CHAPTER 2

STUDY OF BUTTER MADE FROM COW'S MILK AND PREPARATION OF BUTYRIN[1]

809. Butter is regarded as one of the most common foodstuffs and also as the fat with the most complex character. The differences in color, aroma and melting behavior which can be observed among different types of butter seem to set it even further apart from substances that are governed by a well-defined composition. All this has prompted me to describe the chemical history of cow's milk butter in more detail than I have done for other fats, and indeed, butter has been the main subject of my work.

SECTION 1

SEPARATION OF THE FATTY PART OF BUTTER FROM THE BUTTERMILK

810. When fresh butter is melted at a temperature of 60°C in an elongated flask, the buttermilk gradually collects at the bottom of the flask. When the fatty part has become transparent and homogeneous, it is decanted onto a filter positioned between two stoves. The fatty filtrate is then mixed with warm water at 40°C and agitated. When the two materials have separated sufficiently by settling, the fatty part is again decanted and filtered. After this filtration, it looks as though it contains no more water. It has lost some of the aroma and taste of fresh butter. This is the state in which the fatty matter will be investigated; it will be referred to as *butterfat*[2].

811. The buttermilk that has been separated from the butterfat is milky and acid. After filtration, it leaves only a very small amount of solid material on the filter paper, and this solid retains a lot of liquid between its particles. This white, nitrogenous substance seems to be some kind of cheese but in my opinion it would be wrong to believe that the presence of cheese in fresh butter is demonstrated by the observation that buttermilk separates out when butter is melted in a long-necked flask because this liquid consists mostly of water and whatever has been dissolved in it.

812. The filtered buttermilk is transparent and yellow. It has a buttery and milky aroma. It turns litmus paper red and it has an acid, sweetish taste.

813. On distillation, it becomes cloudy as soon as it is heated and then becomes clear again and flakes are formed as it concentrates.

Distillation product

814. It is acid and it smells like cheese and milk or rather like frangipane[3]. After neutralization with baryta water and distillation, it yields ammonia and a residue that when spread on the hand gives off a mixed aroma in which the odors of butyric acid and acetic acid can certainly be distinguished. When this residue is left exposed to air, it produces crystals that after decomposition with phosphoric acid give off a mixed odor of butyric acid and acetic acid and oily-looking droplets that float on the aqueous liquid.

Distillation residue

815. After filtration, what remains on the filter are flakes of a nitrogenous material mixed with calcium phosphate. The filtrate contains a

lot of milk sugar and in short, everything that can always be found in whey. It has an acid odor.

816. To determine the buttermilk content of fresh butter, I put 40 g of butter from Murs in Anjou[4] in a glass funnel, the opening of which had been closed with a stopper made from lead glass. Then I melted the butter. After the fatty part had been well separated from the buttermilk, I let the former solidify and then removed the stopper. I obtained 6 g of buttermilk. I closed the funnel again and remelted the butter and obtained another 0.5 g of buttermilk. Thus 100 parts of fresh butter from Murs contained 16.25[5] parts of buttermilk.

SECTION 2

PROPERTIES OF BUTTERFAT AND HOW IT WAS ANALYZED

§ 1. PROPERTIES THAT CAN BE OBSERVED IN BUTTERFAT WITHOUT SEPARATION OF ITS IMMEDIATE PRINCIPLES

817. The butterfat from Murs in Anjou as obtained by the method outlined above (810)[6] had a very pronounced yellow color and an aroma that I can best describe as that of potatoes cooked with butter. It was partially liquid at a temperature of 26°C; after the butterfat was melted at 40°C, the reading on a thermometer inserted into it dropped to 26.5°C and then rose to 32°C when the butterfat solidified. When left to stand at 17°C, a liquid portion separated from a fat that had crystallized in large granules.

818. When spread on litmus paper, it turned it red[7] and in this respect it behaved like fresh butter. However, I noticed that this acidity is not an essential characteristic of butterfat because samples can be prepared that have no effect on litmus.

819. 100 parts of boiling alcohol with a density of 0.822 (g/mL)[8] dissolved 3.46 parts of butterfat.

§ 2. SAPONIFICATION OF BUTTERFAT WITH CAUSTIC POTASH

820. When an amount of 20 g of butterfat was heated with 8 g of caustic potash dissolved in water, it saponified readily. When the soapy mass was acidulated with tartaric acid, this yielded an *aqueous liquid*[9] and a *saponified fat* that was washed with water until nothing more was removed. The washing water was combined with the *aqueous liquid*.

A. Aqueous liquid

821. It was distilled.

822. The *distillation product* was very acid. It smelled like Gruyère cheese. It was neutralized with baryta water and then distilled again. The product had only a slight smell of glycerin. The dried residue weighed 1 g and it consisted of the barium salts of butyric acid, caproic acid and capric acid.

823. When the *distillation residue* (821) was evaporated almost to dryness, alcohol extracted 2.37 g of glycerin out of it.

B. Saponified fat

824. It weighed 17.7 g. After it had been melted, a thermometer was inserted and the reading first dropped to 39°C and then rose to 40°C when the fat congealed. On solidification, it crystallized partially as narrow needles and partially as fine needles in a star-shaped configuration that formed a wavy pattern on the surface.

825. It was miscible in all proportions with boiling alcohol.

826. 100 parts of the saponified butterfat were dissolved in water containing 15.24 parts of potash and 10.35 parts of soda ash[10]. I should point out that these alkalis contained some chloride, which tends to increase the solubility of the acidulated soaps[11] in the results of the experiment I am describing.

827. The butterfat does not produce non-acid fatty matter when left for a sufficiently long time in contact with the potash, since alcohol extraction of an amount of 25 g of saponified fat originating from butterfat that had been treated with baryta water only yielded 0.38 g of a fatty material that, after a further potash treatment, yielded a water-soluble soap. I noticed that this 0.38 g of fatty material released an amber-like[12] aroma during saponification.

828. With potash, the acidulated butter soaps formed a soap that split easily into a pearly deposit and potassium oleate.

Pearly deposit

829. The fatty acids in the pearly material melted at 56.3°C. They crystallized in shiny lamellae. The neutral combination of this material with potash was treated with boiling alcohol, which split it into potassium stearate and potassium palmitate[13]. The stearic acid melted at 67°C but on slow cooling, it did not crystallize as well as the stearic acid obtained from mutton or beef tallow or lard and when it reacted with potash and dissolved in warm alcohol, it formed a gel.

Potassium oleate

830. The oleic acid that was separated had all the physical and chemical properties of oleic acid from other fats.

§ 3. ANALYSIS OF BUTTERFAT WITH ALCOHOL

831. To investigate any similarities that the immediate principles of the butter from Murs might have with the species of fats I have described in Book II, I treated 100 g butterfat with alcohol. I used about 1 liter of alcohol for each treatment. The first wash was by digestion[14] but the others were carried out at a temperature of 80°C. The washing liquors from the first three treatments were acid but the subsequent ones were not noticeably so. The first five washing liquors were combined and distilled. The resulting oil will be investigated under the denomination of *oil no. 1.* A solid fatty substance precipitated when the solutions of butterfat in boiling alcohol were cooled but it was only from the fourth wash that a significant quantity was separated. I continued washing until all the butterfat had dissolved and the solid part had precipitated in the form of small crystals which I will now examine under the denomination of *stearin* (since the fatty material that separates from the last washing liquors as a liquid that subsequently solidifies has a lower melting point than the fatty material that precipitates as crystals. The former melts at 35°C and the latter at 38 to 39°C). The oil that was separated from the washing liquors from the fifth wash onwards will be examined under the denomination of *oil no. 2.* The aqueous liquid[15] of the first five washes will be referred to as *aqueous liquid no. 1* and that of the last washes as *aqueous liquid no. 2.*

ARTICLE 1

AQUEOUS LIQUIDS Nos. 1 AND 2 AND THE ALCOHOL USED TO ANALYZE THE BUTTERFAT

832. Liquid no. 1 had a slight but distinct aroma of fresh butter[*]. It was slightly acid and faintly colored by the *yellow principle* of butter. It had a bitter and sweetish taste. It was neutralized with baryta water. Although the resulting liquid was quite clear, on concentration it deposited an *orangey oil* that ultimately dissolved again. In addition to this *orange colored oil,* the evaporation residue contained a large amount of water-soluble *yellow principle* and some *barium salts of volatile acids.*

833. Liquid no. 2 was hardly acid at all. It only contained traces of the yellow principle and volatile butter acids.

834. The alcohol that had been separated from the aqueous liquids by distillation was slightly acid, at least the alcohol used for the first washes. When it was distilled again from barium hydroxide, it gave up some butyric acid to this alkali.

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[*] This aroma is found mainly in the distillation residue from the first washing liquor when fresh butter is washed while applying a gentle heat.

835. It can be concluded that the alcohol separated from the butterfat a *yellow coloring principle*, *butyric acid* and another *aromatic principle* that is present in fresh butter (of which I had too little to investigate its properties). I did not examine that part of the butterfat that is mainly composed of oil and stearin.

ARTICLE 2

BUTTERFAT STEARIN

836. The butterfat stearin was treated with alcohol until its melting point reached 44°C. In this state of purity, it had the following properties:

837. It was brilliantly white. Its pearly appearance indicated that is was formed by small needles because I have noticed that nearly all white substances that crystallize into small, intertwined needles look pearly. The stearin was glossier than the stearins from previous fats.

838. After having been melted and allowed to cool slowly, its surface presented small, shiny needles agglomerated into star-shaped configurations.

839. 100 parts of boiling alcohol with a density of 0.822 (gm/L) dissolved 1.45 parts of stearin.

840. On exposure to air, the stearin developed an aroma like that of a candle.

841. 100 parts of stearin saponified more slowly than butyrin. They yielded a soapy mass that on acidulation by tartaric acid split into an *aqueous liquid* and *acidulated soaps.*

A. Aqueous liquid

842. The aqueous liquid was distilled.

Product

843. The product was slightly acid. When neutralized with baryta water, it formed 0.3 parts of salt containing a small amount of butyrate.

Residue

844. The alcohol extracted 7.2 parts of glycerin from the residue.

B. Acidulated soapstock

845. The acidulated soapstock weighed 94.5 parts. It melted at 47.5°C. It crystallized on cooling like the palmitic acid from butterfat soap. It consisted of stearic, palmitic acid and oleic acids.

ARTICLE 3

OIL No. 1.

846. It was colored yellow. After removal of the alcohol, it gave off a slight aroma of fresh butter. It has a pleasant, sweet taste. It turned litmus paper very red. When exposed to a temperature of 10°C for some time, part solidified and the rest remained fluid below 6°C.

847. 100 parts of boiling alcohol with a density of 0.822 (g/mL) dissolved 283.42 parts of the oil no. 1 and the solution was still not saturated. It became very cloudy on cooling. When diluted with a large amount of water, this caused an oil, a little *yellow coloring principle* and *butyric acid* to separate out.

848. 100 parts of this oil saponified much more readily than butterfat and yielded:

A.	An amount of volatile acids expressed as their dry barium salts……………………….	10.5
B.	Glycerin……………………………………………	12.0
C.	Solid fatty acids melting at 35°C………………..	84.9

849. I concluded that oil no. 1 owed its acidity to the presence of a very small amount of free butyric acid because after obtaining a neutral sample by digesting it with milk of magnesium carbonate, I then detected magnesium butyrate in the water. After this treatment, it remained equally soluble in alcohol. This experiment convinced me that it contained no solid fatty acids since these would have reacted with the magnesia.

ARTICLE 4

OIL No. 2.

850. It was slightly yellow and not acid towards litmus. It had a pleasant, sweet taste and was more viscous than oil no. 1.

851. 100 parts of boiling alcohol with a density of 0.822 (g/mL) dissolved 20 parts of oil no. 2. The solution became very cloudy on cooling and it did not release any butyric acid into the water that had been mixed into it.

852. 100 parts were saponified less easily than oil no. 1. The soapy mass was orangey whereas that of oil no. 1 was yellow, like straw.

853. On saponification, 400 parts of oil no. 2 yielded:

A.	An amount of volatile acids expressed as dry barium salts	8.55
B.	Glycerin with a more agreeable taste than the one obtained from oil no. 1	11.00
C.	Solid fatty acids melting at 38°C	84.50

854. Since this oil was much less soluble in alcohol than the previous one and since it yielded less volatile acids on saponification, I concluded that there are two oils in butterfat: the one I called *butyrin* and another that would have shown all the properties of *olein,* if only I could have obtained it without any trace of butyrin.

SECTION 3

THE PREPARATION OF BUTYRIN

855. After having concluded from the experiments reported in the previous paragraphs that there are two distinct species of oil in butterfat, and having been convinced that the high solubility in alcohol of one of them did not stem from any excess of acid it might contain nor from the fact that it had been acidulated, I tried to separate it from the other oil by means of alcohol.

856. First of all, I separated the butterfat from the *buttermilk*. Then I let the fat cool very slowly in a deep porcelain dish and I kept it at a temperature of 19°C for several days. Gradually it became a grainy substance consisting of stearin retaining a certain amount of the two butterfat oils and a liquid formed by these two oils containing some stearin. I expedited the separation of the two substances by pushing the solid substance against the walls of the dish and pressing it with a broad spatula.

857. After filtration, the liquid substance had the following properties: it had a yellow color and it smelled and tasted like warm butter. At 19°C, its density was 0.922 (g/mL) and when spread on moist litmus paper it did not turn it red. 100 parts of boiling alcohol with a density of 0.821[16] (g/mL) dissolved 6 parts and the solution did not change the color of litmus.

858. An amount of 88 g of the liquid substance from butterfat was placed in a round-bottomed flask together with 88 g of alcohol having a density of 0.796[17] (g/mL); the liquids were agitated and macerated at a temperature of 19°C. After twenty-four hours, the alcohol was decanted

and replaced by 176 g of alcohol that was again decanted after a maceration of twenty-four hours. The residue was treated with 176 g warm alcohol. Everything dissolved but on cooling, part of the oil precipitated.

1. Alcoholic solution

859. It was very slightly acid. The alcohol was removed by controlled distillation. The oily residue had a slight effect on litmus and it owed this property to the presence of a very small amount of butyric acid that had been liberated or produced. This was removed by mixing the oil with milk of magnesium carbonate. The magnesium butyrate dissolved in the water. The liquid was decanted and the oil, which was mixed with this excess of magnesium carbonate, was then treated with warm alcohol. The mixture was filtered and by gentle evaporation of the mother liquor, a *butyrin* was obtained that was absolutely neutral towards colored reagents and left virtually no ash on burning. It has been described in Book II, Chapter 16.

860. I went on to compare the butyrin with: 1. the oily substance dissolved in the 176 g of alcohol of the second maceration, and 2. the oily substance that remained dissolved after cooling the 176 g of alcohol that had been heated with the residue of the second maceration, and 3. the substance that was precipitated from the alcohol by cooling. To recap: 100 parts of saponified butyrin yielded:

Dry barium salts..	26.00
Pure glycerin..	12.50
Solid fatty acids melting at 32°C.........................	80.50

2. Alcoholic solution

861. It was less acid than the previous solution (859).

862. The oil that was obtained was yellow but less odorous than the previous one and acid. Its density was 0.920 (g/mL) and 100 parts of boiling alcohol with a density of 0.821 (g/mL) dissolved 17 to 20 parts of this oil: the solution was acid.

863. The saponification of 100 parts of oil that had been neutralized with magnesia yielded:

Dry barium salts..	14.75
Pure glycerin..	11.00
Solid fatty acids melting at 32°C.......................	83.25

2. Oil of the residue of the second alcoholic solution that did not precipitate from the alcohol on cooling

864. It was the same as the previous solution except that it was hardly acid and that it yielded less volatile acids on saponification.

3. Oil of the residue that precipitated from the alcohol during cooling

865. It was yellow with a slight odor of beef tallow. At 19°C, its density was 0.920 (g/mL) and 100 parts of alcohol with a density of 0.821 (g/mL) only dissolved 5.5 parts. The resulting solution had no effect on litmus.

866. 100 parts saponified less readily than butyrin. This yielded:

Dry barium salts	8.6
Pure glycerin	10.0
Solid fatty acids melting at 32°C	90.0

867. The butyrin, the properties of which I have described in Book II, Chapter 16, must have retained some olein and I could probably have isolated part of it by using cold and less concentrated alcohol. The oil of the second alcoholic solution and both the oils from the residue of this solution were mixtures of olein and butyrin from which I could have removed some butyrin by treating the residues repeatedly with hot alcohol. On cooling, this alsohol would have formed a deposit of olein retaining less butyrin than the mixture that would have remained in solution in the cooled alcohol.

Comments

868. This analysis of butterfat is all the more interesting since it shows how easy it would be to draw conclusions from experiments with organic matter that seem to contradict the law of definite proportions. For instance, if somebody, when examining the fluid oily parts extracted from various kinds of butterfat, were to restrict himself to comparing these fluid oily parts with each other 1. with regard to the composition of their saponification products, and 2. with regard to their carbon, hydrogen and oxygen contents, would he not be led to believe that the elementary composition of the fluid oily part of butterfat is not subject to any definite proportions? On the other hand, by following our analytical approach, these results can be explained by assuming that compounds, each of which is subject to definite proportions of its elements, can form mixtures of indefinite proportions.

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[1] The name 'butyrin' will be maintained since 'tributyrin' would be unduly modern.

[2] In the original, the author refers to this material as butter, and the butter from which it has been obtained is called *fresh* butter. Referring to these products as *butterfat* and *fresh butter* respectively eliminates any ambiguity. Nowadays, the former product would be referred to as AMF, anhydrous milk fat.

[3] Frangipane is an almond paste.

[4] Nowadays, this is 49610 Mûrs Érigné in the Maine-et Loire (49) province. Apparently, the custom of mentioning the origin of reagents in the experimental section of research reports and journal articles is quite venerable.

[5] In most countries, food laws prescribe a minimum butterfat content around 80% by weight. They may also prescribe a maximum water content of 16% by weight, which

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has led producers to replace some butterfat and milk solids by salt, which is cheaper. In Europe, spreadable fat products are governed by EC Regulation No.2991/94 subsequently modified by Regulations No. 577/97, No. 1278/97, No. 2181/97, No. 623/98 and No. 568/99.

[6] The 'butter' referred to is the dehydrated product, which is why the author refers to sub-section (810) where he describes its preparation.

[7] This may indicate that the butterfat was not dry and that washing had not removed all acidity.

[8] This density corresponds to 90.3 % by weight.

[9] Butterfat triglycerides contain several short-chain fatty acids that are more or less water-soluble. Accordingly, the aqueous liquid will contain some of the fatty acids.

[10] There is no obvious explanation for these figures. Assuming the fatty acids in butterfat to have an average relative molecular mass of 245, the 100 parts correspond to 0.40 equivalent. On the alkali side, 15.24 parts of potash (MW = 138) correspond to 0.11 equivalent and the 10.35 parts of soda ash (MW = 106) correspond to 0.098 equivalents. Since the fatty acids are monobasic but the carbonates can neutralize two acid groups, there is slightly more alkali than acid: $2 \times (0.11 + 0.098) = 0.416 > 0.40$.

The alkalis could also be translated as caustic potash (MW = 56.1) and caustic soda (MW=40.0). Then the equivalents are 0.27 for the KOH and 0.26 for the NaOH and the excess of alkali over fatty acids is quite a bit larger.

[11] The text says *graisse acidifiée* or acidified fat. In English, the product resulting from the acidulation of soapstock is generally referred to as *acid oil*s so the term *acid fat* could logically be introduced but this could also refer to a non-neutralized fat. Accordingly, the term *acidulated soaps* will be used.

[12] The text says simply 'amber-like' but there are two kinds of amber. There is the yellow amber which is a hard translucent fossilized resin originating from extinct coniferous trees of the Tertiary period, typically yellowish in colour and which has been used in jewellery since antiquity, and there is ambergris, a wax-like substance that originates as a secretion in the intestines of the sperm whale, found floating in tropical seas and used in perfume manufacture. The text refers to the latter meaning.

[13] According to Rossell B. (Ed.) *Oils and Fats Volume 3, Dairy Fats* (Leatherhead Publishing, Leatherhead, England, 2003), butterfat contains about twice as much palmitic acid (27.4% by weight or 24.8 mol%) as stearic acid (13.9% by weight or 11.4 mol%).

[14] This "digestion" appears to refer to a treatment at ambient temperature.

[15] The origin of these aqueous liquids may well be due to the fact that the alcohol used for washing the butterfat contained more water than the alcohol-water azeotrope which contains 96% water by weight. Consequently, evaporation of the alcohol enriches the still bottoms in water until an aqueous liquid results. Another explanation could be that the alcohol is distilled by the introduction of live steam into the distillation flask.

[16] This density corresponding to 90.7 % by weight or 93.7 % by volume pertains to the alcohol used most frequently.

[17] This alcohol is almost absolute.