THE RELATION OF COCOANUT OIL TO THE VARIOUS METHODS OF BUTTER ANALYSIS

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The analytical chemistry of the fats is an undeveloped department of science. The various fats have been discovered, their formulæ determined, and their true nature made known; but analytical processes for separating the various fats and fatty acids from each other with anything like certainty or exactitude, are things for which the student of fatty chemistry is still seeking.

Certain special problems have, however, arisen which have called for an immediate solution, and the stimulus thus given has resulted in a concentration of thought and investigation upon a single question, to which the discovery of many valuable facts is due. A prominent example in this connection can be seen in the case of butter analysis. Various processes were devised, all with the object of distinguishing true butter fat from other fats. The problem was such a difficult one that at one time it was seriously doubted by eminent chemists whether a satisfactory solution could be obtained, since the number of animal and vegetable fats was so great, their character so similar, and their chemistry so little understood.*

It is the purpose of this paper to review briefly the various processes which have been used for butter analysis, and at the same time to bring out more fully and completely, than has hitherto been done, the remarkable chemical and physical relations that cocoanut oil bears to true butter fat.

The melting point of the fat was at one time considered a reliable test, as butter fat melts at an average temperature of 35.8° C, while the ordinary substitutes melt at considerably higher temperatures, viz., ox fat, $48^{\circ}-53^{\circ}$ C; mutton fat, $50^{\circ}-51.6^{\circ}$.

It is, however, easy to find palatable oils and and fats which, when mixed with that animal product which, for want of a better name, is termed oleomargarine, would bring the fusing point of the mixture within the required limits for butter. There is an additional source of uncertainty in the use of this process, due to the fact that butter fat becomes harder by age, and the melting point rises considerably in consequence.

^{*} Hassall, Food. London, 1876, p. 435.

⁺ Bly:h, Foods, etc., p. 294.

In this case cocoanut oil could be mixed with oleomargarine or any other substitute for butter with a higher melting point, since it fuses at a much lower temperature than even pure butter fat, viz.:

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23.5-24.1° (Muter, Analyst, I., 7.)
24.2-24.3° (Original observation.)
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The specific gravity of the fat has also been used as a test, since butter fat has a higher density, viz.: .91246-.91382 at 37.7° ,* than what Blyth terms vegetable butterine .90294, or dripping .90659, But cocoanut oil at the same temperature shows a higher specific gravity than pure butter fat, viz.: .9167,† .9117.‡ Allen gives the specific gravity of cocoanut oil at the temperature of 100° C, as .868, and of butter, .865-.868.§ Thus mixtures of foreign fats could easily be made, of which the specific gravity would be the same as that of butter.

The process of Hehner || was the first one proposed that rested on a purely chemical principle. By this method, as proposed by the author in the original article, the insoluble fatty acids are directly weighed after washing out the soluble fatty acids with boiling water. The limit fixed by Hehner is between 86.5%-87.5% of insoluble fatty acids, while ordinary butter substitutes show much higher figures, in most cases as high as 95%. The investigations of other chemists || have, however, shown that butters are by no means uncommon in which the percentage of insoluble fatty acids will be higher than the limit fixed by Hehner, reaching in some cases as high as 90%.

Cocoanut oil, when examined in strict accordance with Hehner's original directions, yielded 86.43% of insoluble fatty acids,** which would thus enable it to be mixed with other fats in such a manner as to escape detection by this process. It is true, however, that the

- \$ Stillwell. American Chemist, I., 407 (with correction for temperature as directed).
- § Allen, Commercial Organic Analysis, II., 136.
- Fresenius, Zeit. für anal. Chem., XVI., 145.

¶ Flelschman & Vieth, Fres. Zeit, 1878, p. 287. Kretchmar, Ber. Chem. Gesell., X., 2091. Kuleschoff, Wagner's Jahresbericht, 1878, p. 999. Jehn, Archiv. d. Pharm., IX., 1878, p. 535. De la Source, Ibid, 1882, p. 929.

** R. W. Moore, Chem. News, Dec. 5, 1884.

^{*} Muter, Analyst, I., 7.

⁺ R. W. Moore, American Chem. Journa?, VI., No. 6.

subsequent modification of Hehner's process by Dupré, * by which the soluble acids are estimated in the washings from the insoluble acids, would probably detect such a mixture by the low percentage of soluble fatty acids found. The low figures by the Hehner process, in the case of cocoanut oil, are in a measure due to the fact that lauric acid, its principal constituent, is volatilized to some extent at the temperature necessary to dry the insoluble fatty acids, and loss is thus occasioned. Nevertheless, cocoanut oil is a more suitable fat for adulteration with a view to escape this method than any other fat hitherto examined.

Another method brought out by Koettstorfer † depends upon the fact that the comparatively high percentage of glycerides of the lower fatty acids in butter causes it to require a greater amount of caustic potash for saponification than other fats. Experiment justified this view in a measure for oleomargarine, and beef and mutton tallow required about 195 m.g. caustic potash per gm. for saponification, while for pure butter fat 223.5-232.5 m.g. were necessary.

Cocoanut oil in this case also refuses to be classed with the ordinary substitutes for butter, and exhibits figures higher even than pure butter, viz.:

$$257.3-258.3$$

 250.3 246.2

These high figures are due to the presence of large amounts of lauvic acid, together with smaller quantities of caproic, caprylic and capric acids.

It is thus possible to mix oleomargarine with cocoanut oil in such a manner as to bring the results within the limits set by Koettstorfer. In proof of this the following mixtures were made with the object of approaching nearly the limits of Koettstorfer : **

Cocoanut Oil.	Oleomargarine.	Mgs. K O II per grm.
49.3%	50.7%	220.0
70.2%	29.8%	23 4.9
Washed Oil.		
53.1%	46.9	223.6
75.9%	24.1	234.9
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The oleomargarine used required 193.5 mgs. K O H per grm.

* Analyst, I., 87, 114.

+ Fres. Zeit., XVIII., 199, 431.

‡ Valenta, Dingler's Polyt. Journal, 249, 270.

§ R. W. Moore, Chemical News, Dec. 5th, 1884.

The oil was thoroughly washed with hot water.

** R. W. Moore, Chemical News, loc. cit.

A general method for testing oils and fats has been brought out by Hübl* and has been recommended by the author as applicable to the examination of butter for foreign fats. It depends upon the relative capacity for absorbing iodine of the formic, oleic and tetrolic series of acids; the first remaining, under ordinary circumstances, indifferent, while each molecule of the oleic series unites with two atoms of iodine and each molecule of the tetrolic series with four atoms. Thus widely varying figures for various fats and oils are obtained, depending upon the relative amounts of acids of the different series contained in each. Thus, 100 grms. Japanese wax absorb but 4.5 grm. of iodine, while the same quantity of linseed oil, containing 80% linoleic acid, absorbs as high as 160 grms. of iodine.

In this list of iodine figures, butter occupies a place midway between cocoanut oil (8.9 grm.) and the ordinary substitutes. Thus mixtures have been made of oleomargarine and cocoanut oil so as to come within the limits of butter, as the following figures will show.[†]

Oleomargarine, 55%. Cocoanut oil, 45%. Lard, 40%. Cocoanut oil, 60%.

In eight samples Hübl found for butter a maximum figure of 35.1, and a minimum of 26.8.

There is, however, a process, the results of which show butter to be an extreme, and cocoanut oil, though considerably in advance of the figures given by the ordinary substitutes for butter, still falls far below the limits set for genuine butter. This method which was brought out by Reichert,‡ consists in distilling off from the sample under examination a definite amount of acid and estimating the same volumetrically. It is by this method that the fact that butter is comparatively rich in butyric acid which is considerably more volatile than any acid contained in cocoanut oil, is brought into prominence, for the distillation, as recommended by the author, is stopped at a point when the less volatile acids come over in any quantity.

^{*} Dingler's Pol. Journal, 253, 281.

^{*} R. W. Moore, American Chem. Journ., VI., No. 6.

^{\$} Fres. Zeit., XVIII., 68.

If the distillation were continued long and the distillate were not freed by filtration from the acid which condenses in a solid form at the temperature of the condenser, cocoanut oil would give figures very much higher than those of butter, since it is almost entirely cemposed of acids which can be distilled over with water.* In the relative volatility of the more volatile portion of the acids contained. however, butter stands far ahead of cocoanut oil, the prescribed distillate neutralizing, at least, 13. c. c. of $\frac{1}{10}$ normal K O H⁺ while cocoanut oil, treated in the same manner, requires but 3.7 cb. cm.1 Thus mixtures of the latter with butter would lower the figures considerably :

Hehner. Koettstorfer. Hübl. Reichert. Butter, 50 %.) Oleomargarine, 27.5%. 89.50 327.5 35.4 8.7 22.5%. Cocoanut oil,

Thus it can be seen that cocoanut o.1 in four processes for testing butter is characterized by properties which render it, for the chemist, a most dangerous adulterant, making possible a large number of mixtures difficult to detect by chemical methods.

The question naturally arises whether cocoanut oil has actually come into use for this purpose of adulteration, and also whether the mixtures contrived to bathie ordinary chemical tests really re-The first of these questions is most difficult to ansemble butter. swer, since the process which is capable of detecting such mixtures has not, by any means, come into general use, and the results obtained by other processes do not bear upon this question.

There is not, however, a complete absence of evidence on this point since cocoanut oil is mentioned as an adulterant of lard in the Analyst (VII., 193), and Dietzsch || makes note of it as a component of what he terms "Schmalz Butter." The writer also has been informed by an importer of the oil that it has, to his knowledge, been used, with little success, however, for the purpose of adulterating both butter and oleomargarine. The mixtures thus produced were, probably, unpalatable, owing to the fact that the odor of the oil had not been removed.

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^{*} Ondeman's Journ. für prakt. Chem., 81, 367.

^{+ {} Reichert, loc. cit. } Medicus & Scherer, Fres. Zeit., XIX, 159.

[;] Reichert, loc. cit. R. W. Moure, Chem. News, loc. cit.

Nahrungs-mittel und getranke, 4th Ed., p. 212.

It must, however, be taken into consideration that the oil is produced in a warm climate, where decomposition begins easily; that no means are taken to preserve its freshness, and that when met with in colder countries it is already tolerably old, since the transportation occupies a long time. When first made it is, probably, more agreeable to the taste, for the natives of the countries where it is produced use it for the same purposes as we use butter, and if a demand for a palatable article should arise, it would, probably, be supplied.

The smell and taste of the oil, though disagreeable and unpalataole, can both be removed to a great extent. Careful washing with not water will accomplish a great deal, and in this way the writer has succeeded in obtaining a tolerably tasteless article. Also, a German patent has been taken out by Jeserich and Meinert* for rendering vegetable oils, including palm and cocoanut oils, inodorous and edible, so that they can be used in place of butter or in combination with it. The process consists in treating the oil with superheated steam and removing any free fatty acid by saponification with a small amount of calcined magnesia, not exceeding 25%. The patentees claim that in this way a perfectly sweet fat is obtained.

Notwithstanding that cocoanut oil might be, and possibly is, a most dangerous adulterant for butter, there yet remains a process by which it can be infallibly detected, if present, in any amount -the process of Reichert. This method is also the surest and most reliable for testing butter for any other foreign fats. It is easy and elegant in use and requires but one standard solution, and that a permaneut oil, not liable to daily change like the alcoholic potash solution used in the Koettstorfer process. Only one weighing is required of but ordinary exactitude and the transition point of the final titration is as sharp as could be wished. In fact it is a method possessing many merits and few defects, and it is extremely desirable that it should come into general and extended use. Thus far, it has stood all tests in the hands of many chemists. If, then, cocoanut oil should be the means of casting discredit upon all other methods, and thus of bringing that of Reichert into general use, a great and valuable service would be rendered to the subject of butter analysis.

^{*} Wagner's Jahresbericht, 1882, 932.