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THE COMPOSITION AND ANALYSIS OF BUTTER FAT.

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UP to the year 1874 butter fat was regarded as consisting, like other fats, of a mixture of tri-stearate, palmitate, oleate, &c., &c., and with only a trace, 2 per cent. at most, of butyrene. On the strength of this assumption no attempts were made to distinguish butter-fat chemically from other fats, as it was felt that a maximum difference of 2 per cent. gave far too small a margin for safe conclusions to be drawn.

In July, 1874, however, Messrs. Hehner & Angell published a small pamphlet in which they showed that butter-fat yielded only about 86 per cent. of fatty acids insoluble in water, whereas, on the above assumption, it should yield, like most other animal fats, about 95 per cent. Here, then, was a difference, apparently, at once constant and of sufficient magnitude, to be available for the detection of adulteration of butter-fat, with at least such fats as are more commonly used for this purpose. The value of this alleged fact, for the purpose of detecting adulteration, depends chiefly on the constancy of the alleged proportion of insoluble fatty acids, and is independent of the nature of the substance making up the remainder. Nevertheless, it is of advantage to know the nature of this remainder, if for no other reason than to demonstrate why the insoluble acids should be as low as alleged. Messrs. Hehner and Angell accordingly made some attempts to supply this deficiency, and came to the conclusion that it consisted, besides, of course, the necessary glycerine residue, of fatty acids soluble in water, butyric acid chiefly. The method by means of which they endeavoured to show this was, however, open to objection and their explanation was therefore not generally accepted.

In the summer of 1875, I in consequence undertook a series of experiments, in order, if possible, to clear up this point, which seemed to me of considerable interest. The work was frequently interrupted and therefore progressed but slowly. At our meeting in January, 1876, I gave, however, a short description of some of these experiments, which seemed to me to demonstrate that butter-fat really did contain a considerable proportion of fatty acids, soluble in water, as Messrs. Hehner and Angell had alleged. The experiments, it may be recollected, consisting in heating butter-fat either with water alone, or with water and a known amount of alkali in closed tubes, to a temperature of 500° F. In the first case the fat splits up into soluble and insoluble fatty acids and into glycerine, in the second case the soap produced may be decomposed by means of a known amount of acid, the insoluble fatty acids collected as usual, while the soluble fatty acids are estimated in the filtrate by standard alkali. None of the experiments then recorded were, however, quite satisfactory, as owing to constant leakage of the tubes, some loss had taken place in each case. Since then I have overcome this difficulty and now beg to lay the results of these later experiments before you.

Heating with water only. About 5 grammes of the dry filtered butter fat were enclosed in a silver tube, with about 80 cub. cent. of water, and heated to a temperature of from 500 to 550° F for a period of 4 to 5 hours. After cooling, the tube was opened and the contents washed into a beaker, or latterly a flask, as recommended by Dr. Muter, and the insoluble fatty acids thoroughly washed, dried, and weighed without removing them from the flask or beaker. The silver tube was washed out with ether, and the

amount of fatty acids thus obtained, added to that found as above. The aqueous filtrate containing the soluble fatty acids and glycerine, was neutralized with barium carbonate, boiled, filtered and evaporated, at first on a water bath, finally in vacuo over oil of vitriol. The residue obtained was then weighed and the glycerine present extracted with alcohol, or expelled by prolonged heating to a temperature of 130° C, and the rest again weighed, the loss being taken as glycerine. Finally the residual barium salt was converted into sulphate, from which the amount of soluble acids present could be calculated. Neither of these processes is, however, quite satisfactory; in the first some barium salt is dissolved by the alcohol, in the second the glycerine cannot be all expelled without danger of decomposing some of the barium salt. (Owing to this I have not as yet been able to estimate the exact equivalent of the soluble acids present, but I believe that it is very near to that of pure butyric acid. I am now engaged in some experiments to settle this point more conclusively). In some of the experiments I therefore weighed the mixed residue of glycerine and barium salts, added sulphuric acid, evaporated, ignited and weighed again. On the assumption that the soluble acid present is butyric acid, we are then able to calculate both the acid and the glycerine contained in the residue. The general results of the experiments I have already stated, viz. :—that they show the presence of a notable proportion of soluble fatty acids. I may, however, give one experiment in full.

Dry filtered butter fat taken	4.800 grammes.
Insoluble fatty acids obtained	4.202 "
Mixed glycerine and barium salt	1.059 "
Sulphate of barium	0.3395 "

This gives the composition of the fat as follows :—

Insoluble fatty acids	87.54
Soluble " "	5.33
Glycerine	12.62

This still leaves a deficiency, due in part, I have no doubt, to an under estimation of the insoluble fatty acids, owing to difficulties of manipulation, in part to the fact that the soluble acid is not, as assumed, pure butyric acid. In three other experiments, each made with a different sample of butter, I obtained soluble fatty acids 5.3, 6.4 and 5.8 per cent. mean of the four 5.70 per cent., and glycerine 10.86, 11.5 and 11.8 per cent. mean of the four experiments 11.69 per cent.

Heating with standard aqueous alkali. The same amount of butter fat as previously given was heated with 25 cub. cent. of normal soda solution, generally with the addition of some water, in the closed tube as before, to a temperature of 500° F. for four hours. The resulting soap was decomposed by 25 cub. cent. standard acid, slightly stronger than the alkali used, and the insoluble fatty acids washed, dried and weighed as usual. In the filtrate the acidity was estimated by a deci-normal soda solution, and after subtracting the excess of acid added the rest was calculated as butyric acid. Some of the results obtained were very good, but as I found that unless the soda solution used for saponification was very much stronger than that given above, which, of course, is very objectionable on other grounds, nothing was gained by substituting soda solution for pure water, except, perhaps, that the experiments could now be performed in an iron instead of in a silver tube. In either case I had to heat to at least 500° F., for not less than four hours to ensure decomposition. I therefore abandoned this method also, but will give two experiments performed in this manner.

Twenty-five cub. cent. of the standard acid added to 25 cub. cent. of the standard soda required 3·8 cub. cent. deci-normal soda to produce exact regularity.

	1st Exp.	2nd Exp.*
Butter fat taken	4·041 grammes.	3·599 grammes.
Insoluble acids obtained	3·519 „	3·166 „
Cubic cent. deci-normal soda used	28·5	25·8

From this we have—

Insoluble fatty acids	87·08	87·96
Soluble „ „	5·37	5·38

Finally I have adopted the following method which, I believe, leaves nothing to be desired on the score, either of facility of execution or of accuracy. About 5 grammes of the dry filtered butter fat are weighed into a small strong flask. (I always use one of the small assay flasks), 25 cub. cent. of a normal alcoholic soda solution are added, the flask is closed by means of a well fitting caoutchouc stopper, firmly secured by a piece of canvass and string, and heated in a water bath for about one hour. I think a much shorter time would be sufficient, but hitherto I have always heated for one hour. When cool, the flask is opened, the contents, which are semi-solid, carefully liquified by heat and washed into a flask with hot water. This flask is now heated for some time on a water bath to expel the alcohol, some more hot water is added and 25 cub. cent. of diluted sulphuric acid, somewhat stronger than the alkali used, are run in. The contents are now allowed to cool and the acid aqueous solution below the cake of fatty acids is passed through a filter. The fatty acids in the flask are washed by hot water in the manner recommended by Dr. Muter, *i.e.*, each time allowed to cool; all the washings are passed through a filter. I use no cambric, but pass everything through paper. With care scarcely any of the fatty acid will find its way into the filter. At first I used to dry the fatty acids in the flask and on the filter paper separately, making use of a counterpoised filter. I found, however, that the fatty acids evaporate from the filter paper even at a temperature of 105° C., and I now, after the washing with water is completed and the flask drained, wash any fatty acid that may be on the filter into the flask, by means of a mixture of alcohol and ether, boil off the alcohol and ether, on a water bath, and finally dry the fatty acids in the flask at a temperature of 105° C. The drying can be done readily if the melted fat is now and then shaken briskly, so as to subdivide the water as much as possible. In this way the acids, when once in the flask, are not taken out until their weight has been taken, thus reducing the risk of loss to a minimum. Meanwhile the acidity of the aqueous filtrate and washings is estimated by deci-normal soda solution. Subtracting from the amount required the proportion necessary to neutralize the excess of acid added in decomposing the soap, the rest represents the soluble fatty acids contained in the butter taken, and on the assumption of its being butyric acid, we can, of course, calculate the amount of this acid present. When once the equivalent of the soluble acids present in butter is fairly determined, this, of course, will have to be substituted for that of butyric acid. The results thus obtained are, I believe, very accurate, and the process is very simple in execution. I have satisfied myself by repeated experiments that the alkalinity of the alcoholic soda solution by itself is not altered by the process. At one time I had hoped that the process might be conducted in open flasks, but the following experiments will show that a loss of soluble acid is thus occasioned,

* This was a different sample of Butter.

which renders it necessary to use a closed flask. When once the decomposition of the fat is complete, the alcohol may be boiled off without loss. This boiling off of the alcohol is not, I believe, absolutely necessary, for, if we add a sufficient amount of water before adding the sulphuric acid, the fatty acids separated are practically insoluble in the very diluted spirit. As, however, the boiling off is, as far as I can see at present, no disadvantage, it may be as well to do it.

Five portions of the same sample of dry filtered butter fat were treated each with 25 cub. cent. alcoholic soda solution; the first three, contained in open flasks, were heated on a water bath for a $\frac{1}{4}$ hour, $\frac{1}{2}$ hour, and 1 hour respectively, the last two were heated in closed flasks for 1 hour in a water bath. In one of the latter experiments, No. 4, the alcohol was allowed to remain; in the other, No. 5, the alcohol was boiled off previous to the addition of the acid. The following are the results:—

Experiment	1— $\frac{1}{4}$ hours heating,	soluble acid found	5.38 per cent.
"	2— $\frac{1}{2}$	" " " "	"	"	"	4.90 "
"	3—1	" " " "	"	"	"	4.86 "
"	4—1	" " " "	"	"	"	5.49 "
"	5—1	" " " "	"	"	"	5.50 "

The series clearly shows that prolonged heating in an open flask occasions a serious loss of soluble acid. It may perhaps be useful to give one of the above experiments in full. I will give No. 5:

25 cub. cent. of the acid added to 25 cub. cent. of the alcoholic soda required, 29.1 per cent. deci-normal soda solution to produce perfect neutrality.

Dry butter fat taken	4.380 grammes
Insoluble acids obtained	3.885 "
Deci-nomeal soda required	56.5 cub. cent.

56.5—29.1 leave 27.4 deci-normal soda neutralized by the soluble fatty acids present.

From this we obtain:—

Insoluble acids	88.69 per cent.
Soluble acids	5.50 "

The same butter fat had previously been examined, in the usual manner, for insoluble fatty acids only, when 88.56 per cent. had been found.

As a further illustration of the process I will give the analysis of the butter used in the above experiments, and those of the six last samples of butter received in my district, and will add for comparison the specific gravity of the melted fat taken at a temperature of 100° F. compared to water at the same temperature.

	Sp. Gr. at 100° F.	Insoluble Fatty Acid.	Soluble Fatty Acid.
My own butter	912.4	88.69	5.50
District butter, No. 1	912.3	87.83	5.40
" " " 2	912.6	87.61	5.73
" " " 3	913.1	87.31	5.66
" " " 4	913.0	87.40	5.51
" " " 5	912.3	88.10	5.25
" " " 6	912.3	88.03	4.92

Calculating the amount of glycerine residue in each of the above cases, and adding it to the sum of acids found, we do not in any case come up to 100. This is, as before observed, no doubt due in part to the fact that the soluble fatty acid is calculated as butyric acid, whereas some higher acids are also present, in part, however, also to the fact that butter fat, as obtained by simple drying and filtering, does not consist of pure glycerides.

The results given in the foregoing show, I think conclusively, that butter fat really does contain from 5 to 6 per cent. of soluble fatty acids. It will be seen that the fat, whether decomposed with water only at a temperature of 500° F., or with diluted alkali at the same temperature, or with alcoholic soda in an open flask at a temperature not exceeding 176° F., or, finally, with alcoholic soda in a closed flask at a temperature of 212° F. yields substantially the same products. The amount of glycerine found also agrees with this assumption, although but little stress can be laid upon that, as the glycerine cannot be estimated with sufficient accuracy. I am inclined to put more stress on the fact that the amount of glycerine residue calculated, added to the amount of acid found, falls short of 100. In what exact state of combination this soluble acid is contained in butter fat must be decided by future experiments.

In conclusion, a few words in regard to a process (the spec. gr. of the fat taken at 100 F.) first employed by Mr. Bell, and since then strongly recommended by Dr. Muter, who even thinks, going in this somewhat beyond Mr. Bell, that a reputed sample of butter may safely be passed over as good if it shows a spec. gr. above 911. Now, I am sorry to say, I cannot endorse this last statement. I believe that the spec. gr. of the fat is, as one of several factors, of great value in judging of the genuineness of a given sample of butter, but it cannot be safely taken as the sole guide. Within the last week or so, I took the spec. gr. of a sample of mutton dripping, obtained about nine months ago out of my own kitchen, and since kept in my laboratory, and found it to be 917·3. The spec. gr. was taken several times, and otherwise checked, and there can be no doubt of its correctness. On my mentioning this fact to Mr. Bell, he suggested to me that the dripping had probably been strongly heated. I accordingly procured a fresh sample of mutton dripping from my kitchen, and this time found the spec. gr. to be 904·8, when, however, this same sample was heated in a flat porcelain dish, for some time to a temp. of about 300 C., the spec. gr. was raised to 914·4, thus confirming Mr. Bell's suspicion so far. I think it very probable that prolonged exposure to the action of the air, even at ordinary temperature, may have a similar effect. This clearly shows, that taken by itself, spec. gr. cannot be absolutely relied on as showing the genuineness of a sample of reputed butter. On the other hand, I think it will be found that whenever a sample of reputed butter shows a spec. gr. below 911 it may safely be pronounced adulterated. I must express my strong conviction that, as far as I can see at present, no single property of butter fat, taken by itself, is of absolute value as a guide for judging of the genuineness of a given sample of butter, and I would, therefore, advise every one to submit each sample that comes before him to as many tests as possible before he pronounces an opinion.

Dr. Muter had listened to Dr. Dupré's paper very attentively, as it showed an advance in butter analysis to the extent of saponifying in a closed tube, and apart from that, it confirmed his, (Dr. Muter's,) process for the estimation of both soluble and insoluble acids, and of the standards he had laid down. The history of the modern system of butter analysis, was as follows:—In the years 1870-71, he, (Dr. Muter,) began to examine butter, which he did by saponification, first with alcoholic potash, and afterwards with lime and distillation of the whole ley with tartaric acid, so as to estimate the soluble acids. Want of time prevented him from fully publishing his results, and subsequently Messrs. Angell & Hehner saponified with potash decomposed with acid, and estimated

the insoluble acids, published their results, and fixed a standard, this standard Dr. Muter considered too low, and therefore published his process for taking both the soluble and insoluble acids, pointing out the importance of washing in a flask instead of on a filter, giving as a standard for calculation of

Soluble Acids	6·0
Insoluble Acids	88·0
			Total	...	<u>94·0</u>

As representing a fair low class butter, looking as he now did at Dr. Dupré's results done on early summer butter, Dr. Muter was pleased to see therein a complete confirmation of the safety of his insoluble standard. In his paper he had given the barium method of estimating the soluble acids as being, although the most tedious, yet the most accurate, but in the discussion he had mentioned two alternative ways of working, viz, (1) The use of standard alcoholic potash for saponification, and subsequently standard sulphuric acid and (2) The evaporation and ignition of the solution after exact neutralization with standard acid, and the estimation of the alkalinity of the ash and calculation to butyric acid. He saw that Dr. Dupré, had been all along adopting the first of these methods, and he confessed that in practice he himself worked by it to save time, having first carefully standardized his solutions by the barium process. He, however, considered that it was essentially a dangerous method, except in the most practised hands. It was a necessity to save bulk to use a normal solution of potash each C.C. of which represents $\cdot 056$ KHO., so that even the slightest unsteadiness of hand and one drop too much put in, there is at once an appreciable excess of potash which when calculated to per centage of butyric acid gives an enormous error. As the tendency is in this direction, the soluble acids thus estimated come as a rule too low, and he (Dr. Muter) thus viewed Dr. Dupré's results as he rarely appeared to get the total up to 94, without which the speaker considered that no analysis of butter was perfect. He was much gratified with Dr. Dupre's approval of his flask washing, which he was certain would commend itself to highly competent men like Dr. Dupre, for its simplicity and accuracy. Dr. Muter, also from practical experience, upheld the fact that by long boiling in an open vessel, butyric ether is formed and lost during saponification, and although he had not yet gone so far as actually saponifying in a perfectly closed flask, he had, in practice, reduced the boiling to a minimum and partially closed the flask, and had, no doubt, of the value of Dr. Dupré's absolute closing principle.

As to Mr. Bell's specific gravity process he entirely differed from Dr. Dupré, and held that (especially when expressed in "actual density," as modified by himself) it was a very useful process indeed for indicating what butters were worth the trouble of analysis. Mr. Bell's results were, he understood, based on a long course of experiments, as also were his own in confirmation, and he unhesitatingly stated that there was no fat which had a gravity so great as butter. He especially took exception to the case of mutton dripping given, both as regards its gravity and acids, and was certain it could not have been pure. He had again and again examined dripping prepared by his own hands direct from the animal fat, and had found it to have a gravity of about 903 to 904, according to Mr. Bell's system, and that it never, under any circumstances, showed less than 95 of insoluble acids. The lightest fat in the market was the so called "margarine," which had a gravity of 901 to 901·5, and showed when quite fresh 93 per cent, and

when stale and after prolonged melting (the artificially added volatile portion having become dissipated) it yields 95 per cent. This gravity of 901 (= 903 actual density) is strikingly characteristic of the French artificial butter of which he had lately had occasion to examine many samples for members of the butter trade. He did not consider that this one experiment on dripping taken from a kitchen, and which might have really contained an admixture of butter, should weigh for a moment against the results obtained by Mr. Bell and confirmed by himself on undoubtedly pure samples.

Mr. Allen quite agreed with a previous speaker as to the primary importance of the determination of the soluble fatty acid. In confirmation of Dr. Muter's statement that he had been working for some years on the examination of butter by the estimation of the volatile acids, he might remind the Society that in an article contributed some four years since to the *Food Journal*, by Dr. Muter, the author distinctly stated that he was then working on and hoped to perfect a method of determining the butyric acid in butter. Dr. Duprés anomalous result of 92.46 (?) per cent. of insoluble fatty acids in dripping, Mr. Allen thought, might possibly be due to the employment of butter by the cook.

Addendum. Since the foregoing paper was written, I have effected the saponification, decomposition of the soap, and the washing and drying of the fatty acids, at ordinary temperature, thus still further reducing the risk of breaking up the higher into lower acids. The saponification is readily effected by using a sufficiency of alcoholic soda. Between four and five grams. of the dry butter fat were shaken up, for several minutes, with 100 cub. cent. of normal alcoholic soda. The butter soon dissolves, but after a time the solution gelatinizes to a clear transparent jelly. (The temperature of the laboratory at the time of these experiments ranged between 22 and 25°.) This jelly is now allowed to stand over night, during which time the smell of butyric ether, very strong at first, entirely disappears. In one of the experiments the alcohol was allowed to evaporate spontaneously, before the acid was added, in the other (made with a different sample of butter), the soap was dissolved in about half-litre of water, and at once decomposed by the addition of hydrochloric acid. The fatty acids, which separated in white curdy masses, were thoroughly washed on a filter, with cold water, about 4 litres, dried in vacuo over oil of vitriol and weighed. The following are the results:—

1st Exp.	Butter fat taken	4.545 grammes,	insoluble fatty acids obtained	3,888 grammes.
2nd "	"	4,982 "	"	4,299 "
			Percentage of insoluble fatty acids found	1st Exp. 85.5 per cent.
			Ditto	" " " " 2nd Exp. 86.3 "

Butter fat, therefore, yields the same proportion of insoluble fatty acids, whether saponified with or without the aid of heat.

For the sake of completeness, I give the analyses of the samples of mutton dripping referred to in the paper.

	Spec. Gravity at 100° F.	Insoluble fatty acids.	Soluble fatty acids.
1st Sample	917.3	92.43	1.69
2nd Sample, before heating	904.8	95.44	0.09
2rd Sample, after heating	914.4	93.64	0.78

It has been suggested, that the addition of alcohol or ether to the fatty acids, and the subsequent drying, might give either too high a result by the formation of non volatile ethers, or too low a result by the production of volatile ethers. I find, however, that such is not the case. The fatty acids, when alcohol or ether have been added,

certainly require a longer time of heating before the weight becomes constant, than is necessary when no such addition has been made, the ultimate amount found is, however, the same in either case.

A report on "Butter Analysis," by Mr. J. Bell, dated May 31st, 1876, has just been presented to the House of Commons, which contains some useful details, and I hope to return to it at some future time. Meanwhile, I would take this earliest opportunity to refer to two points in this report. Firstly, Mr. Bell is under a great misapprehension in supposing that Messrs. Hehner and Angell's process ever fell practically into abeyance. On the contrary, it was at once taken up by a number of Public Analysts, and at the time of the report was, I believe, adopted by every Public Analyst, who had at all worked on the subject of butter. As evidence of the interest taken in this question, I need only refer to Dr. Muter's paper, published with the discussion in the *Analyst* for March; and my short note read at the meeting of Public Analysts, in January. Secondly, I should like to ask Mr. Bell, if the per centages of fixed fatty acids given in Table III., and from which it is inferred that this per centage increases with the age of the butter, are in each case the results of two or more concordant analyses, or represent a single analysis only? If the latter is the case, the table is I fear of little or no practical value, since the results are then, in four at least out of the six cases given, within the limits of experimental error. A. D.

A TEST FOR THE PRESENCE OF WOOD OIL IN COPAIVA BALSAM,

THE ethereal oil of *Dipterocarpus* Balsam, otherwise known as Gurgun Balsam or wood oil, according to Flückiger, takes a splendid violet colour, when dissolved in about 20 parts of bisulphide of carbon and a drop of a cooled mixture of equal parts of sulphuric and nitric acids added. Fish liver oil and oil of valerian also give a violet colour, but it is transient whilst the colour with wood oil is permanent for some hours. In order to exclude fish oil, a few drops of the liquid may be distilled over and the test applied.

A. W. B.