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**EXAMINATION OF SHREWSBURY AND KNAPP'S PROCESS FOR
THE ESTIMATION OF COCOANUT OIL.**

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LAST year Messrs. Shrewsbury and Knapp described a process for the estimation of cocoanut oil in butter (ANALYST, 1910, **35**, 385). Although a considerable number of English butters were examined, very few of foreign origin were investigated, and of the three examples given in this latter division two were classed as suspicious.

It therefore appeared advisable to examine a number of foreign butters and cocoanut oils by this process. The samples in question were obtained for us from the whole-sale market, and every possible precaution was taken to insure their authenticity. The following results were obtained :

Butter.	Shrewsbury and Knapp Figure.	Iodine Value.	Per Cent. of Triolein (calculated).	Shrewsbury and Knapp Figure of Residual Fats calculated at Triolein = 28.	Shrewsbury and Knapp Figure of Residual Fats calculated as Triolein = 65.
Finnish... ..	31·5	41·3	47·9	18·1	0·4
Danish	30·0	41·5	48·0	16·5	- 1·2
Siberian	33·5	38·7	44·9	21·0	4·3
Swedish	33·0	—	—	—	—
Irish Creamery ...	32·0	34·7	40·2	20·8	6·0
Irish Factory ...	35·5	39·3	45·6	23·0	5·9
Irish Dairy	28·5	39·1	45·4	16·0	- 1·0
St. Ivel (English) ...	30·5	37·5	43·5	18·0	2·2
Kiel	31·5	32·4	37·6	21·0	7·1
Cocoanut stearine ...	138·5	5·4	6·3	136·8	—
Cocoanut oil (Ceylon)...	170·5	5·8	6·7	168·6	—
„ „ (Epicos) ..	165·5	6·5	7·5	163·4	—
„ „ (Cochin)...	166·5	6·6	7·6	164·1	—
„ „ (Colombo)...	168·5	6·3	7·3	166·5	—
Cocoa butter	16·5	31·2	36·2	6·4	—

Shrewsbury and Knapp (*loc. cit.*) give 32 as a suggested maximum, but our results seem to point to a maximum of 35·5.

The effect of variations of the amounts of triolein in butter is dwelt on by these authors. Our experience with triolein is distinctly unsatisfactory, as great variations in the number obtained occur. This is probably due to the fact that a really good separation of the fatty acids in the alcohol-water solution rarely takes place. With oleic acid, however, fairly uniform results were obtained, the figure varying from 25 to 29·5 with the various samples at our disposal.

The figure 65 for triolein, and more so the somewhat higher ones obtained by us, must be excessive, because butters which differ considerably in their percentage of triolein as measured by the iodine value do not differ proportionately in their Shrewsbury and Knapp figure. This would not be likely if 65 or any higher figure were correct for triolein. Probably the number obtained by us for oleic acid is approximately right.

In the table given above the percentage of triolein is calculated from the iodine absorption, and from this the Shrewsbury and Knapp number is obtained by calculation for the residual fats on the assumption of a Shrewsbury and Knapp figure for triolein of 28 for one column and 65, as given in their paper, for the other. From these it is evident that, if 65 were correct, no value could be assigned to anything

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but the amount of oleic acid present, and the whole process would be no better than an iodine value. That this is not the case is seen from the table, where a rise in iodine absorption does not necessarily imply a rise in the Shrewsbury and Knapp figure.

The constitution of the residual fatty acids after separation from the alcohol water solution is given below, and is rather interesting. It seems to point to proportional quantities of all the constituents being dissolved. The main factor in the Shrewsbury and Knapp figure would be dependent then, as contended by the authors, on the proportion of lower and more soluble fatty acids present :

RESIDUAL FATTY ACIDS.

Name.	Iodine Value.	Zeiss at 45° C.	Molecular Weight.	Oleic Acid Per Cent. (calculated).	M - O.
Finnish... ..	44·0	31·5	259·7	49·0	238·2
Danish	47·0	31·5	259·1	52·2	234·1
Siberian	40·2	31·0	263·3	44·7	248·3
Irish Creamery	39·5	30·5	264·0	44·0	250·0
Irish Factory	40·8	31·5	257·0	45·3	236·4
Irish Dairy	43·2	32·0	261·3	48·0	242·3
Swedish	—	31·0	—	—	—

In considering the genuineness or otherwise of a butter, it is doubtless advisable not to rely entirely on any particular figure, but to consider the case as a whole. A figure that we have found to give instructive results is obtained by calculating the iodine value of the fatty acids to oleic acid, and from this the molecular weight of the residual fatty acids, by the following formulæ :

$$\frac{\text{Iodine value per cent.} \times 100}{90} = \text{oleic acid} = O,$$

$$\text{Molecular weight of residual fatty acids} = \frac{100 M - (282 \times O)}{100 - O},$$

where M = molecular weight of the fatty acids and O = oleic acid per cent. The figure thus obtained for genuine butters is generally about 235, and the addition of cocoanut oil tends to reduce the figure considerably.

We find that it is absolutely necessary to follow the process exactly as described by Shrewsbury and Knapp, especially as regards glycerol saponification. With alcoholic potash only extraordinarily high results were obtained ; for example, Swedish butter gave 112, and Danish butter 77. If, however, the correct quantity of glycerol is added after saponification, the results are normal.

The method will probably be of use in helping to determine the approximate composition of margarine. Thus a high-class margarine, A, showed very different

results from a cheap one, B, and the former probably contained a considerable amount of cocoanut oil :

	A.	B.
Zeiss butyro-refractometer (25° C.)	52.5	61.0
Sp. gr. (37.8° C.)	0.9097	—
Shrewsbury and Knapp figure	47.5	19.5
Koettstorfer value	232.8	204.9
Per cent. of insoluble acids left in funnel after Shrewsbury and Knapp	65.8	85.1
Reichert-Meissl	9.0	4.7
Polenske	6.7	1.4

Mr. Knapp sends the following note :

“The figure given by us for triolein was obtained from a single sample, which had a butyro-refractometer reading at 40° C. of 59.0. Lewkowitsch gives 56.5 for pure triolein. I think it would add to the value of the several figures obtained by Messrs. Ross, Race, and Maudsley for oleic acid if they indicated the purity of their samples. With regard to their calculation to show that 65 is too high a figure for triolein, it should be remembered that this calculation is based on the supposition that the various fatty acids do not interfere with each other's solubility. In the process, we are actually dealing with the relative solubilities of oleic, etc., acids in the water-alcohol mixture and in the separated fatty acids. What is required is the figure which olein gives in presence of the other butter constituents, and the calculation very usefully shows that 65 is too high for this figure. Mr. Shrewsbury and I would welcome 28 as the figure for olein, as it would increase the value of the process, and enable us to understand why both cocoanut-oil-free margarine and lard give lower Shrewsbury and Knapp figures than butter.”

