., little more can be done than a rough separation of saturated from unsaturated fatty acids. A quantitative separation of the unsaturated fatty acids has barely been attempted, if we except the determination of the amount of hexabromide obtainable from the mixed fatty acids of linseed and other drying oils, measuring the linoleic acid, to which one of us referred at a recent meeting of the Society of Public Analysts, and concerning which we hope to publish the results of our joint work at an early date. The few figures published by Hazura, based upon the proportions of hydroxy acids obtained by the action of potassium permanganate upon unsaturated fatty acids, are obviously very rough and of no practical value.

For the separation of the solid fatty acids no quantitative method of any kind exists and here again inferences based upon the determination of physical constants and of the equivalents of mixtures have been the only available means. If it be known that a mixture contains two saturated fatty acids only and no more, the determination of the melting point or of the molecular equivalent is a satisfactory way of arriving at their relative proportions. But unfortunately there is no practicable method of proving that two and only two acids are present and, hence, all determinations hitherto made must be accepted with a considerable amount of doubt.

Heintz's well-known method supplies the only means of obtaining an insight into the qualitative composition of a mixture of non-volatile fatty acids, and Liebig's analogous method a means of examining a mixture of volatile fatty acids. Heintz's method is, however, solely a qualitative one and appears unsuited for analytical purposes. Without frequent repetition of the fractional precipitation nothing like a perfect separation of two closely allied fatty acids can be obtained. As, however, we

could find but few data on this point in the literature, we thought it advisable to ascertain to what extent Heintz's method was capable of concentrating the fatty acid of higher molecular weight from a mixture of known composition, by a single precipitation only.

FRACTIONAL PRECIPITATION.

Stearic Acid.—A considerable quantity of fatty acids obtained in the usual manner from cocoa-butter was dissolved in as little hot alcohol as possible, and when cold, the crystallized mass was pressed in a linen cloth. The residue was again dissolved in hot alcohol and the residue again pressed. After repeating this crystallization ten times the melting-point remained constant at 68.5° C. (Heintz gives 69° C. as the melting-point of stearic acid), and had a molecular weight of 283, as determined by the amount of potassium hydroxide consumed and the percentage of barium in the barium salt. (Theory for stearic acid, 284.)

Palmitic Acid.—In most of our experiments we made use of pure palmitic acid obtained from palm oil and prepared by Hopkin and Williams. This melted at 61.8° C. (Heintz, 62° C.), and had a molecular weight of 255.5 (theory 256). Subsequently we prepared palmitic acid from Japan wax. To the experiments made with the latter we shall refer later on.

Precipitation with Barium Acetate.—A solution of barium acetate was prepared containing 8.94 grams of barium acetate in 100 cc. of water, of which solution five cc. contained 0.241 gram barium, capable of combining with one gram of stearic acid. The mixed fatty acids were dissolved in 100 cc. of hot (methylated) alcohol of ninety-eight per cent., and the required quantity of barium acetate solution was added drop by drop from a burette to the hot alcoholic fatty acid solution, which was shaken after the addition of every drop. After cooling the precipitates were filtered off, thoroughly washed with cold alcohol of ninety-eight per cent., dried in the water-bath, and the barium contained in them determined by ignition with sulphuric acid. From the amount of barium sulphate obtained the molecular equivalent of the precipitated fatty acids was calculated and from this the amount of stearic acid by the formula :

$x = \frac{284(m-256)}{m(284-256)}$ where x is the required amount of stearic acid, m the molecular equivalent found, and 284 and 256 the equivalents of stearic and palmitic acids, respectively.

The filtrate and washings from the first precipitate were mixed and a second fraction of the fatty acids remaining in solution precipitated with barium acetate solution and treated as before. In some cases a third and fourth precipitation was made. The results are given in the following table :

I.							
Stearic acid.	Palmitic acid.	Barium acetate solution added.	Barium salt.	Containing barium.	Molecular weight of fatty acids.	Stearic acid in precipitate.	Weight of re-covered stearic acid.
Grams.							
1	1	5	(1) 0.9614	0.1919	275.5	71.7	0.549
		5	(2) 0.4326	0.09	261.75	22.2	0.076
		5	(3) Too small for accurate estimation.				
							0.625
1	2	5	(1) 1.0046	0.2021	272.9	62.8	0.5039
		5	(2) 0.9696	0.1985	273	63	0.4983
		5	(3) 0.5122	0.1066	261.6	22.3	0.0904
							1.0926
1	3	5	(1) 0.8830	0.1827	263.2	27.9	0.1953
		5	(2) 0.9100	0.1863	267.3	42.8	0.3097
							0.5050
1	3	5	(1) 0.8920	0.1842	264.4	30.9	0.2187
		5	(2) 1.0315	0.2125	265.2	35	0.2866
							0.5035
0.5	0.5	2.5	(1) 0.5376	0.1082	272.8	62.7	0.2692
1	1	2.5	(1) 0.5246	0.107	268.3	46.6	0.1946
		2.5	(2) 0.5262	0.1065	270.4	54	0.2266
							0.4212

As a further means of getting some idea of the composition of the precipitated fractions, we recovered the fatty acids by shaking the barium salts with ether and hydrochloric acid in a separating funnel, washing the ethereal solution several times with water, evaporating the ether, and determining the melting-point of the mixed fatty acids. We thought it well to check,

on this occasion, the table of melting-points constructed by Heintz, referring to mixtures of stearic and palmitic acids. The following are our results, in comparison with Heintz's.

II.

Stearic acid. Per cent.	Palmitic acid. Per cent.	Heintz ¹ M. P. ° C.	Hehner and Mitchell. ° C.
100	0	69.2	68.5
90	10	67.2	66.5
80	20	65.3	64.2
70	30	62.9	61.5
60	40	60.3	59.4
50	50	56.6	55.6
40	60	56.3	55.5
32.5	67.5	55.2	54.5
30	70	55.1	54.2
20	80	57.5	56.5
10	90	60.1	59.0
0	100	62.0	61.8

It will at once be seen, by a glance at these tables, that any judgment as to the composition of a mixture of stearic and palmitic acids based on the melting-point can only be very roughly approximate, especially when the acids are present in about equal proportions, there being only about 1.5° C. difference between mixtures containing fifty and thirty per cent. of stearic acid. Still, it enabled us to some extent, to confirm the results given in the first table, obtained by determining the equivalents of the mixed acids. In the following table results are given based on the melting-points only :

III.

Stearic acid.	Palmitic acid.	Barium acetate solution added. cc.	Melting-point. ° C.	Approximate per-centage of stearic acid in precipitate.
0.5	0.5	(1) 2.5	60.8	60-70
		(2) 2.5	54.6	about 30
1	1	(1) 2.5	59.4	60
		(2) 2.5	59.0	nearly 60
		(3) 2.5	58.6	50-60
		(4) 2.5	54.2	30
0.5	1	(1) 2.5	57.0	about 55
		(2) 2.5	55.8	" 50
		(3) 2.5	54.2	30
2.1	0.9	(1) 2.5	64.0	nearly 80
		(2) 2.5	65.0	80-90
		(3) 2.5	65.8	80-90
		(4) 2.5	60.5	60-70
		(5) 2.5	54.6	30-40

¹ *Ann. Chem. Pharm.*, 92, 295.

It is obvious from these results, that by means of an aqueous solution of barium acetate, used in the proportions stated, but a very moderate concentration of the higher fatty acid can be accomplished in one precipitation. Curiously enough, it not infrequently happens, that the second fraction contains a larger percentage of the higher fatty acid, than the first portion. Quantitative results cannot possibly be obtained.

Precipitation with Lead Acetate.—As it might be thought, that owing to the employment of an aqueous solution and the consequent somewhat sudden separation of the precipitate a less perfect fractionation took place than if the precipitate were allowed to form very slowly, we repeated the fractionation with the employment of an alcoholic solution of lead acetate. A solution, containing 6.67 grams of the salt in 100 cc. of alcohol, of which ten cc. were capable of completely precipitating one gram of stearic acid, was made, and the required amount of this solution was added slowly to the hot alcoholic solution of the mixed fatty acids. The fraction crystallizing out on cooling was treated as described in reference to the preceding table.

IV.

Stearic acid. Grams.	Palmitic acid. Grams.	Lead acetate solution added. cc.	Melting-point of liberated acids.	Approximate per- centage of stearic acid. Per cent.
0.5	1	(1) 5	60.2	60-70
		(2) 5	55.0	30-40
		(3) 5	55.4	30-40

Here again the separation was no more complete than in Tables I and III.

Precipitation with Magnesium Acetate.—A solution containing 18.835 grams of magnesium acetate in 500 cc. of which ten cc. were required to precipitate one gram of stearic acid was made and used in the following experiment:

V.

Stearic acid. Grams.	Palmitic acid. Grams.	Magnesium ace- tate solution added. cc.	Melting- point.	Approximate percentage of stearic acid.
0.5	0.5	5	62	About 70

By these results we were confirmed in our opinion, that while by oft repeated fractionation a mixture of fatty acids may be

made to yield the highest fatty acid in a comparatively pure condition, by a single precipitation no sharp separation can even approximately be obtained however slowly the separation be allowed to take place. When more than two fatty acids are present in a mixture, the results must be still more doubtful. For quantitative analytical work, for which, of course, the method was never intended, it is not applicable.

After numerous attempts to separate the liquid and the solid fatty acid from each other by means of glacial acetic acid, which readily dissolves oleic, but at the same time not inconsiderable amounts of palmitic and of stearic acids, and by mixtures of acetic acid, alcohol and water (after the method of David¹), we came to the conclusion that nothing like a sharp separation could thus be effected. Somewhat better were the results obtained by the use of dilute alcohol alone. On grinding up fatty acid, as obtained by the saponification of a solid fat and decomposition of the soap, with dilute alcohol (sp. gr. 0.911) in a mortar, we found that the unsaturated fatty acids were completely dissolved, the palmitic acid partially so, while the stearic acid remained almost completely undissolved. From ten to twenty grams of the various fatty acid mixtures were thus ground up with 100 cc. of dilute alcohol, the latter removed by a filter-pump and the residue was washed with 100 cc. of dilute alcohol of the same strength. After pressing the residue in a filter-cloth, placed between blotting paper, a pearly white mass was obtained, which after drying, showed an iodine absorption of from two to three per cent. From the molecular weight, ascertained by means of alcoholic alkali, the proportions of palmitic and stearic acids were calculated on the assumption that nothing but stearic and palmitic acids were present, an assumption which cannot be very incorrect, because the lower fatty acids are soluble to a considerable extent in alcohol of the strength mentioned.

¹ *Compt. rend.*, 86, 1416.

			VI.				
	Fatty acids. Grams.	Washed resi- due. Grams.	Molecular weight.	Per cent. stearic acid in the washed acids.	Per cent. stearic acid in original acid.	Iodine number of original fatty acid.	Melting-point of original fat- ty acids.
Butter (Brittany)...	10	2.0	260.8	15.0	3.0
Same sample.....	259.3
	260.3
Butter (Danish)	20	2.5	263.6	29.0	3.6
	263.8
Butter (Danish)	10	1.85	258.0	7.0	1.29
Oleomargarine.....	10	4.0	267.3	428.	17.12	46.5	43.2
Margarine	10	3.7	266.2	40.0	14.8	43.23	38.0
Margarine	10	4.0	265.0	34.4	13.76
Mutton tallow	10	5.5	264.0	30.0	16.5	39.5	43.8
Mutton tallow	20	11.0	265.8	37.4	19.47	35.6	47.8
Lard.....	20	7.5	258.8	8.6	3.2
Lard.....	20	7.0	260.0	15.0	5.2

Although, when working under exactly the same conditions, fairly constant results could be obtained, the method effected at best only a concentration of the stearic acid and afforded no certainty that the final product consisted of only two fatty acids, from the equivalent of which the proportion might be calculated. Although we worked as nearly as possible at a uniform temperature, variations could not be avoided, leading us to abandon the search in this direction.

The following reasoning gave much greater hopes of success. Imagine a mixture of fatty acids to be treated with an amount of solvent sufficient to dissolve the whole of the various components of the mixture. If the solvent were already saturated with one of the constituents of the fatty acid mixture to be examined, it was to be expected that the totality of the corresponding fatty acid contained in the mixture would remain undissolved. Or, if a mixture were heated with a solvent saturated at a certain temperature with one of the constituents sought to be determined, then on cooling down to a corresponding temperature, the whole of the particular constituent might be expected quantitatively to crystallize out, provided that the other constituents of the fatty acid mixture exercised no restraining influence by adding to the solubility.

In principle this is the method of Casamajor for the quantitative separation of cane sugar from invert sugar. Casamajor washed the sugar to be examined with methyl alcohol saturated with cane sugar.

We chose the freezing-point of water as the most suitable constant temperature, it being easily maintained and the solubility of stearic and the other acids occurring in fats being suitable for accurate work.

After some preliminary experiments with ether and other solvents which we had to reject as taking up too much stearic acid, we finally fixed upon alcohol (methylated) of a specific gravity of 0.8183, containing 94.4 per cent. of alcohol by volume. It will be seen, in the following experiments, that the exact strength of alcohol is a matter of no consequence, but the solubility determinations here to be given apply only to alcohol of that strength.

For maintaining a constant temperature we employed an ice-chest, constructed of a metal box, to the interior side of which were soldered suitable sockets to receive the clamps necessary to hold the small flasks in which the determinations were carried out, submerged up to the neck in ice-water. The metal box was fitted in a wooden box and the space between metal and wood was packed with wool and saw-dust, while a cushion of wool and flannel was placed between the lids of the metal and wooden boxes.

For the preparation of the stearic solution about three grams of pure stearic acid were dissolved in about a liter of warm alcohol of 0.8183 sp. gr., and the stoppered bottle containing the solution was placed over night in the ice-water (in which were lumps of ice) in the chest, so that the bottle was submerged up to the neck. After twelve hours a considerable portion of the stearic acid had crystallized out. The saturated mother liquor was siphoned off without removing the bottle from the ice-water. The filtering siphon used consisted of a small thistle funnel twice bent at right angles, fitting with its smooth limb in a flask attached to a suction pump, while the bulb of the funnel, which was submerged in the ice-cold solution, was covered over with a piece of fine calico. On applying suction a perfectly clear stearic

solution was obtained, saturated at 0° C., or rather at 0.2° C., which was the temperature almost constantly shown by a standard thermometer.

A precisely similar mode of filtration was also adopted in the quantitative experiments on mixed fatty acids, the thistle funnel used being a miniature one, with a bulb not larger than about one-quarter of an inch in diameter. The accompanying drawing will sufficiently explain the apparatus.

VII.

SOLUBILITY OF STEARIC ACID IN ALCOHOL (SPECIFIC GRAVITY 0.8183),
AT 0° C.

Stearic acid taken. Gram.	Alcohol. cc.	Time of cooling. Hours.	Residue obtained by evaporating ten cc. of the filtered solution. Gram.
0.2	100	12	0.0155
0.2	100	36	0.0153
0.2	100	84	0.0153
0.5	100	12	0.0158
0.5	100	36	0.0145
0.5	100	84	0.0140
0.3	100	48	0.0144
0.3	100	84	0.0142
0.3	100	12	0.0157
0.3	100	36	0.0149
0.4	100	12	0.0158
0.4	100	36	0.0148

VIII.

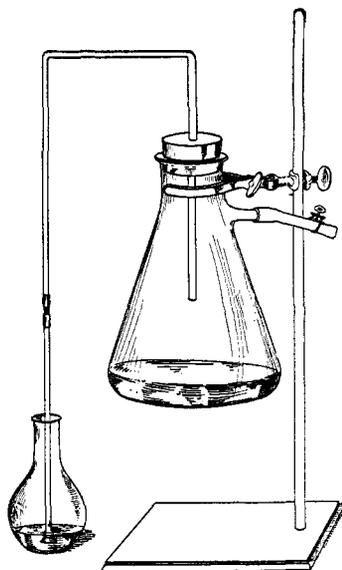
SOLUBILITY OF PALMITIC ACID IN ALCOHOL (SPECIFIC GRAVITY 0.8183)
AT 0° C.

Palmitic acid taken. Gram.	Alcohol. cc.	Time of cooling. Hours.	Residue obtained by evaporating ten cc. of filtered solution. Gram.
2	100	12	0.1298
2	100	36	0.1244
2	100	60	0.1211
2	100	84	0.1134
2	100	108	0.1086
2	100	132	0.1044
2	100	156	0.1028
2	100	12	0.1320

From the two preceding tables it appears that it is easy to obtain constant results with stearic acid, and that supersaturation does not readily occur. The solubility of the palmitic acid in alcohol of the same strength as that employed for stearic acid is about eight times greater than in the case of stearic acid, and constant results are far less easy to obtain.

Experiments with Known Amounts of Pure Stearic Acid.—Accurately weighed quantities of pure stearic acid were placed in weighed flasks capable of holding about 150 cc., provided with a rubber cork. From fifty to 100 cc. of the saturated stearic solution were added, the flask closed and the contents gently warmed on a water-bath till all stearic acid had dissolved. The flask was then clamped in the ice-chest and kept in ice-water over night. In the morning the contents of the flask were, as a rule,

gently shaken, without being withdrawn from the ice-water, in order to promote crystallization and again left for at least half an hour. The alcohol was then filtered off by means of the arrangement described, care being taken to draw off the solution as completely as possible. The residue was washed three times successively with ten cc. of the saturated stearic solution, cooled down to 0° C. The small funnel was then detached from the suction arrangement and washed with hot pure alcohol, the washings falling into the flask containing the residue, the flask



being previously taken out of the ice-chest. The alcohol was then evaporated, and the residue dried at 100° C. to constant weight.

Since the interior sides of the flask, as well as the residue of crystallized stearic acid, retained a small amount of the stearic alcohol, a small correction, experimentally found to amount to 0.005 gram had to be applied, this amount having to be deducted from the total weight found. In almost all cases the precipitated stearic acid formed a small, but compact mass after filtration, retaining a very minute amount only of the washing solution.

The following results were obtained.

IX.

Stearic acid taken. Gram.	Saturated alcohol. cc.	Total residue found.	Stearic acid after deducting 0.005 gram. Gram.
0.0188	100	0.021	0.016
0.0220	100	0.025	0.020
0.0320	100	0.0381	0.0331
0.0381	50	0.0445	0.0392
0.1072	50	0.113	0.108
0.1356	100	0.1414	0.1364
0.1414	100	0.1440	0.1390
0.2137	100	0.2206	0.2156
0.2282	100	0.2334	0.2281

As a check we also made a number of experiments by dissolving weighed quantities of the stearic acid in the saturated alcohol, leaving the flask over night in ice and, instead of weighing the crystallized deposit, evaporated measured quantities of the filtrate, thus determining the amount of stearic acid in solution. If this corresponded with the amount previously found to be soluble in ten cc. of alcohol, it followed that the whole of the added stearic acid had separated.

X.

Stearic acid. Gram.	Saturated alcohol. cc.	Residue in 10 cc. after twelve hours. Gram.
0.1955	100	0.0155
0.5090	100	0.0150
0.3130	100	0.0157
0.4010	100	0.0158

It will be seen that the amount left in solution perfectly corresponded with that contained in the stearic alcohol, and that therefore none of the added stearic acid could have remained in the solution.

Having thus satisfied ourselves, that pure stearic acid could be determined with a satisfactory degree of accuracy, it remained to be seen, whether in the presence of other fatty acids, equally satisfactory results could be obtained, or whether other fatty acids would themselves exercise a solvent action upon the stearic acid.

XI.

INFLUENCE OF LOWER SATURATED FATTY ACIDS.

Stearic acid taken. Gram.	Lower fatty acid employed. Gram.	Stearic acid found after deducting 0.005 gram. Gram.
0.0556	5 cc. butyric acid.	0.0582
0.0476	5 cc. acetic acid.	0.0468
0.0990	1.5 gram cocoanut fatty acids.	0.1070
0.1060	0.9079 cocoanut acids.	0.118
0.2020	0.5130 " "	0.220

XII.

INFLUENCE OF PALMITIC ACID.

Stearic acid taken. Gram.	Palmitic acid added. Gram.	Stearic acid found, after deducting 0.005 grams. Gram.
0.2026	0.5472	0.2032
0.1016	0.5354	0.1074
0.0520	0.600	0.055

Influence of Unsaturated Fatty Acids.—The oleic acid used for the following experiment was commercial oleic acid, and was not free from stearic acid. Three grams crystallized in the manner described from stearic alcohol, giving 0.025 gram of stearic acid. A corresponding deduction had therefore to be made in the following experiment :

XIII.

Stearic acid. Gram.	Crude oleic acid. Gram.	Stearic acid found. Gram.
0.2997	3.200	0.3355

Deducting from the latter figure 0.0278 gram, the amount of stearic acid obtainable from the three and two-tenths grams of oleic acid, and 0.005 gram for correction, there remain 0.3027 gram of stearic acid recovered from the 0.2997 taken, or one per cent. too much.

Influence of Saturated and Unsaturated Fatty Acids Together.—Fatty acids prepared from hog's lard were first crystallized by themselves and afterwards with different quantities of added stearic acid, with the following results :

XIV.

Lard acids taken. Gram.	Stearic acid added. Gram.	Stearic acid obtained. Gram.	Added stearic acid recovered. Gram.
0.5	none	0.0242
0.5	0.050	0.0738	0.0496
0.5	0.080	0.1058	0.0816

It is thus shown, that stearic acid added to a mixture of fatty acids can be completely recovered in the manner described.

Experiments with Commercial Stearic Acid.—The sample employed had an iodine absorption of two and three-tenths per cent. and melted at 56.2° C.

XV.

Commercial acid taken. Gram.	Stearic alcohol added. cc.	Amount of deposit minus 0.005 gram. Gram.	Per cent. of stearic acid found.
0.1042	50	0.0490	47.02
0.1480	50	0.0702	48.7
0.2510	50	0.1223	48.7
0.2900	50	0.1468	50.6
0.3984	100	0.1932	48.5

XVI.

EXPERIMENTS WITH COMMERCIAL LARD.

Lard.	Iodine number.	Stearic acid minus 0.005 gram. Gram.	Stearic acid in fatty acids. Per cent.
1 0.9794	61.2	0.1338	13.06
2 0.5065	not taken	0.0635	12.53
2 0.8328		0.1090	13.08
2 1.0604		0.1359	12.90
3 0.4970	57.5	0.0801	16.11
3 1.0178		0.1634	16.05
4 1.0987	61.2	0.0669	6.09
4 0.9990		0.0764	7.6
4 1.2878		0.0782	6.07
5 0.5150	65.66	0.0548	10.64
5 1.0410		0.1030	9.89
6 0.5000	63.58	0.0372	7.4

Determination of Stearic Acid in Fat from Different Parts of the Same Pig.—It is well known that the proportion of liquid and solid fat varies very considerably in the fat taken from different parts of the same animal. We thought it would be of interest to ascertain whether in this case the alteration affected only the proportions of fluid (unsaturated) and solid fatty acids, or whether the latter themselves varied in composition. The animal from which the fat was taken was a Somersetshire pig six months old. The following table contains the results :

XVII.

Part of pig.	Fatty acids taken. Grams.	Melting-point.	Iodine absorption.	Stearic acid minus 0.005 gram. Gram.	Melting-point of deposit.	Stearic acid. Per cent.
Head	0.5212	34.8 ^j	67.7	0.0452	67.8	8.67
"	1.0481			0.0993	66.2	9.47
Ham	0.5006	34.6	61.6	0.0438	67.5	8.74
"	1.0044			0.0906	67.3	9.02
Breast	0.5152	36.8	64.2	0.0610	67.2	11.84
"	1.0219			0.1114	66.8	10.90
Flare	0.4936	40.0	52.8	0.0774	66.5	15.70
"	1.0096			0.1450	67.2	14.40
Back	0.5002	35.6	67.9	0.0430	67.0	8.59
"	0.9998			0.0910	66.5	9.2
Flare from another pig :						
	1.5221			0.1940	67.2	12.70
	1.1320			0.1386	67.0	12.24

It will be observed that the melting-points of the deposits obtained were in all cases slightly lower than that of pure stearic acid, but a mere trace of liquid fatty acid would be fully sufficient to account for the depression.

Assuming that the iodine number measures only oleic acid, and that 100 parts of the latter absorb ninety parts of iodine, it is easy to calculate the percentage of stearic acid in the saturated fatty acids contained in the total fatty acids from the fat of the animal referred to. On making this calculation it is found that the following are the percentages of stearic acid in the saturated fatty acids: Head, 35.0 per cent.; ham, 28.1 per cent.; breast, 39.6 per cent.; flare, 36.4 per cent.; back, 36.1 per cent.

It follows that in the case of this particular animal, at least, the variation in the consistency of the fat from various parts was almost entirely due to fluctuations in the amount of oleic acid.

Stearic Acid in Fat from Different Parts of the Same Sheep.—The different specimens of fat were taken from a Scotch sheep eighteen months old :

XVIII.

Part of sheep.	Fatty acids taken. Grams.	Iodine No. of fat.	Melting point of fatty acids.	Stearic acid minus 0.005 gram. Gram.	Percentage of stearic acid.
Back	0.5280	61.3	41.4	0.1310	24.8
Neck	0.5324	48.6	42.2	0.0876	16.4
Breast	0.7146	58.2	33.8	Very slight.	About one.
Ham	0.5100	50.6	40.8	No deposit after 2 days.	
Kidney	0.5030	48.16	45.6	0.1318	26.2
"	1.0175			0.2820	27.7

Calculating, as before, the percentage of the stearic acid in the saturated fatty acids we find: Back, 78.0 per cent.; neck, 36.0 per cent.; breast, 3.0 per cent.; ham, none; kidney, 58.0 per cent. The ham fat was liquid at ordinary temperature and that from the breast almost liquid.

In connection with these numbers, the following experiments may here find a place.

The molecular equivalent of the fatty acids from the sheep-kidney fat was found by titration with potassium hydroxide to be 271.6. The iodine number was 48.16, corresponding to 56.0 per cent. of oleic acid, assuming the whole of the iodine absorption to be attributable to oleic acid. The amount of stearic acid found being 26.2 per cent., there remain 17.8 per cent. for other saturated fatty acids. Assuming these to be palmitic, the calculated equivalent of the fatty acids is as follows:

$$\begin{aligned} \text{Oleic acid, } & 0.56 \times 282 = 157.92 \\ \text{Stearic " } & 0.262 \times 284 = 74.71 \\ \text{Palmitic " } & 0.178 \times 256 = 45.57 \end{aligned}$$

277.90

A very fair approach to the 276.1 directly determined.

XIX.

DETERMINATION OF STEARIC ACID IN MISCELLANEOUS FATS.

	Taken.	Iodine No.	Stearic acid minus 0.005 gram. Gram.	Percentage in fatty acids.
Beef-stearine	0.3024	...	0.1516	50.19
"	0.4174	...	0.2131	51.05
Oleomargarine	1.0107	...	0.2295	22.00
"	0.5192	...	0.1104	21.26
"	1.1100	...	0.2630	23.6
Margarine 1	1.0035	...	0.2495	24.8
" 2	0.5000	...	0.0586	11.72
Horse kidney-fat	0.701	85.4	No deposit.	

	Taken.	Iodine No.	Stearic acid minus 0.005 gram. Gram.	Percentage in fatty acids.
Cotton 'stearine'	0.9945	0.0334	3.3
Stillingia tallow		22.87	No deposit.	
Cocoa-butter	1.0168	0.4064	39.9
"	0.9548	0.3878	40.6
Maize oil	5.4186	No deposit.	
Almond oil	5.0236	No deposit.	
Olive oil	5.5558	No deposit.	
Earthnut oil	1.0648	0.0751 (M. P. 67° C)	7.00

XX.

Examination of Lard Crystals Separated from Ether.—It is well known to those who are accustomed to test for beef stearine in lard, that the form of the crystals obtained from pure lard is subject to considerable variation. While from some lards (the softer kinds) nothing but broad plates with pronounced chisel-shaped ends are obtained, from the harder kinds (flare lard) bunches of more pointed, though still chisel-edged, broad needles, crystallize. When the crystals are repeatedly recrystallized from ether, they as a rule become more and more needle-like, until they are practically undistinguishable from beef stearine crystals. One of us illustrated this point some time ago, before the Society of Public Analysts, by the exhibition of a large number of photo-lantern slides. After finding the remarkable differences in the amounts of stearic acid contained in various parts of the fat of the same pig, stated above, we thought that determinations of stearic acid in lard crystals might throw light upon this subject. No one as yet has attempted to explain the cause of the difference between the shapes of lard crystals and of beef stearine crystals, and it is not known whether the phenomenon is due to different isomerides, or simply to the proportion of stearic to palmitic or other acids contained in the deposits.

140 grams of a sample of flare lard, with an iodine absorption of 57.5 and a stearic acid contents of 16.11 and 16.05 per cent. in the fatty acids, were dissolved in a liter of warm ether. This is nearly the proportion of ether to lard generally employed in Stock's mode of working the Belfield test. Next morning there was an abundant deposit of crystals, showing the characteristic chisel-shaped ends. The crystals were separated, a small por-

tion saponified and the free fatty acids obtained. They were found to contain 32.4 per cent. of stearic acid. The ethereal solution, poured off from the crop of crystals, was evaporated, and part of the resulting fatty residue was decomposed to obtain free fatty acids. These contained only fifteen per cent. of stearic acid.

The main crop of crystals was then recrystallized from ether. The crystals were now needle-shaped, but had still distinct chisel-shaped ends. The fatty acids obtained from these contained 47.6 per cent. of stearic acid, while the fatty acids obtained as before from the second solution contained 17.23 per cent. stearic acid.

For a third time the crystals were crystallized from ether. The percentage of stearic acid had now risen in the fatty acids from the crystals to fifty-nine per cent., while the fat in solution contained 33.2 per cent. This third crystallization was, in form, hardly distinguishable from beef stearine crystals.

It can hardly be doubted, from a consideration of these results, that the form of the beef crystals is solely due to a larger proportion of stearic acid, than can be obtained from a pure lard by a single crystallization. When it is considered that pure lard contains, as far as our results go, not more than about fifteen per cent. of stearic acid, while beef stearine contains fifty per cent., it is intelligible, that from a beef-stiffened lard a deposit with a larger percentage of stearine is likely to result than from lard alone. At the same time the subject is quite worthy of a much more extended investigation.

The results also show that very many crystallizations would be required to separate the glycerides of palmitic and stearic acids fairly completely, as has been pointed out by Heintz many years ago.

XXI.

Examination of Samples of Butter.—We have made considerably over one hundred determinations of stearic acid in butter fatty acids, utilizing for this purpose the fatty acids remaining behind in the Reichert method. In the large majority of cases no deposit at all, or only a very minute quantity separated from

the stearic alcohol. In some cases, however, phenomena apparently of supersaturation, occurred. Occasionally on examining the flasks after opening the ice-chest in the morning, the solution was perfectly clear, but after shaking the contents and leaving them for some time longer in the ice, a small, but increasing, crystallization formed. We have not quite concluded our investigation into the cause of this phenomenon, and as the question of the examination of butter, with a view to distinguish it from margarine mixtures, is of very great practical importance, we propose to deal with this part of the subject in a separate communication. Inasmuch as all constants which are now utilized for the discovery of admixtures with butter-fat, are occasionally breaking down, it would be a matter of obvious importance, if a constituent which is never absent from butter substitutes, *viz.*, stearic acid, could be shown to be absent from butter-fat, or to occur in it only in minute quantities. Analysts would then for the first time be in a position to distinguish absolutely between pure and adulterated butter. For the purpose of the investigation we would thank those of our colleagues who take an interest in the subject to kindly furnish us with small samples of undoubtedly genuine butters, normal and abnormal, together with their results of analysis, including any or all of the following: Reichert number, insoluble fatty acids, refractive index, together with any details that may be of interest or importance.

XXII.

On the Abnormal Behavior of Palmitic Acid Obtained from Japan Wax.—Japan wax, consisting or supposed to consist mainly of palmitine with free palmitic acid, is considered to be a ready source of palmitic acid. We prepared a quantity of the acid from Japan wax, possessing apparently all the properties of palmitic acid. On making mixtures of this acid with known amounts of stearic acid, we were surprised to find that only a part, or none at all, of the added stearic acid could be obtained by crystallization from stearic alcohol, as the following figures will show:

Stearic acid. Gram.	Japan-wax acid. Gram.	Time of standing.	Stearic acid found. Gram.
0.1440	0.5	8 days	0.0438
0.2500	0.5	12 hours.	0.1542
0.0200	0.5	12 hours, turbidity only.	
0.2000	0.5	60 hours.	0.1800
0.4000	0.5	12 hours.	0.3800
0.2370	0.5	4 days.	0.2217
0.1500	0.5	4 days.	Turbidity only.
0.1000	0.100	12 hours.	Very slight precipitate.
0.0500	0.1	3 days.	" " "
0.05	0.2	"	" " "
0.025	0.225	"	" " "
none.	0.5	2 days.	none.

Without extended investigation it is impossible even to guess at the reason of the abnormal behavior of Japan-wax acids. Whether they combine with the added stearic acid, or cause the latter to be etherified by the alcohol, we are unable to say. The whole subject of Japan wax is quite worthy of investigation, as the statements made concerning it are somewhat contradictory. In any case, the failure to apply our method to Japan-wax acids does not directly bear upon the question of determination of stearic acid in ordinary fats and oils, in which we are quite satisfied that acid can be determined with reasonable accuracy.

The principle underlying the method described may be applied also to the determination of other fatty acids, such as palmitic and arachidic. In the former case the results would of necessity be less exact on account of the far more considerable solubility of palmitic acid and the greater correction number to be applied. For arachidic acid, on the other hand, the method ought to do good service, as it may safely be assumed that its solubility is far less than that of stearic acid. We hope to recur to the subject at some future time.

To summarize in a few words the method which we recommend :

Prepare a supply of alcohol saturated with pure stearic acid, or with stearic acid containing not much palmitic acid, at 0°C. Dissolve from one-half to one gram of the fatty acid mixture to be examined, if these are solid, or about five grams if fluid, in about 100 cc. (exact measurement is not necessary) of stearic alcohol. Leave in an ice bath over night, agitate the mixture next morn-

ing and allow to stand in ice for a short time, filter off while the mixture remains in ice, wash with stearic alcohol at 0° C., dry and weigh. Determine the melting-point of the product, which should not be much less than 68.5° C.

11 BILLITER SQUARE, LONDON, NOV. 23, 1896.

THE DETERMINATION OF SOLID FATS IN COMPOUND LARDS.

BY GEORGE F. TENNILLE.

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IN March, 1896, there appeared in this Journal an article by J. H. Wainwright entitled, "The Determination of the Solid Fat in Artificial Mixtures of Vegetable and Animal Fats and Oils."

Samples of compound lards had been submitted to the United States laboratory for the determination of the relative proportion of their constituents in order that the claim of the exporters for "drawback" of duties paid on one of the constituents might be verified, and the paper consisted in a description of a mechanical process which had been adopted by the United States laboratory for use in such determinations.

Though no great claim for accuracy in results or of scientific principles involved was made yet the conclusion arrived at was that the process would give correct results to within about one and one-half per cent.

Having been connected with one of the companies interested in the collection of this "drawback" of duties paid on the oleostearine used in compound lard, and having personally supervised the making of the lard which was sent to the United States laboratory for analysis, and hearing that the result obtained by the chemist often fell short of the actual amount of oleostearine which I knew to be contained in the samples, I made a great many trials of the process and came to the conclusion that, though under certain conditions it might give concordant and fairly accurate results, it could not be relied upon at all under certain other conditions.

I have selected a series of ten from the many analyses which were made with a view of showing in a rather exaggerated manner perhaps the possible results when the test is carried out under those conditions which prohibit accuracy.