

XVIII.—*On certain Isomeric Transformations of Fats.*

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Chevreul gave the name of stearic acid to a particular acid derivable from certain natural fats, while, at the same time, he used the word stearine as a synonyme for the most solid portion of any natural fat which furnished glycerine; thus, he speaks of the stearine of human fat, while, at the same time, he shows that stearic acid is not derivable from it. Lecanu afterwards prepared from mutton fat a substance which, on decomposition by alkalis, yielded an acid consisting chiefly of stearic acid, and proposed to restrict to this substance the name of stearine. Most chemists, adopting the principle of nomenclature contained in Lecanu's proposal, now understand the names stearine, margarine, &c., to signify bodies which, if they were obtained, would, on decomposition by alkali, furnish respectively only stearic acid, margaric acid, &c., and glycerine, and, in the absence of such substances, apply them to those which most nearly approach them. The origin of this nomenclature for the fats, belongs, however, not to Lecanu but to Chevreul; for, throughout his work on the fats, stearine is the only exception to it. This exception, I wish to remark, has been rather unfortunate: for many physiologists and some chemists, still employing the word in the sense in which Chevreul used it, have particularized by it bodies which other chemists have described as margarine or palmitine. This diversity of nomenclature has already introduced many apparent discrepancies into works upon the fats, and, as a consequence, some real difficulties in the way of further investigation. I refer to the circumstance here, not because I have any change of name to propose, but because I think allusion to it will be sufficient to render obvious the advantages of allowing stearine to signify the substance, whether hypothetical or not, which, on decomposition by alkali, affords stearic acid and glycerine, instead of forming an exception to a convenient and established system of nomenclature.

Chevreul\* prepared what he called stearine from five different sources, viz., human fat, fat of swine, fat of the goose, mutton fat, and beef fat. As he gives, instead of the melting point, the point of solidification after melting, and as other chemists, in speaking of the stearine prepared by them, have given only the melting point, we are

\* *Recherches Chimiques sur les corps gras.* Paris, 1823, p. 261, &c.

restricted to use, as the standard of comparison for their results, the melting point of the acid furnished on saponification. The acid from the substances prepared by Chevreul, even after the removal of a portion of oleic acid, melted only in one case so high as  $64.8^{\circ}\text{C}$ . Since the melting point of stearic acid, as found by him and confirmed by others, (Redtenbacher,\* Laurent and Gerhardt†) is  $70^{\circ}$ , none of the substances which he called stearine, can be regarded as a close approximation to pure stearine.

Braconnot,‡ by using essence of turpentine as the purifying agent, instead of alcohol, which Chevreul used, succeeded in procuring a substance which melted at  $61.25^{\circ}$ , and furnished an acid fusible at  $62.50^{\circ}$ .

Afterwards Lecanu§ prepared from mutton-fat, by means of ether, a substance which melted at  $62^{\circ}$ , and furnished an acid melting at  $64^{\circ}$ . He states that he found it impossible to raise the melting point of this acid by purification higher than  $66^{\circ}$ , and adds that M. Bussy, in researches which he was then pursuing, had not found stearic acid to melt higher than  $66^{\circ}$ . Hence he concluded that what he called stearine was a pure substance.

Since then stearine has been prepared in the same manner by Liebig and Pelouze,|| who do not mention its melting point in their paper; by Artzbächer,¶ who brought its melting point to  $60.6^{\circ}$ , and by Heintz,\*\* who agrees with Lecanu in its melting point. Although these chemists may not concur with Lecanu in regarding any of these substances as pure stearine, they yet admit that it is impossible to raise its melting point above  $62.25^{\circ}$ .

There are three ways in which the chemical purity of the glycerine-fats may be estimated—1st. That further crystallisation produces no change in the melting point of the fat itself; 2nd. That when crystallised, the crystallised portion and that remaining in the mother-liquor differ not at all, or only slightly, in melting point; 3rd. That on saponification, the resulting acid be not susceptible of having its melting point changed, or in other words, of further purification.

The first of these tests is that by which chemists have hitherto been guided in the purification of fats; but although competent, it

\* Ann. Ch. Pharm. XXXV, 46.

† Compt. Rend. trav. chim. 1849, p. 337.

‡ Ann. Chim. XCIII, 252. J. Pharm. XXV, [2], 307.

§ J. Pharm. XX, 325. Ann. Ch. Phys. LV, 192.

|| Ann. Ch. Pharm. XIX, 264. J. pr. Chem. 173.

¶ Ann. Ch. Pharm. LXX, 239. Compt. Rend. trav. chim. 1849, p. 343.

\*\* Pogg. Ann. LXXXIV, 229.

is calculated to deceive unless very delicately applied, and, as will be seen, has really done so.

In the treatment of mutton fat by ether for the preparation of stearine, I have found that, although between two successive crystallisations after the fifth, the thermometer can scarcely distinguish, yet if these two crystallisations be melted under the same circumstances, a difference of time in the commencement of melting will be perceived, a difference which is still greater, the more widely separated in respect to the number of times two specimens may have been crystallised; and although the thermometer may fail to point out a difference in the melting point of two immediately successive crystallisations, yet that long after the melting point of stearine has reached  $62^{\circ}$ , the difference of melting point between substances, one of which has been crystallised two or three times oftener than the other, is quite sensible to the thermometer.

Instead, however, of relying entirely on this test, I took as guide the second, one which consists, theoretically speaking, in carrying on the crystallisation from ether, till the portion which remains in the mother-liquor, has the same melting point as that crystallised out. I say theoretically speaking: for, even after thirty-two crystallisations, the residue in the mother-liquor, after removal of a second crop of crystals, differed in melting point from the first crop by  $2^{\circ}$  or  $3^{\circ}$ .

It might be supposed that, instead of the impurities being so persistent as this represents them, the difference of melting point arose from some decomposition taking place every time the substance was dissolved; but this was not the case, for I found the melting point and composition of stearine to remain unchanged after ten weeks' contact and partial solution in ether.

Each of the thirty-two crystallisations spoken of, was made on an average with a quantity of ether at least fifty times that of the substance dissolved, and the mother-liquor was poured off when the temperature fell to  $16^{\circ}$ . At first the crystals were then washed with warm ether and afterwards strongly pressed by the hands in folds of linen; but as the substance approached to purity this was discontinued, and the mother-liquor removed by decantation alone. A second, and sometimes a third, crop of crystals was obtained from the mother-liquor, and, after being sufficiently purified, added to the first crop. In the first five or six crystallisations, the quantity of ether employed was not more than from ten to fifteen times the volume of the substance dissolved, but towards the end it was increased to upwards of one hundred times the volume. In this manner not more

than eight grammes were obtained from two kilogrammes of the crude fat.

After thirty-two crystallisations, the substance which I obtained melted, not at  $62^{\circ}$ , but at least  $2^{\circ}$  higher, and furnished an acid melting at  $66^{\circ}5$ . It possessed characters hitherto unsuspected in the class of substances to which stearine belongs.

The method of taking the melting point consisted in fusing on a hook at the end of a platinum wire a bead of the substance, and suspending the wire in a beaker containing water previously boiled, to expel air. The temperature of the water in the beaker was regulated by placing the latter on a small sand-bath over a gas-lamp. The perfect contact between the bead and the water ensured the identity of their temperature, which was given by a thermometer suspended in the water. The temperature at which a small ring of limpid fat surrounding the bead first appeared was taken as the melting point. The melting point of substances which, like stearic acid, solidify after fusion, not in an amorphous, but in a crystalline condition, is best observed by enclosing them in thin-walled capillary tubes; for when directly exposed to the contact of the water, the latter entering the interstices among the crystals, and afterwards remaining suspended in the fused mass, gives it an opalescent appearance, and renders it difficult to distinguish the true melting point.

During the preparation of stearine in the foregoing manner, I had occasion to take its melting point at various stages of the purification. Observing that after being melted it did not, in harmony with the laws of latent heat, always solidify at the same temperature as that at which it melted, I made a register of its solidifying point in a number of cases, and found that the solidifying point was, in most cases, from  $12\cdot2^{\circ}$  to  $12\cdot8^{\circ}$ , and never more below the melting point, but in a few cases not even  $2^{\circ}$  below it. These observations were made long before I had brought the stearine to a state of purity; but although made on an impure substance, they remained good for the purer substance. It was next observed that these variations of the solidifying point were not due to agitation in one case, and its absence in another; in short, that in those cases in which the temperature fell  $12\cdot2^{\circ}$  below the melting point before solidification commenced, the passage into the solid condition was not precarious; it was impossible to produce it by any mechanical means at a higher temperature. For those specimens then under examination, the conditions of these variations were found to be, that, when the temperature was raised only  $1^{\circ}$  or  $2^{\circ}$  above the melting point, solidification set in as soon as the temperature fell  $1^{\circ}$  or  $2^{\circ}$  below the melting point; but that when

the temperature was raised  $4^{\circ}$  above the melting point, solidification could be induced only when the temperature fell  $12.2^{\circ}$  below the melting point.

When the stearine which had solidified  $12.2^{\circ}$  below its melting point was again heated about  $1^{\circ}$  above the solidifying point, it became less opaque, indeed almost transparent, suggesting the impression that it was melting, but, whether the temperature remained stationary or rose, quickly resumed its opacity. Inasmuch as the precaution of enclosing the fat in dry close tubes made no difference in this phenomenon, it was concluded to be the effect of temperature alone.

In the circumstances of the foregoing experiment, where the fat was continuously heated from below to above the point at which the change presented itself, the conditions were in favour of its appearing at the lowest temperature capable of producing it. As it was shewn to be the effect of temperature, it appeared probable that if the fat were suddenly submitted to a temperature a few degrees higher, but not necessarily so high as the melting point, this appearance would present itself with greater intensity. A bead of substance, of melting point  $63^{\circ}$ , which was the purest I had at the time, was placed in a small glass tube, at one side of the part which had been previously drawn out to a capillary diameter; the tube was plunged, the end containing the bead undermost, into water at  $53.6^{\circ}$ ; the air was now sucked out of the other end, whereupon the fat passed through the capillary part of the tube, which, had it not been fluid, it was impossible it could do. Hence, there remained no doubt whatever that the fat really melted at the temperature at which the forementioned transparency appeared, and afterwards solidified at the same or even at a higher temperature.\*

The question now arose: is the stearine the same in every respect after as before this melting? that is, has it the same properties, and, among the rest, that of melting at this lower temperature? When taken after melting and again solidifying at  $53.6^{\circ}$ , and plunged into water at that temperature, it did not melt; in short, it melted only when the temperature rose to its ordinary melting point,  $63^{\circ}$ . The

\* Since I finished my experiments on this point, my attention has been called to the fact that Dr. Heintz, of Halle (Ber. d. Berl. A. 1849, 222. J. pr. Chem. XLVIII, 382. L'Institut. 1849, 390) had also noticed that stearine from mutton fat, melting at  $62^{\circ}$ — $62.25^{\circ}$ , became transparent when immersed in water at  $51^{\circ}$ — $52^{\circ}$ , and afterwards resumed its opacity when the temperature rose to about  $58^{\circ}$ . He has, however, given no explanation of what takes place, but merely stated that the stearine does not become fluid. His reasons for this conclusion consisted in the fact, that a thin layer of stearine did not change its form, although it became transparent when plunged into water at  $52^{\circ}$ . In repeating the experiment, I have found that, whenever the stearine becomes entirely transparent, it takes the form that would be assumed by a fused mass of any other substance.

stearine had therefore, by melting and again solidifying at  $53.6^{\circ}$ , passed into a different isomeric modification. The only evident difference between these two modifications is, that one melts immediately above its solidifying point, the other only at  $12.2^{\circ}$  above it, and that the former approaches slightly more to translucency, and is more reflective of light than the latter.

Before melting and solidifying at  $53.6^{\circ}$ , the stearine had the property of melting at that and even at lower temperatures, so low, that when we take the consequences, instead of the actual appearance, as evidence, we must admit that the proper point for placing the first melting point at is as nearly identical with the point at which it solidifies, after being heated  $4^{\circ}$  above its hitherto known melting point, as the melting point of any metal is with its solidifying point. What I mean by taking the consequences as evidence is, that the appearance of melting at  $53.6^{\circ}$  being succeeded by the transition into a modification which melts only at  $63^{\circ}$ , if we find that this transition is a consequence of keeping it a sufficient length of time at  $51^{\circ}$ , then, although we may see no appearance of melting, we must consider that it does melt at that temperature. In the case of this specimen, which melted at  $63^{\circ}$ , and solidified about  $50.5^{\circ}$ , it was found that although a temperature of  $51^{\circ}$  required a long time to produce the change into the modification melting at  $63^{\circ}$ , it was yet sufficient to do so, and for that reason I conclude that the first melting point is at least within  $0.5^{\circ}$  of the solidifying point. A reason why this transition at the lowest sufficient temperature is not preceded by the appearance of melting, consists in the fact "that next to water, fat possesses the greatest capacity for heat;"\* and "is also one of the worst conductors of heat when fluid;"† so, that, after the heat of the water in the experiment has melted the surface of the bead, the surface, or say the superficial stratum, will have again solidified in the modified state before the heat has penetrated to the next interior stratum; hence, at the lowest temperature sufficient to produce the change, a portion is always in one or other solid state, and at no one moment is the whole transparent, but only different portions in successive moments.

It will be readily perceived that the temperature of the first melting point is dependent on that of the solidifying point (the solidifying point after heating  $4^{\circ}$  above the second melting point). As all temperatures above the solidifying point, and below the second melting point produce the modification of higher melting point, if the

\* Lehmann's Phys. Ch. translated for Cavendish Soc. by Day, I, 261.

† Id. p. 260.



solidifying point was higher than it is, the first melting point must also have been higher, or it could not have existed at all.

It yet remained to be found what was the cause that, when the temperature had not been raised  $4^{\circ}$  above the second melting point, solidification set in before the temperature fell  $12\cdot2^{\circ}$  below this melting point.

This depended on the fact that there was yet another melting point, and another isomeric condition corresponding to it.

When the temperature was raised only  $1^{\circ}$  or  $2^{\circ}$  above the second melting point, and then allowed to fall slowly  $1^{\circ}$  or  $2^{\circ}$  below it, solidification commenced, and proceeded, not suddenly, as at the ordinary solidifying point, but slowly, and when complete, the appearance of the fat was entirely different from what it had been in either of the foregoing modifications, it was more opaque and friable, and melted only at  $66\cdot5^{\circ}$ , or  $3\cdot5^{\circ}$  above its ordinarily known melting point.

To distinguish these different modifications, they will be called in the order of their melting points, the first, second and third; that melting at  $51^{\circ}$ , the first modification; that melting at  $63^{\circ}$ , the second; that melting at  $66\cdot5^{\circ}$ , the third. The latter may be also called the crystalline condition, for it really is so; and what is very remarkable, as well from its connexion with the other facts in this paper, as from its having so long escaped observation, the crystals from ether have the third melting point only.

From what has been said it will be observed, that both the second and third modifications are producible in the interval between the first and second melting points; the second modification in the lower extremity of this interval, the third in the higher. There is, however, no particular point in this interval forming a marked boundary by which the two ranges of temperature that produce the two different modifications are separated. In the case of the specimen taken for illustration, and having its melting points respectively at  $51^{\circ}$ ,  $63^{\circ}$ , and  $66\cdot5^{\circ}$ , the second modification was alone producible under  $56^{\circ}$ , at least within any moderate time; at  $56\cdot5^{\circ}$  a mixture seemed to be the result, whilst at  $57^{\circ}$ , and all temperatures between that and the third melting point, the third modification alone was produced.

It may also be collected from what has been stated, that neither the second nor third modification can be produced from a substance which has been heated to the third melting point; for the liquid which is then formed, solidifies only when the temperature falls below the first melting point, and is then necessarily in the first modification, unless after the lapse of hours.

What has been said of the specimen hitherto spoken of, may be summed up by saying that it has three melting points; it melts at the temperature of the first, solidifies; melts at the temperature of the second, solidifies; melts at the temperature of the third, and then solidifies only when the temperature has fallen below all three; and after solidifying here, it may be made to melt again at the first, at the second, and at the third melting points respectively, solidifying, as before, below all three; and these changes are producible in this succession to any extent without the slightest loss or gain of weight.

In specimens where the impurities predominate, as those having their second melting point at  $61^{\circ}$ , or below it, the third modification is procurable only by obtaining crystals from ether or some other solvent.

On the other hand, as the stearine approached to purity, the appearance of the second melting point subsided, insomuch that when a substance having its first melting point at  $52^{\circ}$ , and its third at  $69^{\circ}7$ , was obtained, it did not, on being heated continuously from the first to the third melting point, become fluid at any intermediate temperature; however, when it was melted at or near its first melting point, and allowed to solidify at the same temperature, and then suddenly removed to a temperature which by inference was judged to be a little above its second melting point, as  $65^{\circ}5$ , it did melt.

At the same time that the second melting point was thus disappearing, the highest temperature for producing the second modification, instead of rising along with the melting points, was approaching more and more nearly to the first melting point, thus narrowing the limits for the production of the second modification and extending those of the third, so that in the specimen having its first and third melting points at  $52^{\circ}$  and  $69^{\circ}7$  respectively, the highest temperature for producing the second modification was about  $55^{\circ}$ , or  $3^{\circ}$  above the first melting point, while in the less pure substance, having its first melting point at  $51^{\circ}$ , the corresponding point was  $56^{\circ}$ , or  $5^{\circ}$  above its first melting point.

These facts, along with the melting point, specific gravity, and external appearance\* of the second modification being intermediate between those of the other two, lead to the inference that if stearine were obtained quite pure, the highest temperature at which the second modification would be producible would coincide with the first melting point; and there being consequently no range of temperature for producing the second modification, there would be no second modifi-

\* Although the appearance is intermediate, it is quite distinct. It is described further on.



cation and no second melting point, but only a first and third melting point, or in that case, a first and second melting point; and that what I have called the second modification is a mixture of the other two modifications, owing its existence, somehow or other, to the impurities. But even were we certain that this were the case, there would still remain the difficulty of explaining how they could produce it. The following seems to me also a strong reason for believing it not a mixture. In the assumption that it is such, is implied that the relative quantities of the first and third modifications in it are such that when the melting point of the former is exceeded, its solvent action on the latter is sufficient to make the whole melt some distance below the third melting point. Now if this were correct, we ought, by increasing the proportion of the first modification, or, in other words, of the solvent, to be able to depress the melting point of the whole still more. But experiment showed that when a bead of substance having its second melting point at  $63^{\circ}$  was brought into the second modification by being melted and allowed to solidify at a little above its first melting point, it became limpid at the same temperature,  $63^{\circ}$ , as it did when it was allowed to solidify, only very partially, or when after solidifying, the greater part of it was again reduced to the first modification.

Dr. Hittorf\* has lately shown in an interesting paper on selenium, that this substance has two allotropic modifications and two melting points to correspond; and that, after melting at the higher of the two, it solidifies only when the temperature has fallen considerably below both. Now it is also known that selenium softens considerably below what he calls its first melting point; but whether the changes which accompany this softening are those consequent upon a real fusion, has not been investigated; but should they be found to be such, there would be the closest analogy between its characters and those of stearine.

The following is a short table of the melting-point of mutton stearine at different stages of the purification:

No. of crystallizations.	Solidifying Points.	Melting Points.		
		1.	2.	3.
5	$49^{\circ}$	$49.5^{\circ}$	$61.3^{\circ}$	$64^{\circ}$
17	$50.5$	51	63	$66.5$
32	$51.7$	52	$64.2(?)$	$69.7$

From this table, it will be observed that the second melting point

\* Pogg. Ann. LXXXIV, 214.

rises much more quickly than the first, with the removal of the impurities, and the third still more quickly than either of the other two. This is explained by what we know to be the general action of solvents; for the influence of the impurities is a solvent one, or in other words, one which tends to depress the melting point; and for any given quantity of impurities, this is greater at the temperature of the higher than of the lower melting point, so that this quantity of impurities being removed, the higher melting point rises in consequence more than the lower. The different modifications have probably also different solubilities, even at the same temperature; indeed, the fact of the third modification being always deposited from ether, whatever modification may have been dissolved, shows that it is the one most insoluble in ether. The property in question should, therefore, be ascribed in part to each of these causes.

Considering that in general an increase of specific gravity corresponds to a loss of latent heat, and that doubtless these different modifications of stearine depend on differences of latent heat, it became an object to take their specific gravities with as much precision as possible.\*

The following table shows a decided difference in the density of the different modifications. Where two observations on the same substance at the same temperature are given, they were made on different quantities in different bottles as a test of the method. Whatever tem-

\* As there are other instances where the method employed might be used with some advantage, a description of it may be useful. A portion of dry stearine was put into a dry stoppered specific gravity bottle and weighed. The bottle was then filled with distilled water, inverted in a beaker containing distilled water, and the whole heated to 100°; in this way the fat melted, and allowed any adhering air, as well as that expelled from the water, to collect in a single globule; after cooling, the bottle was taken out of the beaker, and being placed in its ordinary standing position, the greater part of the globule of air rose into the neck of the bottle, whence it was expelled by filling its place with water. To remove the air which still adhered to the fat, a tube about two inches long, and wide enough to admit the head of the stopper, was attached by a piece of vulcanized caoutchouc tubing to the neck of the bottle, and filled with distilled water. The temperature of the water being about 30° degrees, the apparatus was placed in a beaker, under the receiver of the air-pump. On exhaustion, the remaining air in the bottle rose, by its elastic force, through the orifice in the stopper and through the water in the little reservoir. On readmission of the air to the receiver, the water in the reservoir was forced into the bottle to supply the place of the removed air. The bottle being thus filled was, after removal of the tube, again placed on its side, and the orifice immersed in a beaker of distilled water; by bringing the temperature of the water in the beaker to the required point, that in the bottle was brought to the same, and all the different modifications of the fat successively produced. Before taking the bottle out to weigh it, it is necessary to keep the temperature a considerable time at the point to which the determination refers, otherwise the slow cooling of the fat, arising from its great specific heat and bad conducting power, will occasion serious errors.

perature the determination is referred to, water at the same temperature is the unit.

## SPECIFIC GRAVITIES.

3rd M.P. of substance.	Temp. at which determination was made.	Modifications.			
		1.	2.	3.	Fluid.
65°	15°	0.9872	—	—	—
66.5	15	0.9877	—	—	—
	15	0.9867	1.0101	1.0178	—
69.7	15	—	—	1.0179	—
	51.5	0.9600	—	1.0090	—
	65.5	—	—	0.9931	0.9245
	68.2	—	—	0.9746	—

The volumes corresponding to these densities are as follows :

3rd M.P. of substance.	Temp. at which determination was made.	Modifications.			
		1.	2.	3.	Fluid.
65°	15°	1.0129	—	—	—
66.5	15	1.0124	—	—	—
	15	1.0134	0.9900	0.9825	—
69.7	15	—	—	0.9824	—
	51.5	1.0416	—	0.9910	—
	65.5	—	—	1.0069	1.0816
	68.2	—	—	1.0260	—

From these tables it may be seen that the density does not change sensibly with the condition of purity; that the third modification is denser than the second; the second than the first; and, as might be supposed, that the fluid modification is less dense than any of the others; that the first and third, at least, although solids, expand much more rapidly with increase of temperature than does water, a property long known of the liquid fats, but not previously determined, I believe, for any solid fat; that between 15° and 51.5°, the first modification expands more than the third; it is however to be remarked, that at the higher extremity of this interval, the first modification approaches its melting point, which probably influences its rate of expansion. We also observe, that within the range of 2.7° between the temperatures 65.6° and 68.2° the third modification expands 0.0191 parts more than water; within the range of 14° between the temperatures 51.5° and 65.5°, it expands only 0.0159 parts more than water; while within the range of 36.5°, between the temperatures 15° and 51.5°, it expands only 0.0086 parts more than water.

There can be no doubt that a greater number of these data taken

by the more convenient and exact method of a volumenometer, would point out some interesting relations.

None of these modifications conduct electricity. When a small portion of any of them formed part of the circuit of a very intense current produced by a powerful induced magnet with three Daniell's cells, the galvanometer was not sensibly deflected.

Not the least interesting fact, however, is that this property of existing in three modifications is not peculiar to stearine from mutton fat; it is possessed by many other fats.

At the same time that I prepared stearine from mutton fat, I also sought it in beef fat with the view of submitting to investigation the question of the constitution of the glycerine fats in general, as regards their products on saponification, by a method proposed to me by Dr. Williamson. The results of this investigation are reserved for a future communication.

Artzbächer\* seems the only chemist besides Chevreul who has attempted to prepare stearine from beef fat. The stearine obtained by him from it melted at  $60\cdot6^{\circ}$ .

Commencing with the same quantity of it as of the mutton fat, viz., two kilogrammes, I obtained, after eighteen crystallisations from ether, not more than a gramme of substance melting at  $63^{\circ}$ ; the quantity being now so small, it was useless to pursue the purification further, although the melting point of the residue in the mother-liquor, after removal of a second crop of crystals, was  $2\cdot8^{\circ}$  below that of the first crop. It possessed, however, all the properties of mutton stearine of the same degree of purity, so that  $63^{\circ}$  was only its second melting point.

A substance which is probably a vegetable tallow, but of whose history I know little, has also been the subject of investigation. In its crude state, it is of a pale yellow, cheese-like appearance, somewhat motley from parts of it being crystalline and others waxy; it has a slightly disagreeable smell. On saponification, it yields a dirty white soap which forms a brown solution, and on decomposition by strong acid, liberates an acid of a deep brown colour.

After one crystallisation of this substance from alcohol, and five from ether, there remained a glycerine fat, which melted only  $1\cdot2^{\circ}$  higher than the residue in the mother-liquor, so that it is not difficult to purify. Its properties were then analogous to those of stearine, but like the purer stearine, it does not, on being heated continuously from its first to its third melting point, viz., from  $45\cdot6^{\circ}$  to  $64\cdot5^{\circ}$ , melt at any intermediate temperature, but when the temperature comes to  $62^{\circ}$ , its appearance quickly changes from waxy to crystalline;

\* Ann. Ch. Pharm. LXXX, 239. Compt. Rend. trav. chim. 1849, 343.

this, and the results of some experiments similar to those by which the existence of the second modification was shown in stearine after its second melting point had disappeared, make me believe that this substance really has a second melting point at  $62^{\circ}$ . After melting at the third melting point, it solidifies in less time than does stearine above the first melting point; so that in order to bring it into the first modification, it must be cooled somewhat quickly, in less than an hour at most; but at whatever temperature it solidifies, it has the same properties as if it had been melted as well as solidified at that temperature. This is universally the case; the properties of the solid fat are regulated by the temperature at its own formation, not by that at which the antecedent liquid may have been formed.

The corresponding modifications of this substance, of mutton-stearine and of beef-stearine have the same appearance under the microscope. There is not much to be said of the first modification, unless that it appears as mamillæ radiated like hematite; when watched under the microscope, these mamillæ are seen to form suddenly when the temperature falls to the solidifying point; the second modification has an exfoliated appearance, somewhat suggestive of incipient crystallisation; the third is perfectly crystalline, and by proper attention, particularly in the case of the vegetable fat, the crystals can be obtained in the dry way as definite in form, as from ether, but smaller. So far as the eye can judge without means of measurement, the crystals of these three substances seem isomorphous, but I regret I have not been able to measure their angles.

Palmitine, from palm oil, after twelve or thirteen crystallisations from ether, margarine from butter, and also margarine from human fat, or at least the more solid portion of that substance after two crystallisations from alcohol, and one from ether, exhibited similar phenomena with respect to variety of modification and melting point.

On the other hand, neither elaidine, cocinine, nor any other of the substances in the subjoined table, has the property of existing in more than one modification.

In seeking for some feature in the constitution of the substances that have this property, which would separate them from those that have not, the attention is arrested by the fact, that most of the substances which possess it, as stearine, palmitine, margarine, are unquestionably the glycerine-fats, corresponding to certain members of the series of acids of the formula  $(\text{CH})_{2n}\text{O}_4$ , while among those substances which do not possess it, there is not one, unless we except cocinine, which has such a constitution. In reference to cocinine, I may

observe, that although St. Evre's\* analysis of cocinic acid agrees with the formula  $C_{22}H_{22}O_4$ , yet he, as well as Bromcist† describe it as destitute of one character, crystallisation and opacity on cooling, which, so far as is known, belongs to every other member of the series of acids to which his formula assigns it.

In the following table, instead of the formula of the fats themselves, are written those of the acids derivable from them; for as yet considerable doubt must exist as to those of the fats. In the other cases the formulæ of the substances themselves are written.

	Formulæ.	Solidi- fying Points.	Melting Points.		
			1.	2.	3.
Mutton-stearine . . . . .	$C_{34}H_{34}O_4$	51·7°	52·0°	64·2° <sup>p</sup>	69·7°
Beef-stearine . . . . .	$C_{34}H_{34}O_4$	50·5	51·0	63·0	67·0
Substance from vegetable tallow	—	45·0	45·6	62·0	64·5
Palmitine from palm oil . . .	$C_{32}H_{32}O_4$	45·5	46·0	61·7	62·8
Margarine from butter . . .	$C_{34}H_{34}O_4$	40·0	40·5	51·0	52·6
Margarine (?) from human fat .	—	43·5	44·2	54·5	56·0
—					
Cocinine . . . . .	$C_{22}H_{22}O_4$	29·3	33·5		
Elaidine‡ . . . . .	$C_{36}H_{34}O_4$	23·7	38·0		
		28·0			
Stearic acid . . . . .	$C_{34}H_{34}O_4$	65·8	68·0		
Palmitic acid . . . . .	$C_{32}H_{32}O_4$	59·0	61·0		
Margaric acid from butter . .	$C_{34}H_{34}O_4$	50·5	52·3		
Stearic ether . . . . .	$C_{38}H_{38}O_4$	33·0	33·7		
Cerotic ether§ . . . . .	$C_{58}H_{58}O_4$	60·0	60·3		
Cerotin (alcohol) . . . . .	$C_{54}H_{56}O_2$	81·0	81·0		
Cerotene . . . . .	$C_{54}H_{54}$	57·0	57·8°		
Chinese wax . . . . .	$C_{108}H_{108}O_4$	80·5	81·0		
Paraffin . . . . .	$(CH)_{2n}$	43·5	43·5		