Analytical Method——The amount of the product extracted with BuOH from alcoholyses reaction mixture were determined through the following procedure. To 200 cc. of a reaction mixture neutralized with conc. H_2SO_4 to pH 6.0, 400 cc. of hot BuOH and 600 cc. of hot aqueous solution of NaCl (15%) were added, and the resulting two layers were separated. Aqueous layer was washed with 100 cc. of hot BuOH twice, then BuOH layer and washings were combined and washed twice with 100 cc. of hot aqueous solution of NaCl (15%). After removal of BuOH, the residue was dried at 90° for 2 hr. under a reduced pressure. The dried residue, obtained from BuOH extract, was weighed, while the total solid content in the product was weighed after removal of DMF from an aliquot of the reaction mixture.

Unreacted methyl stearates in dry reaction mixture of alcoholyses were determined by the method, which was applied by Osipow, *et al.*[1]

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Summary

Alcoholyses of methyl stearate by sucrose were investigated, and the contents of Ester Parts produced under various molar ratios of sucrose/methyl stearate were determined. From the results obtained, in comparison with theoretical values, the composition of the alcoholysis product obtained by the reaction was assumed to be governed by the random distribution rule.

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86. **Kazuya Kunugi**: Studies on the Syntheses of Sucrose Fatty Acid Esters. II. Separation of the Alcoholyses Products by Liquid Column Chromatography and Determination of the Contents of Sucrose Monostearate.

(*Research Laboratory, Asahi Denka Kogyo Co., Ltd.**1)

In the previous paper of this series,*2 the author investigated the composition of the alcoholyses products, Ester Part (EP), of methyl stearate by sucrose. To find the rule which governs the composition of the EP, the sum of sucrose mono-, di-, and polystearates, the random distribution rule has been postulated and found to be in good accordance with the theoretical value.

In the present work, the contents of sucrose monostearate in the alcoholyses products were determined and compared with the calculated values to confirm the random distribution rule.

For the analysis of sucrose monostearate obtained by alcoholyses of methyl stearate by sucrose, separation by liquid column chromatography and determination by saponification value were applied in this work. Recently M. Gee, *et al.*,[1] showed that sucrose monostearate can be analyzed quantitatively by gas chromatography after methylation,

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*2 Part I: This Bulletin, **11**, 478 (1963).

1) M. Gee, *et al.*: Chem. & Ind. (London), **1961**, 829.

saponification and molecular-distillation. However, since this method was not yet reported when the present work was carried out, the author applied the liquid column chromatography for the determination of sucrose monostearate, as will be described later.

Complete determination of all components in alcoholyses products, i.e., sucrose mono-, di-, tri-, and higher polystearate were not carried out, because of the experimental difficulty in separation of each of these components. The determination of sucrose monostearate only was carried out and compared with the theoretical value in this work. Hydrophillic property of sucrose monostearate and relatively large difference of the saponification value between sucrose mono- and distearate were useful to analyze quantitatively by liquid column chromatography.

In order to separate and determine sucrose monostearate, butanol-extracts described in the previous paper,*[2] a mixture of sucrose mono-, di- and other polystearates were subjected to the chromatographic separation. Alumina powder acidified by ordinary procedure was used as the column packings, and benzene-butanol (9:1 v./v.) (solvent A) and butanol saturated with water (solvent B) were used as the elution-solvent. These solvents were found most suitable for the effective separation of sucrose monostearate, and gave good solubilities of every sample. Sample solution in solvent A was put and developed on the top of the column, and then eluted by solvent A at first. Sucrose polystearates were eluted as the first fraction, and then, by elution with solvent B sucrose monostearate and a part of sucrose distearate were collected as the second fraction. After distillation of the solvent from the eluate, the saponification value of dry product of each fraction was determined.

The experimental results of various samples are shown in Table I. Two examples of the chromatograms are shown in Figs. 1 and 2. In Table II, the saponification values of various sucrose stearates are shown.

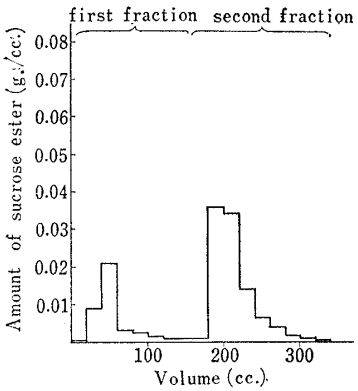

Fig. 1. Chromatogram for Ester Part obtained by Experiment No. 3 in Table I $\left(\frac{\text{Sucrose}}{\text{Methyl stearate}} = 1.05\right)$

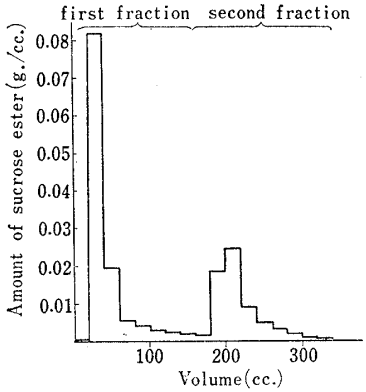

Fig. 2. Chromatogram for Ester Part obtained by Experiment No. 5 in Table I $\left(\frac{\text{Sucrose}}{\text{Methyl stearate}} = 0.35\right)$

As can be seen in the figures, the separation was nearly complete between the first fraction and the second fraction. Tables I and II show that the saponification value of the first fraction is higher than that of sucrose distearate, while the saponification value of the second fraction is lower than that of sucrose distearate except for No. 6. Summing up these results, sucrose tri- and higher polystearates were collected in the first fraction and sucrose monostrearate in the second fraction, while sucrose distearate seemed to be contained in both fractions.

Table I. Experimental Results of Column Chromatography

Experimental No.	Amount of Al_2O_3 (g.)	Amount of sample (g.)	Dry product of first fraction: % in sample	Dry product of first fraction: sapon. value	Dry product of second fraction: % in sample	Dry product of second fraction: sapon. value	Sucrose monostearate content (%)
1	50	2.018	3.8	—	93.0	97.8	79.5
2	50	2.498	1.8	—	90.1	104.0	61.6
3	30	2.990	29.2	129.5	68.6	97.8	58.8
4	30	2.995	38.4	141.6	45.6	113.4	19.3
5	30	3.985	61.0	147.1	31.4	124.1	3.9
6	30	5.000	82.6	161.9	10.3	138.9	—

Table II. Saponification Value of Various Sucrose Stearates

Sucrose ester	mono-stearate	di-stearate	tri-stearate	tetra-stearate	penta-stearate	hexa-stearate	hepta-stearate	octa-stearate
Saponification value	92.6	128.6	147.8	159.5	167.2	174.0	178.0	181.8

Furthermore, a part of sucrose distearate seems to be left on the column, since it is only partially soluble in solvent B, while sucrose monostearate is readily soluble.

Thus, the content of sucrose monostearate in each sample can be determined from the saponification value of the second fraction by the following equation :

$$x=\frac{128.6-A}{36.0}\times d \qquad (1)$$

where; x indicates the content of sucrose monostearate in the sample, A the saponification value of the second fraction and d the content of the second fraction in the sample.

In this equation, 128.6 is the saponification value of sucrose distearate and 36.0 is the difference of the saponification value between sucrose mono- and distearate. The calculated results of sucrose monostearate content are also shown in Table I.

On the other hand, the contents of sucrose monostearate and other stearates in various alcoholyses products obtained at various molar ratios of sucrose/methyl stearate can be calculated by the random distribution rule assuming that the stearoyl radical will distribute on the sucrose molecules randomly. The method of calculation by this rule was described in the previous paper.*[2]

The theoretical values of sucrose mono-, di-, tri-, and higher polystearates in various products are shown in Table III.

The comparison of the contents of sucrose monostearate between observed and theoretical values are shown in Table IV, quoted from Table I and III. In this Table, both values gave a reasonable accordance.

Table III. The Composition of Sucrose Stearates calculated from Random Distribution Rule (wt. % in Ester Parts)

Sucrose / Methyl stearate molar ratio	3.13	2.11	1.05	0.54	0.35	0.21
Sucrose monostearate	81.7	73.7	51.5	22.5	7.2	0.3
distearate	16.5	22.7	34.9	34.0	20.2	2.4
tristearate	1.6	3.4	11.4	26.9	29.2	9.1
tetrastearate	0.1	0.2	2.0	12.4	25.0	20.6
pentastearate	—	—	0.2	3.6	13.2	28.8
hexastearate	—	—	—	0.6	4.3	24.6
heptastearate	—	—	—	—	0.8	11.8
octastearate	—	—	—	—	0.1	2.4

Table IV. Contents of Sucrose Monostearate observed and Theoretical Values at Various Molar Ratios

No.	Sucrose / Methyl stearate molar ratio	Sucrose monostearate (%)	
		Found	Calcd.
1	3.13	79.5	81.7
2	2.11	61.6	73.7
3	1.05	58.8	51.5
4	0.54	19.3	22.5
5	0.35	3.9	7.2
6	0.21	—	0.3

In the case of Nos. 2 and 3 in Table IV there were found considerable discrepancies. It seems that these discrepancies are mainly due to the errors of the saponification value. As can be regarded from the equation (1), an error of the saponification value found is enlarged two or three fold when expressed in term of amount of sucrose monostearate.

According to the observations concerning with EP in the previous paper, and concerning with the contents of sucrose monostearate described above, it is concluded that the composition of the product obtained by alcoholysis is governed by the random distribution rule. Thus, as well as EP and sucrose monstearate, the contents of di-, tri- and higher polystearate in the various products are as shown in Table III. It is possible, therefore, to predict the composition of alcoholysis product at an arbitrary molar ratio of sucrose/methyl stearate.

In Osipow's report,[2] the product was consisted of only sucrose distearate, when the molar ratio of sucrose/methyl stearate was 1/2. According to the random distribution rule, however, about 20 % of sucrose monostearate should be obtained, and the experimental results proved this assumption.

Experimental

Samples of Chromatography——Alcoholysis of methyl stearate with sucrose was performed at various molar ratios of the reactants. (sucrose/methyl stearate was 3, 2, 1, 1/2, 1/3, 1/5). The products were extracted with BuOH to remove unreacted sucrose and BuOH extracts were dried by distillation of the solvent. The details of the alcoholysis reaction and the extraction were reported in the previous paper.*[2] These BuOH extracts were applied for the following chromatography.

Liquid Column Chromatography——A column with 1.8 cm. of diameter, 40 cm. length and with a glass filter at the bottom was used. This column was packed with acidified alumina, and an aliquot of the sample solution in benzene-BuOH (9:1 v./v.) was chromatographed. The quantities of the alumina and sample used were shown in Table I.

After development of the sample solution, it was eluted with 150 cc. of benzene-BuOH (9:1 v./v.), and the eluate was collected as the first fraction. The chromatogram was succeedingly eluted with 150~200 cc. of water-satd. BuOH and the eluate obtained thereby was collected as the second fraction.

From each fraction, on removal of the solvent by distillation or evaporation of the solvent, dry product was obtained, which was applied for determination of the saponification value after weighing. These results were also shown in Table I.

Examples of chromatograms were shown in Figs. 1 and 2, which correspond to Nos. 3 and 5 in Table I respectively.

The author expresses his sincerest gratitude to Prof. Dr. T. Ukita, University of Tokyo, and to Prof. Dr. T. Kwan, University of Tokyo, for their kind guidance. The author is deeply grateful to Mr. T. Shoji, the President of this Company, to Mr. J. Huruyama, the executive managing Director of this Company, and to Dr. H. Murata, the Director of this Laboratory, for their guidance and encouragement throughout the course of the present work and for giving permission for publication of this work.

2) L. Osipow, *et al.*: Ind. Eng. Chem. 48, 1459 (1956).

Summary

Mixed sucrose stearates extracted from alcoholyses products at various molar ratios of sucrose/methyl stearate were separated by liquid column chromatography, and the contents of sucrose monostearate were determined. According to the comparison of the observed values with the theoretical ones, it was concluded that the composition of the alcoholysis product is governed by the random distribution rule, and it can be predicted by calculation with this rule. The compositions of various products were shown.

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87. **Kazuya Kunugi**: Studies on the Syntheses of Sucrose Fatty Acid Esters. III. Re-esterification of Sucrose Monostearate.

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In the previous paper of this series,[*2] the author reported that the composition of the alcoholyses products of fatty acid esters with sucrose were governed by the random distribution rule. The above conclusion was obtained from comparison of the observed contents of free sucrose and sucrose mono-stearate in the alcoholysis product with the theoretical values calculated by the random distribution rule.

In the present work, the author attempted to investigate this rule concerning with re-esterification of a sucrose stearate. The random distribution rule was proposed by Bailey[1] in order to calculate the composition of a re-esterified fat, assuming that the acyl radicals would migrate and distribute randomly on glycerol molecules in the presence of catalyst. According to this assumption, it is regarded that, in the case of sucrose stearate, the composition of inter molecular-esterification products depends upon the molar ratio of sucrose/stearoyl radical, and is independent on the structures of the ingredients used.

Osipow, *et al.*,[2] had suggested that re-esterification of sucrose polyester with addition of excess sucrose would produce sucrose monoester, and this suggestion had been confirmed in this laboratory.

On the contrary, by re-esterification of sucrose partially substituted stearate, sucrose and higher polystearate can be obtained in consequence of random distribution. In this work, this possibility was investigated in the case of re-esterification of sucrose monostearate.

Since sucrose monostearate can be obtained more easily than other various stearates by recrystallization of the alcoholysis product obtained from the reaction mixture of excess sucrose and methyl stearates, it was chosen as a typical compound of partially substituted stearates.

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*2 Part II : This Bulletin, **11**, 482 (1963).

1) A. E. Bailey : "Industrial oil and fat products." 834, Interscience Publishers INC., New York (1951).

2) L. Osipow, *et al.* : Ind. Eng. Chem., **48**, 1459 (1956).