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THE ANALYSIS OF BUTTER.

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(Abstract of a Paper read on March 19th.)

IN making examinations of butter, the smell of butyric ether has been observed when the butter is saponified in the usual manner, *i.e.*, by the action of alcoholic solution of potash on the butter, but until we called attention to the subject, in the course of last year, the butyric ether arising during this action was regarded as an insignificant by-product. We have shown* that the butyric ether is a main product, and that by

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* Chemical News, vol. 48, page 49, and in a paper read before the chemical section of the British Association, Southport meeting, 1883.

restricting the action of the potash it is possible to cause all of the butyric acid—which is derivable from butter—to assume the form of butyric ether. At any rate we have proved that much more than half of the butyric acid may be made to assume the form of butyric ether. Very important theoretical and practical consequences follow from a knowledge of this fact.

The theory has a bearing on the analysis of butter, and we propose to deal with that on the present occasion, and have to offer a rapid and accurate method of analyzing butter by means of a measurement of the quantity of butyric ether, which is evolved under certain specified conditions.

The working details of our method are the following:—

The butter is clarified in the usual way, and then 5 grammes are weighed and taken for the analysis. The butter is placed in a small retort of about 200 c.c. capacity, and fitted to a condenser. About 100 c.c. of alcohol (sp. gr. 0·838) is added to the butter in the retort, and then 0·5 grms. of solid potash is added. The retort is then gently heated, and the contents are distilled, the distillation being continued to dryness. The distillate is received in a bottle fitted with a stopper, and containing 40 c.c. of accurately measured normal caustic potash or soda. When the distillation is complete the stopper is placed in the bottle and the contents are shaken for a short time, and presently it will be found that the smell of butyric ether has vanished. Phenol phthalein is now added to serve as an indicator, and the solution is titrated with normal sulphuric acid. The following results have been obtained:—

	I.	II.	III.			
Butter sample I.	3·20	3·46	—	per cent. $C_4H_8O_2$		
„ „ II.	2·96	2·96	3·17	„	„	
„ „ III.	3·17	—	—	„	„	
„ „ IV.	3·00	2·85	—	„	„	
„ „ V.	3·40	—	—	„	„	
„ „ VI.	3·26	3·13	3·40	„	„	
						Mean of insoluble fatty acids, 87·30 per cent.

Three samples of butter received by Mr. Wanklyn from Buckingham, gave—

No. I. ..	2·86	3·15	2·97	per cent. $C_4H_8O_2$, insoluble fatty acid	87·86
„ II. ..	none	—	—	„	95·16
„ III. ..	3·20	—	—	„	88·60

No. II. therefore contained no butter fat whatever, and was reported on to that effect.

Several samples of “one shilling butter” bought at various shops gave no trace of butyric ether, and consumed no alkali when treated as above described. The insoluble fatty acids in these samples was found to be a little more than 91 per cent.

In like manner cocoanut-fat and various other fats and oils, some of which yield less than 95 per cent. of insoluble fatty acids, have been found to yield no butyric ether when treated by our process.

We are of opinion that slight admixtures of butter with foreign fat are of very rare occurrence in commerce; either the fat which is sold under the name of butter, is butter altogether, or else it is devoid of butter.

And certificates that a given specimen of commercial butter contained, say 20 per cent. of foreign fat mixed with the butter or say 80 per cent. of foreign fat mixed with the butter, are open to grave suspicion.

In the course of the discussion which ensued after the reading of the original paper.

Mr. ALLEN said:—The formation of butyric ether during the saponification of butter is certainly an exceedingly curious reaction, of which I do not venture to offer any explanation further than that put forward by Mr. Wanklyn. I wish, however, that gentleman had brought forward some further facts in confirmation of his isoglycerine theory; still, we can take it as a fact, that butyric ether is produced in saponification, and that when the operation is carried out in the manner described by the authors, slightly over 3 per cent. of butyric ether is obtained. I do not gather that the quantity which distils over is necessarily all the ether that is formed. It would be interesting to know whether the volatile product is butyric ether only, or contains ethers of other volatile acids besides. When the paper is printed I hope we shall see actual analytical figures, and we shall then be able to judge how far the process is capable of giving constant results. Since the introduction of Hehner and Angell's process many modifications have been proposed, but these, unfortunately, have not always stood the test of experience, and in the present case it will be most desirable to know how much this process can do. I have myself attempted other plans, but have not succeeded in working out a process which would give absolutely constant figures on repetition.

The figures given by the authors of the paper seem to me to be very low, and a grave source of error exists in the possible variation in the proportion of alkali used. It is all very well to assume that we have to deal with butter or with butterine, but, unfortunately, we have to do sometimes with mixtures, and how do we then know whether we have not more caustic potash than is sufficient for this reaction? Supposing for instance, that we have 20 per cent. only of butter in a mixture, would not then the excess of potash be very considerable? This, it seems to me, wants further explanation and experiment before we know how far the process is likely to give reliable results.

It is not so many years ago that Mr. Wanklyn used to pooch-pooch Hehner and Angell's method on the ground that the true proportion of butyric in butter was a mere fraction of 1 per cent. I do not know whether Mr. Wanklyn is not even now prepared to hold the same view, on the ground that butyric acid is not contained as a glyceride in the butter, but that the acid is formed in the process itself. It would be interesting to know what should happen if butter-fat were decomposed with sulphuric acid instead of alkali; would we then still get butyric acid? In this manner more light might be thrown on this interesting reaction.

Mr. HEHNER said: No analyst can be more desirous than I am myself to see butter analysis further improved, and I am sure no one appreciates the difficulties of the methods at present in use more keenly than I do. I hail every improvement in butter analysis with delight, for every one affords further evidence that the seed sown by Mr. Angell and myself, now a good many years ago, is growing and flourishing. I am, however, sorry to think that the method suggested by Messrs. Wanklyn and Fox, instead of being anything like an improvement, is decidedly a retrograde step; it brings us back almost to the position in which butter analysis found itself when first taken up by me. Ten years ago it was said that butter fat contained about two per cent. of glyceride

of soluble fatty acids, and it was not without strong opposition—mainly, also, on the part of Mr. Wanklyn—that we demonstrated that the actual quantity was very much larger. Six to seven per cent. or more of soluble fatty acids being readily obtainable from butter fat. Now, after the lapse of ten years, Mr. Wanklyn comes to us with a method by which he actually gets from $2\frac{1}{2}$ to 3 per cent. of butyric acid. This is, for Mr. Wanklyn, a decided advance; if he continues his labours he may, *in time*, reach the quantities readily obtained by other analysts.

Now, if we look at the paper just read, we see that it consists of a great deal of theory, and of a very little bit of fact. I have heard a very eminent lawyer say in Court, that he preferred one grain of common-sense to a cartloadful of chemistry. I might paraphrase, and say “one grain of fact is better than a ton of theory.” Analytical methods should, before all things, stand upon solid facts, not be merely pegged on to theories. The original foundation of Mr. Wanklyn’s isoglycerine theory was the supposed fact, that from some fats after saponification, he was unable to obtain any glycerine whatever. He “rushed into print,” and announced his great discovery in the *Chemical News*, in a paragraph of a few lines, never afterwards, as it ought to have been, amplified by the publication of actual experiment. True, he read a paper on the same subject before the British Association, but as far as I am aware, that paper has not been printed. Somewhat later the inventors of isoglycerine find that the fats, from which they were unable to extract any glycerine after all could be made to yield up their alcohol in a tangible form. With that observation one should imagine the isoglycerine would have collapsed, but it was too excellent a theory to be allowed to die in this manner. In order to keep it alive, Mr. Wanklyn now comes to us and transfers the production of his mind to butter fat. Because it is a remarkable fact that butterfat on saponification with alcoholic potash yields some butyric ether, the butyric acid combining, to a small extent, with ethyl instead of potassium, and because, according to Mr. Wanklyn’s distinct statement, butyrate of glycerine, on being saponified, does not yield any butyric ether whatever, therefore butterfat is devoid of any compound of butyric acid, but must contain *isoglycerine*. The foundation, in fact, then, of his theory as it now stands is his allegation that butyrine on saponification cannot yield butyric ether. I have, myself, prepared some tributyrine, by heating together glycerine and butyric acid to 260° C., and thoroughly washing the product. This most easily yields a powerful odour of pineapple when saponified in the presence of alcohol, Mr. Wanklyn’s statement notwithstanding (the experiment was here shown).

With this one little fact Mr. Wanklyn’s theory vanishes and collapses.

If it must then be admitted that a glyceride containing the butyric radical can yield butyric ether in the presence of potash, why does the butyric acid combine with ethyl instead of potassium? You will notice that the authors of the paper are careful to use a quantity of alkali only just sufficient to saponify the fat employed. They avoid an excess. As the butter fat gradually dissolves it must indeed be locally in excess. The molecule is broken up by the alkali, part of the acid combines with it, but the rest of the acid is free to do what it likes, and accordingly takes hold of the alcohol. If we have butyrine $(C_4H_7O_2)_3$ $C_3H_8 + 2KHO + C_2H_5HO$ we could get $2C_4H_7KO_2 + C_4H_7C_2H_5O_7 + C_3H_8(HO)_3$

Be this the explanation of the fact or not, it is quite evident that Mr. Wanklyn's explanation is not an explanation at all; he attempts to explain things which are unknown, by others still more unknown. He has to *invent* a substance, isoglycerine, to explain an observation apparently in opposition to our knowledge of the behaviour of organic ethers. But admitting for the sake of argument that isoglycerine exists, is it intelligible why the butyric acid, formed by its decomposition, should be able to combine with ethyl in the presence of potash, whilst that power is expressly denied to butyric acid present in a glyceride? The acid, whatever its origin, cannot have different properties in the one case from the other.

So much for Mr. Wanklyn's theory. Now as to his facts, which, as I have said, are very small indeed.

We all know that, however much alkali be taken to saponify butter fat, some butyric ether always forms. With a great excess of alkali the quantity yielded is small. I have found as little as .3 per cent. With a barely sufficient amount of alkali, as the authors of the paper show, as much as 33 per cent. may be obtained. It is quite evident that the resulting percentage is necessarily only a function of the quantity of alkali, and as in this new process no particular provision is made to use an absolutely exact proportion of the two agents, fat and potash, it follows that the quantity of ether which is obtained is quite accidental. The whole of the facts come to this, that the formation of butyric ether affords a good *qualitative* test for the presence of butter in a mixture of fats. We knew this years ago, when a once notorious member of this Society first alluded in a police court to a "saponification test" he was possessed of for the examination of butter. Messrs. Wanklyn and Fox bring us no further than this. Unless they study the subject much more intimately than they have done, I would advise them rather to bear the ills they have than fly to others that they know not of.

Mr. Wanklyn replied: I have listened with very great attention to the remarks made by Mr. Hehner, and I am delighted that I have induced him to experiment on this matter. The subject of ethers is one upon which I have been engaged for the last seventeen years, and is, as everyone knows who has worked on it, one of the most difficult subjects in organic chemistry and full of pitfalls. Mr. Hehner has shown us a very beautiful experiment; but I think I may mention that it is possible to produce a trace of butyric ether from butyric acid, alcohol, and potash alone—a possibility owing to causes which are pretty well known to chemists; this fact we can verify in a variety of ways. When we bring butyric acid and alcohol together no combination takes place, but if a trace of potash is added, immediate combination is obtained, and in this way we might get a little butyric ether.

Mr. Hehner, to judge from his remarks, has evidently not made himself acquainted with the grounds which inspired the isoglycerine theory, and as to his remarks on theories generally I was sorry to hear them. I have been accustomed to work in a laboratory nearly all my life, and in my opinion a good chemical theory is worth a lifetime of experiment. The most valuable possession a scientific man has is a theory,

which may be true or false, but which leads to investigation. I have reason to believe that my theory will stand complete investigation. As to my paper before the British Association, it will be published in the report of the Association when this appears.

The theory of isoglycerine depends upon this: No natural fat yields the proper theoretical quantity of glycerine. I have taken the trouble to get information from manufacturers who only get five per cent. of glycerine from the total fat taken, the fatty acids being 95 per cent. and 5 per cent. of glycerine being obtained by the manufacturer, he is satisfied with his yield, the figures summing up to 100; nevertheless, half of the theoretical amount of glycerine is missing. My explanation of this circumstance is that only one half of the glycerine there is here, and the other half exists as isoglycerine.

Reverting to butter, a good many chemists have worked on this subject but not one has succeeded in getting the theoretical quantity of glycerine from it. Last summer I worked at the subject and saponified with hydrate of lime; first of all there is a curious combination of lime with the butter. I expected a loss of water, but remarkably enough there was no loss. Afterwards, when the action is completed the lime combines bodily with the glycerine and the fatty acids, and from this no glycerine can be extracted. It is only after prolonged extraction with boiling alcohol that the compound is broken up and yields its glycerine. I do not mean to recommend the use of lime for this saponification; I merely warn analysts against its use.

It is not only the smell of butyric ether that we obtain, but from 3 to 4 per cent., and I believe it is even possible to get a higher percentage. The process described in the paper is a practical method for examining butter, and I do not agree with Mr. Hohner that it is a step backwards. By our process one is enabled to turn out in about an hour a very fair examination of butter or fats containing butter, and I expect that the degree of accuracy to which we shall rise will be that we shall be able to measure 20 per cent. of butter in a fat, and that within an hour.