BOG BUTTER

"BOG BUTTER"

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BOG BUTTER

Bog Butter is a name given to the waxy substance, which is formed when ordinary butter undergoes chemical change other than decay, after being buried in bogs for an indefinitely long time.

HISTORICAL - Animal or vegetable fats, which have been buried for a long time in moist surroundings, without the access of air, lose their characteristics of natural fats and are sometimes classed among organic minerals.
There are three types of these organic minerals:-
1 - Ozocerite, a brown, hard, amorphous wax, which is really solid paraffin and consists of carbon and hydrogen only.
2 - Oxygenated compounds of a bituminous character allied to amber, such as Succinelite, which contains carbon and hydrogen, as well as oxygen.
3 - Brücknellerite, a fat-like mineral of the consistence of butter, which is found associated with certain deposits of brown coal. It gives an acid containing carbon, hydrogen and oxygen.

Some fat-like masses, found in bogs or swamps, which are popularly known as "Bog Butter", or in Germany as, "Sumpf Butter", are described as a mineral by Dana (1), and called Butyrellite in his text book on Mineralogy. He defines it as follows, - "Crystallisable in needles;butter-like

in consistence; color, white; melting point impure native material 47°C. Brazier; after solution in alcohol 51°C. Luck; 52-52.7°C. Brazier; easily soluble in alcohol or ether, contained carbon, hydrogen and oxygen."

Chemists in the early eighties who examined this, made ultimate organic analyses and obtained a ratio of carbon, hydrogen and oxygen very close to that of palmitic acid. In 1885, MacAdam analysed ten samples of bog butter and found that the melting point of the ether soluble portion varied from 40-47°C. He described it as a white, fryable substance, with a greasy feeling and a cheese-like odour, containing some cows' hairs. One sample gave a faint odour of acrolein, and he concluded that butyrellite had no claim to be called a mineral, but that it was just butter.

Bog butter has been found in kegs and wrapped in rushes, also in cloths, which left their markings on the outside of the fat. In the folk lore of Ireland, there are many references to the butter dyke or butter safe, being dug in the bogs, in which the butter, known in some districts as "Fairy Butter", had been stored to keep it sweet and cool during the summer.(2) The fairy origin of the butter might be ascribed to the active imagination of the Celtic brain, many of the inexplicable things in nature being put down to the

good or evil doings of the indigenous fairies of Erin. Mr. Plant, (3) mentioned a mineral, waxy resin, called "Guyaquillite", which was found in extensive deposits in marshy places near Guyaquil, in South America, similar in composition to Bog Butter. He considered bog butter to be produced from the decomposition of vegetable matters forming the peat or bog. Later, after analysing some bog butter, he obtained an acid, similar in composition to palmitic,which could not possibly have arisen from this decomposition.

Some butter two thousand, five hundred, years old, which was discovered in a sealed vase, in the tomb of Queen Hasheps of the Eighteenth Egyptian dynasty was analysed and found to be just rancid butter (4). In the absence of moisture the changes characteristic of bog butter were not observed and the fats were only slightly hydrolysed.

Wigner and Church (5) analysed a sample of bog butter and found that it had the composition already referred to, but all these chemists failed to recognize the changes which butter had undergone.

"Adipocere" is the name given to animal fats, which have been buried for a long period of time under similar conditions to bog butter, that is, in the absence of air, and the presence of a large amount of water. Dr. Ruttan (6) made

a thorough and a very complete study of both pig and human adipocere. He found that the fat had been broken up into the fatty acids, glycerol, and a small quantity of soaps. The soluble portions had been removed mechanically and part of the unsaturated oleic acid had become hydrolysed, forming the two waxy characteristic acids of adipocere, namely, the iota and theta hydroxy stearic. He found, in brief, that adipocere was a mixture of palmitic and stearic acids, with a varying proportion of the two hydroxy stearic acids, with calcium soaps and traces only of fats or oleic acid.

The object of this study of bog butter was to compare its composition and properties with those of adipocere. In other words, to find out if the products of hydrolysis of all fats, whether of animal or vegetable origin, were the same. Further the bog butter was examined in order to prove that it was composed of the decomposition products of ordinary butter, due to prolonged hydrolysis in the absence of air.

Dr. Ruttan obtained fourteen samples of bog butter from Ireland, eight from the Royal Irish Academy of Dublin and six from the Belfast Public Art Gallery and Museum.

These samples had been found in the bogs of Tyrone, Antrim, Mayo, Westmeath, Derry and Queens, and were

undoubtedly genuine specimens of bog butter.

The color of the butter varied from white or pale yellow through biscuit color to a light brown, In some cases there was a layer of clear, chocolate brown, stratified material, around the outside of the sample, notably numbers, 2, 3, 8 and 12. Matted fragments of leaves, cones, and woody fibre were found associated with the butter and some hairs, which were presumably cows' hairs. These were black, straw yellow, and red in color, and occurred in samples number, 4, 6, 11 and 14.

The nature of the bog butter may be described as a soft, waxy, granular and subcrystalline solid, with a greasy feeling. Other samples, such as number 7 and 5 were extremely hard and waxy, very similar in appearance to adipocere. The samples from Belfast, numbers 9 to 14, were preserved by the Museum authorities in Petroleum, and Number 10, had a very strongly marked odour of resin, whereas, the other samples were practically odourless.

The samples were small, varying from 10.25 grammes in number 9 to 38.7 grammes in number 13, the average being 21.7 grammes.

EXPERIMENTAL - As the samples were not homogenous, they were very finely ground up in a mortar, and in this

manner a good average of the whole sample was obtained for study.

The samples so obtained were dried to constant weight over sulphuric Acid, in an evacuated dessicator at a pressure of 15 millimetres. The loss in weight was calculated as moisture, and this varied from 0.011% in number 7 to 0.382% in number 9, the average was 0.157%. These results showed that the samples were comparatively dry.

The melting point varied from 46.0°C. in number 11 to 53.5°C. in number 2, and the average was 49.4°C. Ordinary butter melts at 32°C. The samples which contained the waxy stratified material, numbers 2 and 3, melted at a slightly higher temperature than the others, namely, 53.5°C. and 52.0°C. There were hard globules of orange, waxy appearance, several millimetres in diameter, in four of the samples, numbers 1, 3, 6 and 13, and these had a melting point of 78°C. which corresponds to that of the mixture of the mono hydroxy stearic acids found in adipocere. These globules were so large in number 13 that it was quite easy to separate them from the main sample for purposes of identification . The outside layer of number 8, which was semi-transparent and distinctly harder than the rest of the sample, melted at 54.6°C. The following tables, numbers 1 and 2 contain some of the physical properties of the original Bog butters.

Table 1. ORIGINAL BOG BUTTER From Dublin Between pages 6 and 7.

No.	Museum Designation	Where Found	General Description
1	S.A.1899-63 R.I.A. Dublin	Townland Derryaghan County Tyrone,1898	Pale Biscuit yellow,soft granular with crystals & hard glassy lumps,Melting Point 78°C. earthy staining.
2	14.1908 No. 3 Lower Shelf,R.I.A.Dublin	Found when cutting turf,Lough Eske,near Donegal	Partly granular and sub-crystalline,white waxy & soft. Covered with black vegetable matter,below this clear,hard waxy stratum.
3	Ireland No. 4 Lower Shelf,R.I.A. Dublin	Not stated	Stained chocolate brown for 2 mm. of waxy stratified mass. Interior granular & sub-crystalline material with harder, waxy globules.
4	Ireland No. 2 Lower Shelf,R.I.A. Dublin	Not stated	Soft granular material of biscuit color with slight darkening on outside.Leaves & hair found.
5	R.I.A. Dublin	Co.Westmeath,38/1915	Extremely hard, waxy,white mass, similar to Adipocere.Matted fragments of leaves & scales from cones.Very little soft granular material.
6	R.I.A. Dublin	Foxford Co.Mayo	Very waxy soft granular material, white to light brown,and some hard globules,Melting Point 77.2°C. Red hairs.
7	R.I.A. Dublin	Abbeyleix,Queens Co. W.37.	Very hard,waxy,granular,similar to 5,small cavities with crystals,vegetable mold.
8	No.1,Lower Shelf R'I.A. Dublin	Not stated	Granular,waxy,biscuit color,with darker brown streaks,outside layer semi transparent & amorphous, distinctly harder, Melting Point 54.6°C.

Table 1. Cont'd. ORIGINAL BOG BUTTER Between pages 6 and 7.

from Belfast

No.	Museum Designation	Where Found	General Description
9	No.1,L-16,Public Museum,Belfast	Clough Mills,County Antrim	Biscuit color,waxy,granular, homogeneous,very slightly stained,almost free from foreign matter.
10	1-23,No.2	Near Broughshane County Antrim	Light brown,granular,waxy, similar to 9, but more deeply stained,peculiar odor.
11	No. 3.	Not stated	Soft,fatty,granular,carrying small hairs,quite a greasy feeling,homogeneous.
12	No.4,1911-351	Near Portadown	Granular,white,waxy,hard materials,containing stratified brown substance,woody fibre.
13	No. 5,1911-352	Boveva Bog,County Derry,1830	Yellow amorphous,orange,waxy masses,several mm. in diameter, Melting Point 78°C.
14	No. 6,1911-350	County Derry	White,porous,granular,with hairs cavities lined with harder materials

Table 2. ORIGINAL BOG BUTTER Between pages 6 and 7.

No.	Weight in grams.	Moisture	Melting & Solidification Point		% Soluble in Ether
1	15.25	0.15%	49.0°C.	45.0°C.	95.275%
2	18.25	0.3	53.5	43.0	94.3
3	25.	0.17	52.0	43.2	96.0
4	21.85	0.068	49.5	44.6	98.64
5	18.17	0.055	50.3	46.0	98.77
6	26.25	0.07	51.5	47.0	98.06
7	18.	0.011	49.5	46.3	98.85
8	21.5	0.265	49.1	42.0	96.69
9	10.25	0.382	46.8	42.0	96.94
10	16.25	0.275	49.9	47.0	95.86
11	24.85	0.24	46.0	42.0	98.66
12	24.5	0.033	48.0	42.0	97.88
13	38.7	0.093	48.3	42.0	98.09
14	29.9	0.092	47.5	40.0	97.69

Table 2. Cont'd. ORIGINAL BOG BUTTER Between pages 6 and 7.

No.	% Insoluble in Ether	% of Total Ash	Notes on Insoluble Residue
1	4.725%	0.69%	Trace of Calcium soap,no soluble salt, vegetable fibre.
2	5.7	0.523	Trace of soap. Humus & some volatile material,no calcium.
3	4.0	0.574	Small trace of soap.No calcium,fibrous vegetable tissue
4	1.36	0.484	Small amount of soap & no calcium.Humus
5	1.23	0.116	Trace of soap,no calcium. Mostly humus
6	1.94	0.443	Humus & some fusible matter,mostly sand, sodium salts & trace of calcium.
7	1.15	0.321	Some calcium,appreciable amount of soap, vegetable matter
8	3.31	0.226	Trace of soap,organic woody brown material, no calcium.
9	3.06	0.577	Small amount of soap. No calcium.Organic matter
10	4.14	0.535	Sticky brown substance left on evaporation of ether. Trace of calcium,fibrous woody residue.
11	1.34	0.308	Trace of calcium,mostly sodium,fibrous material with few grains of sand,trace of soap,peculiar odor.
12	2.12	0.262	Trace of soap,no calcium,woody material.
13	1.91	0.336	Trace of soap,sand and calcium,woody material.
14	2.12	0.485	Trace of soap & calcium,humus & spongy mass of mold.

PRELIMINARY SEPARATION OF FATS BY SOXHLET EXTRACTOR -

The extraction of the fat and the fatty acids was carried out in a Soxhlet Extractor, using ether as a solvent. A Schleicher and Schull extraction thimble was loosely filled with asbestos, dried at 95°C. cooled, and weighed in a glass thimble holder, closed with a ground glass stopper. The dried sample was packed in the thimble with alternate layers of asbestos and weighed as before. After extracting for six or seven hours, the ether was evaporated, the last portion removed under diminished pressure, and the residue dried in vacuo to constant weight. The percentage of soluble matter was calculated by loss in weight of the thimble and contents, and this checked by the actual weight of the extracted substance in the flask. The extracted matter calculated by these two methods gave concordant results.

THE INSOLUBLE ETHER RESIDUE.

The average amount of insoluble material from the ether extraction was 2.75%, varying from 1.15% in number 7 to 5.7% in number 2. This was tested for calcium and sodium, both of which were found to be present in very small quantities in numbers 1, 6, 7, 10, 11, 13 and 14. There was some infusible matter in numbers 5 and 6, which was quite insoluble in hydrochloric acid or nitric; probably sand.

The main portion consisted of humus, traces of soap, and fibrous vegetable mold. The soap was detected in all the samples, except numbers 6 and 10, by setting free the fatty acid with hydrochloric acid. This solution was shaken up with ether to dissolve the fatty acid, and the mineral acid was washed out with water in a separating funnel. The ether was evaporated and the residue had the appearance and odour of fat acids. Sample number 10, which had been preserved in petroleum, gave a sticky brown resinous substance, when the ether was evaporated.

The amount of ash in the original bog butter was determined by slowly igniting a weighed quantity of the ether insoluble residue in a small platinum dish, and this was found to be fairly constant. The average was 0.42%, and this varied from 0.116% in number 5 to 0.577% in number 9.

ETHER SOLUBLE MATERIAL -

A solid waxy cake was obtained after the ether had been evaporated completely. This was quite hard and of a straw yellow color. It contained the fatty acids, small quantities of unsaponifiable matter, and some neutral fat.

The average of these extractions gave 97.25% soluble in ether; this varied from 94.2% in number 2 to 98.85% in number 7.

THE PHYSICAL CONSTANTS OF THE ETHER SOLUBLE RESIDUE.

The physical constants of the ether soluble material are tabulated in the following tables, numbers 3 and 4.

The melting and solidification points of the extracted matter were determined and the average melting point was found to be 47.4°C.; the lowest was 44.7°C. in number 11, and the highest, 50.3°C. in number 5.

The refractive indices were determined, by means of the Abbe Zeiss refractometer, of the solid extracts at temperatures slightly above their melting points, and from these the refractive index at 55°C. was calculated for each, and found to average 1.4420. This varied from 1.4377 in number 4 to 1.4459 in number 13. The highest value was found in number 10, namely, 1.4463, but this was not a pure sample.

The acid value was determined in the usual manner, in order to find the amount of free fatty acids. This varied from 153.0 in number 1 to 203.2 in number 4, with an average of 173.8. This shows a large proportion of fatty acids in bog butter, whereas, the acid value of ordinary butter is practically nil.

The saponification value was determined, and this showed the total amount of fat acids, free and combined, present in the Bog butter. The mean molecular weight of the fatty acids, was calculated from this and found to be near the mean molecular

Table No. 3 ETHER SOLUBLE RESIDUE Between pages 9 and 10.

No.	Melting & Solidification Point	Solidification Point	Refractive Index at 55°C.	Acid Value	Neutral Fat
1	46.9°C.	43.0°C.	1.4412	153.0	25.81%
2	46.6	43.1	1.4424	171.4	21.0
3	47.9	45.5	1.4404	194.0	6.5
4	48.3	44.2	1.4377	203.2	7.25
5	50.3	48.5	1.4399	189.2	9.83
6	47.6	44.7	1.4435	155.7	24.0
7	47.2	44.9	1.4395	187.2	11.2
8	49.8	45.0	1.4436	165.2	19.55
9	46.0	43.9	1.4427	192.6	9.63
10	50.3	42.7	1.4463	107.6	30.9
11	44.7	41.3	1.4420	153.7	14.25
12	46.0	42.2	1.4405	188.0	8.0
13	47.1	39.6	1.4459	154.0	16.92
14	45.5	40.2	1.4423	153.2	25.15

Ordinary Butter
32.0

Table No. 4 ETHER SOLUBLE RESIDUE Between pages 9 and 10.

No.	Saponification & Value	Mean Molecular Weight	Iodine Value	% Olein	% Oleic Acid
1	203.1	276.1	12.36	14.32%	13.71%
2	214.0	262.1	15.27	17.70	16.91
3	206.8	271.5	15.99	18.51	17.74
4	218.2	257.0	14.11	16.38	15.59
5	208.5	269.0	7.40	8.58	8.21
6	201.8	278.1	18.24	21.14	20.23
7	209.5	268.0	8.95	10.39	9.93
8	203.0	276.5	15.14	17.56	16.8
9	212.0	264.9	13.70	15.89	15.20
10	153.5	366.0	12.89	14.93	14.30
11	178.0	315.5	15.70	18.20	17.41
12	203.6	276.0	11.25	13.04	12.48
13	183.7	306.0	14.56	16.89	16.16
14	201.4	279.0	12.08	14.0	13.40
Ordinary Butter	226.0	248.0	38.	44.0	42.15

Table No. 4, Cont'd. ETHER SOLUBLE RESIDUE Between pages 9 and 10.

No.	Saponification value of Acetylated fat.	Acetyl Value	% Hydroxy Acid
1	212.0	18.50	11.3%
2	209.1	17.40	10.6
3	217.6	16.09	9.8
4	216.98	27.51	16.8
5	219.0	11.94	7.2
6	212.0	24.80	15.1
7	225.6	27.28	16.6
8	206.5	24.95	15.2
9	218.4	26.9	16.4
10	166.3	53.70	32.8
11	213.9	32.0	19.5
12	204.15	11.7	7.1
13	222.9	41.7	25.4
14	184.8	15.2	9.2
Ordinary Butter		1.9-8.6	~~3.2~~

weight of a mixture of Stearic and Palmitic acids in molecular proportions, namely, 270; the molecular weight of palmitic acid is 256, and that of stearic acid, 284. The saponification value varied from 178 in number 11 to 218.2 in number 4, giving an average of 203.4. In some instances this value was lower, showing an excess of palmitic acid. The saponification value was lower than that of ordinary butter, which was as high as 233, and this corresponded to a mean molecular weight of 240.5 and showed that in the passage of ordinary butter to bog butter, the lower fatty acids disappeared. The two samples, numbers 11 and 13, which had the highest mean molecular weights, of 315.5 and 306.1, were the ones which contained the largest quantity of the hydroxy stearic acids. The molecular weight of the latter is 300.

The ester value is determined from the difference between the saponification and the acid values, and shows the average amount of neutral fat, present in bog butter, to be 15.3%. The least amount of fat found was, 6.5% in number 3 and the largest amount, 25.81% in number 1. Sample number 10 which contained the petroleum gave abnormal results, and these were omitted from the averages.

THE INVESTIGATION OF THE PRESENCE OF UNSATURATED FATTY ACIDS.

In order to find the amount of unsaturated acids present in bog butter, the iodine number was determined. Wijs' solution was used for this determination and iodine was absorbed, showing the presence of an unsaturated acid.

The iodine number varied from 7.4 in number 5 to 18.2 in number 6,

with an average of 13.44. From this value the calculated average percent of olein was found to be 15.5%, or as oleic acid 14.9%. The average iodine number for butter is 38, which is equivalent to 42.15% oleic acid, or 44% olein. The oleic acid in bog butter is, therefore, about one third this amount, showing that two thirds of the unsaturated acid in butter has disappeared; a portion of the oleic acid has been converted into the hydroxy stearic acids, but most of it has probably been carried away mechanically.

ESTIMATION OF VOLATILE FATTY ACIDS.

One of the chief characteristics of ordinary butter is the amount of volatile fatty acids present, namely, 12.15%. In order to detect the presence of any volatile fatty acids in bog butter the Reichert Meissl method (6) was followed. Five grammes of the ether soluble residue were saponified, and after the alcohol had been evaporated, the soap was dissolved in hot water, and the fatty acids liberated with normal sulphuric acid. The volatile acids were distilled over with steam and 150 C.C. of the distillate collected for titration with tenth normal potassium hydroxide. The Reichert Meissl value so obtained was 3.3 which corresponded to 0.58% volatile fatty acids, calculated to Butyric acid. This value is almost negligible compared with the same value for ordinary butter, which is 27.6, corresponding to 12.15% volatile fatty acids. No volatile

acids were detected in adipocere, although the same method was employed for their separation.

HYDROXY STEARIC ACIDS.

Preliminary tests showed the presence of acids of high melting points, corresponding to the hydroxy stearic acids found in adipocere. These hydroxy acids are comparatively insoluble in petrolic ether, although just as soluble as the fatty acids in ordinary ether. Therefore, for the purpose of separation and identification of these hydroxy stearic acids, the ether soluble residue was extracted with light petrolic ether (B.P.30°-45°C.) and the insoluble residue recrystallised from warm ether at room temperature and also at zero. Two well defined acids were separated from each sample after a series of recrystallisations. One acid crystallised in elongated prismatic needles which had oblique terminal planes. The melting point of this acid was 84.5°C. and as much as 4.55% was obtained pure from sample No. 13 of bog butter. This acid corresponded to iota hydroxy stearic acid, which was found in adipocere. The other mono hydroxy stearic acid, crystallised in glistening waxy plates, which were rhombic or hexagonal in form. The melting point of these plates was, 78°C. There was always a larger proportion of the prisms than of the plates. The lowest melting point of any known di-hydroxy stearic acid is about 100°C., therefore, these acids are most

probably mono-hydroxy stearic acids. These two acids were found to be identical with the two hydroxy stearic acids found in adipocere. It has been shown that there is a trace of a di-hydroxy stearic acid in butter (7) namely, 0.38%. One fraction from number 6 had a melting point of 91.5°C. which indicated the possible presence of a trace of a di-hydroxy stearic, whose melting point was in the neighborhood of 100-125°C.

The constitution of the acid melting at 84.5°C. has been definitely established, by Shukoff and Schestakoff, to be iota hydroxy stearic acid, that is, the hydroxyl group is attached to the iota carbon atom. The position of the hydroxyl group in the other acid (M.P. 78°C.) has not been established. However, unless there is another oleic acid in bog butter, with the double bond in a different part of the molecule from ordinary oleic acid, it seems most probable that the hydroxyl group is attached to the theta carbon atom. Therefore, these two acids obtained from bog butter are isomers and their relation to oleic acid is evident from the following formulae,-

Oleic Acid $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$

Iota Hydroxy Stearic acid $CH_3(CH_2)_7\underset{OH}{CH}-\underset{H}{CH}(CH_2)_7COOH$

Theta Hydroxy stearic acid $CH_3(CH_2)_7\underset{H}{CH}-\underset{OH}{CH}(CH_2)_7COOH$

These two waxy acids were the ultimate products of hydrolysis of the olein in butter, the first compound formed being oleic

acid, which combined with another molecule of water to form the saturated hydroxy acids.

The acetyl value was determined to find approximately the amount of hydroxy acids in the ether soluble residue. A definite portion of the fat was boiled gently in a round bottom flask with a reflux condenser for six hours, with an equivalent weight of fused anhydrous sodium acetate, and three times its weight of acetic anhydride. The filtration method was employed as described by Lewkowitsch (8). The acetyl value varied from 11.7% in number 12 to 41.7% in number 13, and the mean value found was 22.71 corresponding to 14.86% mono hydroxy stearic acid. The per cent of hydroxy acids varied from 7.1% in number 12 to 25.4% in number 13. This value was exceedingly high in the samples which contained hard globules in the original bog butter. The acetyl value for butter is 1.9-8.6. The Bog butter has a much higher value as some of the unsaturated oleic acid of butter has been converted to the hydroxy stearic acid.

FATTY ACIDS OF THE ETHER SOLUBLE MATERIAL.

After a series of recrystallisation of the residue, soluble in petrolic ether, a white cyrstalline solid was obtained, which when dry gave a melting point of 58°C. This was, in all probability, a eutectic mixture of stearic and palmitic acids.

The ether soluble residue was saponified with a large excess of alcoholic potash and the fatty acids were liberated with concentrated Hydrochloric acid. The acids separated in a layer on top of the aqueous solution and on cooling, hardened. The acid value was 220.9 and the mean molecular weight 254. This was recrystallised from warm alcohol at 5°C. After four hours a precipitate was obtained, which, when filtered gave a melting point of 57.8°C. By a series of fractional recrystallisations 4.1% of an acid was obtained with a constant Melting point of 69.2°C. which corresponds to stearic acid.

SUMMARY - The conclusions to be drawn from the analyses and other determinations described in this paper is that bog butter results from the slow hydrolysis of butter in the absence of air, with the time factor of indefinite value; and that it has the same general composition as adipocere. The following table shows the comparison between the physical constants of the ether extract of bog butter and that of adipocere. -

	BOG BUTTER	ADIPOCERE
Melting Point	47.4°C.	61.5°C.
Acid Value	173.8°C.	201.7
Saponification Value	203.4	207.0
Mean Molecular weight	276.0	288.0
Acetyl Value	22.7	34.75
Iodine number	13.44	6.04
Specific Gravity at 100° C.	0.8332	0.8436

The iodine number is larger in bog butter than in adipocere and this indicates a larger amount of oleic acid, which accounts for the slightly lower melting point of the bog butter.

There is a greater difference between the acid and saponification values in bog butter, than in adipocere, which shows that there is more neutral fat in bog butter than in adipocere.

In adipocere there is 4.41% of calcium soaps, whereas in bog butter only the most minute traces could be detected. This is due to the fact that the calcium soaps in adipocere, are formed from the calcium in the bones, while in bog butter these conditions are absent.

The similarity between bog butter and adipocere is not evident from the fact that the two isomeric mono-hydroxy stearic acids found in adipocere (9) are also present in bog butter. Brown's analysis of butter (10) is as follows,-

Olein 34.99%	Lauric 2.7%
Stearin 1.91	Capric 0.34
Palmitin 40.51	Caprylic 0.53
Myristic 10.44	Caproic 2.32
	Butyric 6.23%

During the conversion of ordinary butter into bog butter the fat in the presence of a large excess of water is gradually

broken down into the fatty acids and glycerol. The olein is partially converted to oleic acid and afterwards to the hydroxy stearic acids. The Stearin and Palmitin leave behind the corresponding insoluble fatty acids, and the glycerol so liberated is washed away mechanically, as are also most of the lower fatty acids, which are water soluble, and the alkaline soaps.

We conclude that all fats when hydrolysed under the conditions stated above yield identical products, in varying proportions; and that bog butter is a waxy derivative of ordinary butter; and not a mineral derived from bog products as some of the early chemists believed.

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STEARIC AND PALMITIC ESTERS OF PROPYLENE AND TRIMETHYLENE GLYCOL.

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IN PART QUALIFICATION FOR DEGREE OF MASTER OF SCIENCE.-

THE FAT ACID ESTERS OF PROPYLENE & TRIMETHYLENE GLYCOL.

Historical.- The fat acid esters of ethylene glycol were prepared by Dr. R. F. Ruttan, F.R.S.C.(1) in 1915, when their properties and physical constants were ascertained. It was found that they could best be prepared by the direct union of the acid with the glycol at a comparatively high temperature, with constant stirring. The separation of the mono and di derivatives could only be effected by prolonged fractional crystallization.

Previous to this only one compound had been prepared in 1895 by Würtz, namely, the distearate of ethylene glycol. He used the silver salt of the acid with ethylene bromide, but this gave only the di-compound, and although many experiments were performed it was found quite impossible to obtain any trace of the mono derivative. To prepare the silver salt of the fat acid, a solution of the acid in alcohol was saturated with dry ammonia, and an equivalent proportion of an alcoholic solution of silver nitrate added. After the Ammonia and some of the alcohol had been distilled, the salt precipitated out in fine needles. However, this process is very tedious and has now been replaced by the direct esterification method.

In this paper is described the preparation and properties of the fat acid esters of the two isomeric propylene glycols,namely, 1.2. di hydroxy propane, and 1.3. di hydroxy propane or trymethylene glycol, and their chemistry compared

with that of the Ethylene Glycol esters.

Experimental.- Only the very purest materials were employed in the following experiments, and these were carefully tested before use. The charge, consisting of the glycol with the fat acid was esterified at a constant temperature for several hours in the electric oven with a platinum stirrer, which was run by a small electric motor. At this comparatively high temperature the water formed during the reaction was driven off. A hard cake of fat was obtained, which was washed with hot water to remove the excess of glycol. The free uncombined acid present in this fat was determined and the calculated amount of sodium bicarbonate added to neutralize the free acid. This was fused in a porcelain dish on the water bath for one hour. The ester was washed out with hot ether, using a hot filter. This was allowed to crystallise at room temperature, then about zero, and the residue dissolved in 95% alcohol. From their relative solubilities these crystals could be separated into the di and mono compounds for purification. A series of fractional recrystallisations were made until the mono and di esters were obtained pure, as shown by their constant melting points. When these esters had been prepared by this method and purified, their physical properties were determined.

The melting point was taken in the usual way.

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The refractive indices were determined by the Abbe Zeiss refractometer at various temperatures, slightly above the melting points of the esters, and from these the refractive index at the melting point was calculated.

The solubility of each of the purified fats was found by saturating a solution of absolute alcohol at a temperature slightly above that at which the solubility was wanted. These saturated solutions were kept for sixteen hours at a constant temperature of 15°C. About 10 C.C. of the clear supernatant solution were drawn off by means of a warm pipette and weighed accurately in a closed weighing bottle. After the alcohol had been evaporated very slowly on a hot plate, the residue was dried to constant weight at 95°C. The rest of the saturated solution was placed in a mixture of melting ice and kept at zero for several hours, when the solubility at this temperature was determined in a similar way.

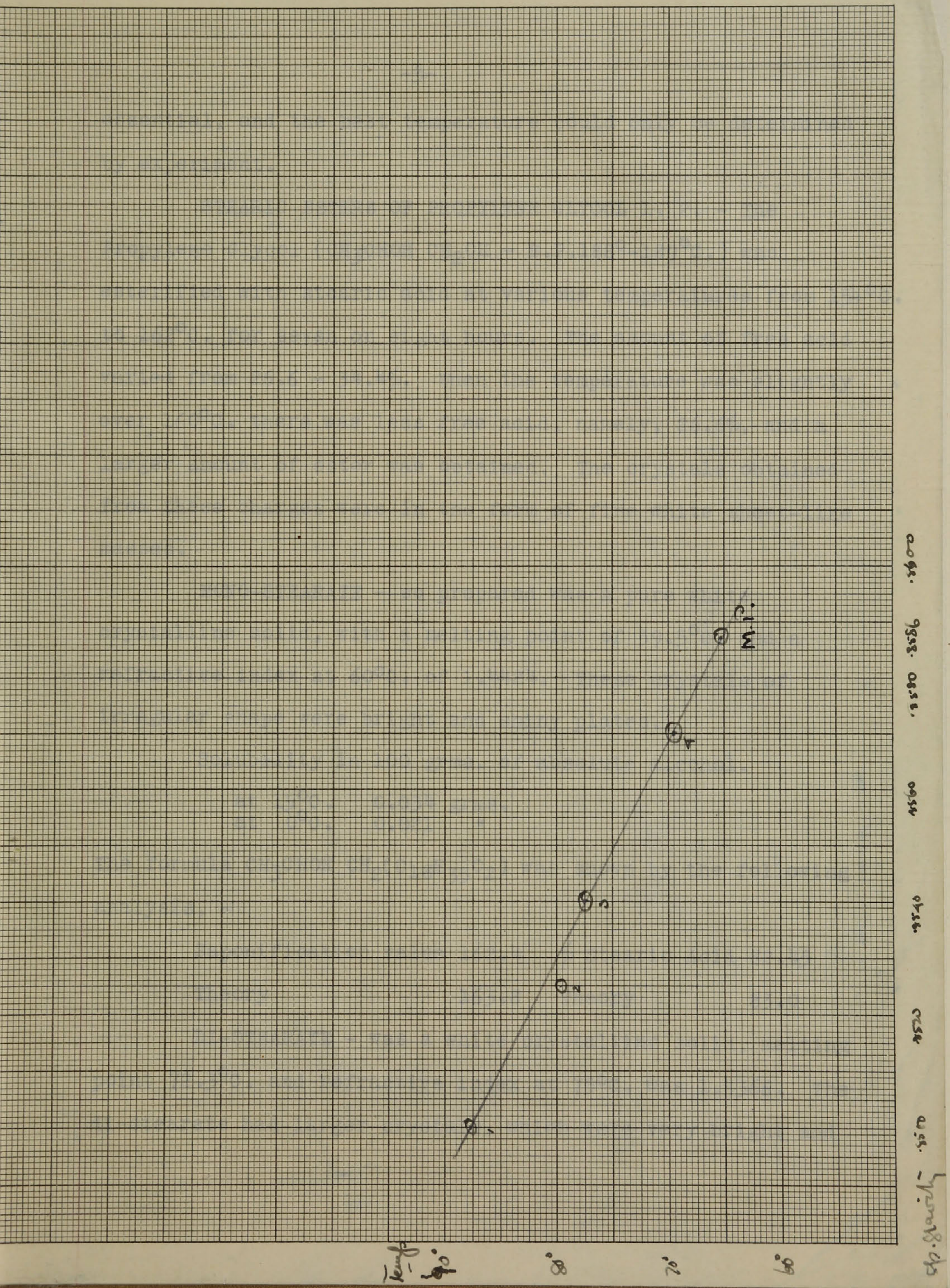
In order to find the specific gravity of a solid fat, the dilatometric method was found to be the most satisfactory as well as a very exact method. The dilatometer was first carefully calibrated with pure mercury. To fill it, the tube was heated in the electric oven, and then suspended in hot water and the melted fat was drawn in through a very fine capillary, with aid of a suction pump. When the bulb of the dilatometer was filled with the fat, the whole apparatus was

quickly transferred to the inner tube of a double walled glass vessel. In order that the fat would not solidify, this tube was previously heated by boiling in the outer jacket, connected to a reflux condenser, some pure liquid such as Ethyl Alcohol, chloroform or Benzol, whose boiling point was above the melting point of the fat. A great number of readings had to be taken, in most cases it required about two hours for the temperature and also the reading on the dilatometer to become constant. The dilatometer was cooled in an evacuated dessicator and weighed, from this the weight of a carefully measured volume of the fat would be obtained. In the case of the distearate of trimethylene glycol, methyl alcohol, ethyl alcohol, benzol and trichlorethylene were the constant boiling liquids used to give a series of readings as follows:-

Trichlorethylene	87.2°C.	Specific Gravity	0.8500
Benzol	78.8°C.	" " "	0.8525
Ethyl Alcohol	77.6°C.	" " "	0.8540
Methyl Alcohol	69.0°C.	" " "	0.8570

These points were plotted and by extrapolation the specific gravity at the melting point of the fat could be found, which in this case, was 64.7°C. and the specific gravity was found to be 0.8586 as seen on the accompanying diagram.

The following is a detailed description of the preparation of these fats. It was found that the temperature at which the esterification took place was most



essential, and the best temperature could only be determined by experiment.

STEARIC ESTERS OF PROPYLENE GLYCOL 1. 2. - The Propylene Glycol ($CH_3CHOH\ CH_2OH$ - B.P.188°-189°C.) was esterified with stearic acid at various temperatures from 154°C. to 162°C. for seven or eight hours. The amount of free acid varied from 26.6 - 34.4%. When the temperature was slightly over 160°C. there was less free acid, namely, 26.6%, and a larger amount of ester was obtained. The crystals obtained from these charges were in the form of fine white sheet-like masses.

MONO-STEARATE - so prepared was a pure white crystalline solid, with a melting point of 59.5°C. and a refractive index at 60°C. of 1.4424. These crystals of irregular shape were bright and shiny plates.

Solubility in 100 grms. of absolute alcohol.

at 15°C. 0.034 grms.
at 0°C. 0.021 "

The formula $CH_3CHOH\ CH_2(C_{18}H_{35}O_2)$ was shown by the following analysis, -

Saponification value	162.4	% Stearic Acid	82.45
Theory	163.8	Theory	83.0

DI-STEARATE - was a white crystalline solid, melting point 72.3°C. and refractive index at 75°C. was 1.4366. The di-stearate had larger crystals, which were very bright and

flaky. This was found to be less soluble than the mono.

Solubility in 100 grms. of absolute alcohol.

at 15°C. 0.0063 grms.
at 0°C. 0.0012 "

The formula $CH_3CH(C_{18}H_{35}O_2)CH_2(C_{18}H_{35}O_2)$ was shown by the following analysis:-

Saponification value	184.1	% Stearic Acid	93.4
Theory	184.2	Theory	93.4

STEARIC ESTERS OF TRIMETHYLENE GLYCOL 1. 3. - The trimethylene glycol ($CH_2OH\ CH_2\ CH_2OH$) employed had a boiling point of 214 - 216°C. It was always necessary to have a large excess of the glycol in order to obtain any of the mono derivative. The temperature necessary for a complete reaction was 180°C. and at this temperature there was only 6% of free acid, while at 178°C. there was 8.19% free acid.

MONO-STEARATE - of trimethylene glycol was obtained in the form of irregular white scale-like crystals. The melting point was 60.5°C. and the refractive index at 60°C. was 1.4437.

Solubility in 100 grms absolute alcohol.

at 15°C. 0.0305 grms.
at 0°C. 0.01431 "

The formula $CH_2OH\ CH_2CH_2(C_{18}H_{35}O_2)$ was shown by the following analysis:-

Saponification value	165.0;164.4	% Stearic Acid	83.75;83.3
Theory	163.8	Theory	83.0

DI-STEARATE - crystallised in small pure white shining plates which had a melting point of 64.7°C. and a refractive index at 75°C. of 1.4397. This crystallised in smaller crystals than the corresponding ester of Propylene Glycol.

Solubility in 100 grms absolute alcohol.

at 15°C. 0.00381 grms.
at 0°C. 0.00126 "

The formula $CH_2(C_{18}H_{35}O_2(CH_2\ CH_2(C_{18}H_{35}O_2)$ was shown by the following analysis:-

Saponification value	184.0;184.5	% Stearic Acid	93.5;93.3
Theory	184.2	Theory	93.4

PALMITIC ESTERS OF PROPYLENE GLYCOL 1. 2. - The Palmitates of propylene glycol were prepared by heating 25.6 grammes of palmitic acid with 12 grammes of the glycol for eight hours at temperatures from 157 to 167°C. The free acid varied from 26.6 to 36.6%. It was found that the highest temperature gave the best results. This cake of fat contained less free acid, namely, 26% and more of the mono palmitate crystals.

MONO-PALMITATE - crystallised in white shiny crystals. It had a melting point of 54.2°C. and a refractive index at 60°C. of 1.4405.

Solubility in 100 grms. absolute alcohol.

at 15°C. 0.0907 grms.
at 0°C. 0.0193 "

The formula $CH_3CHOH\ CH_2(C_{16}H_{31}O_2)$ was shown by the following analysis:-

Saponification value	178.0	% Palmitic Acid	81.4
Theory	178.25	Theory	81.5

DI-PALMITATE - had a melting point of 68.8°C. and a refractive index at 75°C. of 1.4364. The white crystals obtained were large and shiny. The di-compound always had a melting point higher than the mono.

Solubility in 100 grms. absolute alcohol.

at 15°C. 0.0115 grms.
at 0°C. 0.00516 "

The formula $CH_3CH(C_{16}H_{31}O_2)CH_2(C_{16}H_{31}O_2)$ was shown by the following analysis:-

Saponification value	202.5	% Palmitic Acid	92.68
Theory	202.9	Theory	92.75

PALMITIC ESTERS OF TRIMETHYLENE GLYCOL 1. 3. - The temperature of esterffication for the palmitates was 171°C. but as the fat obtained had a very high percentage of free acid, namely, 14%, this temperature was about four degrees too low. It was impossible to repeat the experiment as the supply of glycol was exhausted, and no more could be obtained. Only the di-palmitate was crystallised from this charge.

DI-PALMITATE - was a white crystalline solid with a melting point of 56.2°C. and a refractive index at 75°C. of 1.4374.

Solubility in 100 grms. of absolute alcohol.

at 15°C. 0.0517 grms.
at 0°C. 0.0244 "

The formula $CH_2(C_{16}H_{31}O_2)CH_2CH_2(C_{16}H_{31}O_2)$ was shown by the following analysis:-

Saponification value	202.6; 203.1	% Palmitic Acid	92.7; 92.8
Theory	202.9	Theory	92.75

The solubility of the palmitates was found to be greater than that of the stearates.

COMPARISON OF THE FAT ESTERS OF THE GLYCOLS - The esters of ethylene glycol had a habit of crystallisation very similar to the esters of propylene and trimethylene glycol. They all resembled the true glycerol esters by crystallising in thin shiny plates of irregular outline. Their leaf-like crystals often arranging themselves in rose-like masses. The stearates of the three series had a higher melting point than the corresponding palmitates and the saturated esters were higher than the corresponding mono-derivatives.

There was a marked difference in the melting points and the solubility of the esters of the two isomeric propylene glycols. The mono-derivatives were more soluble than the di, and the palmitates much more so than the stearates.

The principal properties of these glycol esters are tabulated below for easy comparison.

Table 1.

Ester	M.P.	Refractive Index	Solubility in Grammes at 0°C.	15°C.
Ethylene Glycol				
Mono Stearate	58.5°	1.4310	0.670	2.0
Di Stearate	75.0	1.4385	0.010	0.020
Mono Palmitate	51.5	1.4411	1.62	10.0
Di Palmitate	68.7	1.4378	0.018	0.055
Propylene Glycol				
Mono Stearate	59.5	1.4424	0.0211	0.034
Di Stearate	72.3	1.4366	0.0012	0.0063
Mono Palmitate	54.2	1.4405	0.0193	0.0907
Di Palmitate	68.8	1.4364	0.00516	0.0115
Trimethylene Glycol				
Mono Stearate	60.5	1.4437	0.01431	0.0305
Di Stearate	64.7	1.4397	0.00126	0.00381
Di Palmitate	56.2	1.4374	0.0244	0.0517