becam brown. 3% H_2O_2 (10 cc.) was successively added three times and 30% H_2O_2 (2 cc.) ten times at the interval of 30 min. and then 30% H_2O_2 (6 cc.) two times at the interval of 1 hr. After acidification with dil. HCl and salting out with NaCl, the reaction mixture was extracted with Et_2O. After drying with anhyd. Na_2SO_4, the ethereal solution was distilled off to give colorless crystals, which were recrystallized from water to m.p. 217°, $C_9H_{11}O_5N$ (Ⅷ). Yield 50 mg. It was proved to be identical with 4-carboxy-α,α,3-trimethyl-5-isoxazoleacetic acid by mixed fusion and by comparison of IR spectra. *Anal.* Calcd. for $C_9H_{11}O_5N$: C, 50.70, H, 5.20. Found: C, 50.52, H, 5.18.

The authors wish to express their deep gratitude to Dr. Y. Asahina, Emeritus Professor of University of Tokyo, for his encouragement throughout the course of this study and Dr. S. Shibata, Professor of University of Tokyo, for the gift of usnic acid. The authors wish to thank Dr. M. Takeuchi and Japan Electron Optics Laboratory Co. Ltd. and Dr. S. Matsuoka of this University, for discussing and measurement of NMR spectra. Thanks are due to Mr. Y. Itatani, this Faculty, for elemental analysis.

Summary

The structure of isoanhydromethyldihydrousnic acid, one of the products by the acetylation of methyldihydrousnic acid has been shown as being (Ⅱa). The reaction mechanism of the dehydration reaction has been discussed to show that it involes the fission and reformation of -C-O-C- linkage in the furan nucleus and successive Dienone-Phenol rearrangement. The difference in the mode of reaction at the intermediate dehydration process would result anhydromethyldihydrousnic acid (Ia) or iso-anhydromethyldihydrousnic acid (Ⅱa).

(Received August 10, 1962)

UDC 547.458.2'29

85. **Kazuya Kunugi**: Studies on the Syntheses of Sucrose Fatty Acid Esters. I. Contents of Ester Parts in the Products of Alcoholyses.

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Since Osipow, *et al.*,[1] have developed the syntheses of sucrose fatty acid esters, interests about these compounds have increased in their application to food-additives and emulsifiers.

In order to synthesize the sucrose stearate, for example, Osipow, *et al.*, applied the alcoholysis reaction of methyl stearate by sucrose. These were reacted in the solvent of dimethyl formamide (DMF) with a catalyst K_2CO_3, the reaction mixture being boiled and the volatile methyl alcohol, which was produced during reaction, being stripped off through a fractionating column.

In the industrial manufacturing, the composition of the product of the alcoholysis under various conditions, especially under various molar ratios of sucrose/methyl stearate is an important problem. As for the composition of the product of the reaction, almost no report in the literature is available except the one mentioned above.

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1) L. Osipow, *et al.*: Ind. Eng. Chem., **48**, 1459 (1956); J. Am. Oil Chem. Soc., **34**, 185 (1957).

The report of Osipow, *et al.*, however, involves only two cases of the molar ratios of sucrose/methyl stearate 3, 1/2 and as will be described in the following paper of this series, their communication contains certain problems for further research.

In the present series of work, the author attempted to investigate the composition of the product and to find out the rule governing the alcoholysis reaction.

Bailey[2] has proposed a random distribution in the calculation of the composition of re-esterified fats or partially acylated glycerides produced by alcoholysis reaction. According to Bailey, the calculation of the amounts in percentages of mono-, di-, and triglycerides and of free glycerol in a reaction mixture of fat and glycerol are achieved by probability considerations. In alcoholysis of methyl stearate by sucrose, the similar considerations could also be capable to calculate the composition of the reaction product.

In the present work, several investigations on alcoholyses at various molar ratios of sucrose/methyl stearate were carried out. In each condition, the products were consisted of unreacted sucrose, sucrose monostearate, distearate and higher polystearates, and small amounts of free stearic acid formed in neutralization step of the reaction mixture.*[2]

The resultant mixture of the alcoholysis was dissolved in aqueous solution of sodium chloride and extracted with butyl alcohol. Afer removal of solvent from the extract (BuOH extract), the residue obtained was consisted of Ester Part (EP) and free stearic acid, while unreacted sucrose was found remained in aqueous layer. Thus, the content of EP was determined readily by measurement of the acid value, i.e., of the content of free stearic acid in BuOH extract. In order to compare the experimental results with theoretical values, according to the random distribution rule, E in the following equation was taken as the content of EP, because the content of free acid is not considered in the random distribution rule :

$$E=\frac{\beta}{\alpha+\beta}=\frac{\sigma-\gamma}{100-\gamma} \qquad (1)$$

where α and β are percentages in weight of unreacted sucrose and EP respectively, σ is the percentage in weight of the product in BuOH extract, and γ is that of free stearic acid. Experimental results are shown in Table I.

On the other hand, according to the random distribution rule, each component of the alcoholysis product is calculated by the following equation :

$$(H+S)^8=H^8+8H^7S+28H^6S^2+56H^5S^3+70H^4S^4 +56H^3S^5+28H^2S^6+8HS^7+S^8 \qquad (2)$$

where, H and S are mole fractions of unreacted hydroxyl radical and of reacted one respectively. In this equation, H^8, for example, represents mole fraction of unreacted sucrose in the product, $28H^6S^2$ represents mole fraction of sucrose distearate, and $56H^3S^5$ of sucrose pentastearate, etc. Therefore, mole fraction of EP is calculated as $(1-H^8)$, and thus, its percentage in weight is also calculated readily. The pathway of calculation of H and S in equation (2) will be shown later.

Experimental results and calculated ones of EP in various reactions are given in Table III. Both results were found in good consistency, and so it was concluded that the random distribution rule seemed to govern the compositions of the products in these reactions. Now, it is possible to predict the composition of alcoholysis product at an arbitrary molar ratio of sucrose/methyl stearate.

*[2] The amounts of unreacted methyl stearate were negligible, as shown in Table II.

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

Table I. Experimental Results of σ and γ, and E calculated from Equation [1]

Reaction No.	σ Dry product of BuOH extract (%)	γ Free stearic acid (%)	E Ep (%)
1	43.5	0.92	43.0
2	55.3	1.56	54.6
3	79.5	2.14	79.1
4	94.2	5.71	93.9
5	94.1	4.20	93.8
6	100.0	3.31	100.0

Table II. Unreacted Methyl Stearates in Products of Various Reactions

Reaction No.	1	2	3	4	5	6
Unreacted methyl stearate (%)	1.0	0.03	0.05	0.01	0.27	0.60

Table III. Experimental and calculated Results of EP in Various Reactions

Reaction No.	Sucrose / Methyl stearate molar ratio		EP (%)	
	$n^{a)}$	$m^{b)}$	Found	Calcd
1	3	3.13	43.0	42.2
2	2	2.11	54.6	55.2
3	1	1.05	79.1	79.2
4	0.5	0.54	93.9	95.0
5	0.33	0.35	93.8	99.1
6	0.2	0.21	100.0	100.0

a) cf. equation (3) *b*) cf. equation (4), (6)

Table IV. Experimental Results in the Case of Using Excess Methyl Stearates over Sucrose

Methyl stearate used, mole/mole of sucrose	Catalyst	Period of reaction (hr.)	Degree of esterification (mole/mole)
8	K_2CO_3	18	5.9
8	〃	12	5.2
8	〃	12	5.3
11	〃	15	4.7
11	CH_3ONa	8	3.9
11	TBAC[a)]	10	4.8

a) Trimethyl benzyl ammonium carbonate

Table V. Reactants used and Period, in each Reaction

Reaction No.	Sucrose (g.)	Sucrose (mole)	Methyl stearate (g.)	Methyl stearate (mole)	DMF (cc.)	K_2CO_3 (g.)	Period of reaction (hr.)
1	308	0.9	90	0.3	1190	4.5	5
2	206	0.6	90	0.3	890	6.0	5
3	171	0.5	149	0.5	960	6.0	6
4	68	0.2	119	0.4	560	6.0	9
5	51	0.15	134	0.45	560	6.0	9
6	34	0.1	149	0.5	600	6.0	9

In the above discussion, it was assumed that sucrose should have eight reactive hydroxyl groups in a molecule. However, as shown in Table IV, the maximum average degree of esterification obtained was 5~6 ester groups per sucrose molecule, when excess (eight or more moles) of methyl stearate was used per mole of sucrose. Recently, Bobalek, *et al.*,[3] also observed similar behavior on the synthesis of sucrose polylinseedate.

3) E.G. Bobalek, *et al.*: Official Digest, 453 (1961).

It is expected that more additional investigations concerning with sucrose polyesters will make clear the reason why the maximum average degree of esterification is not eight.

Method of calculation——In order to calculate mole fractions H and S in equation (2), the following relations must be considered at first.

$$n=\frac{A}{B+C} \quad (3), \qquad m=\frac{A}{B} \quad (4)$$

A is quantity of sucrose used (moles)
B is quantity of reacted methyl stearate (moles)
C is quantity of methyl stearate converted to stearic acid (moles)
n is molar ratio of sucrose/methyl stearate used
m is molar ratio of sucrose/reacted methyl stearate

And,

$$x=\frac{M_sC}{M_hA+(M_s-18)B+M_sC}\times 100 \quad (5)$$

where; x is percentage of free stearic acid in the dry product, M_h is molecular weight of sucrose, M_s is molecular weight of stearic acid.

Therefore, the following equation is derived from (3), (4), and (5),

$$m=\frac{\left(M_s-18\times\frac{x}{100}\right)n}{M_s-(nM_h+M_s)\times\frac{x}{100}} \quad (6)$$

Various values of m were shown in Table III.

Then, H and S are calculated from the following equations (7) and (8).

Since reacted hyroxyl group corresponds to esterified methyl stearate,

$$S=\frac{B}{8A}$$

therefore, from equation (4),

$$S=\frac{1}{8m} \quad (7), \qquad \text{and} \qquad H=1-S \quad (8)$$

Experimental

Methyl Stearate——The mixture of 100 g. stearic acid, 100 g. of conc. H_2SO_4 and 400 g. of MeOH was boiled with stirring and refluxing over a period of 3 hr. From the cooled reaction mixture which separated into two layers, the upper layer was taken and washed with water repeatedly. After removal of free acid with NaOH, the raw methyl stearate was purified by distillation under reduced pressure. (b.p_4 177~179°). *Anal.* the following;

	Found	Calcd.
Acid value of stearic acid	195.8	197.2
Saponification value of methyl stearate	188.0	188.0

Alcoholysis——The amounts of sucrose, methyl stearate, solvent DMF, and catalyst K_2CO_3 used in each reaction were given in Table V. A reaction mixture consisted of the four components was boiled under 90±5 mm. of mercury pressure, and MeOH formed during reaction was stripped from the system through a fractionating column. The period of each reaction was also given in Table V.

Reactions shown in Table IV were carried out analogously.

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]

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 guidances. 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 guidances and encouragements throughout the course of the present work and for giving permission for Publication of this work.

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.

(Received August 21, 1962)

UDC 547.458.2'29

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.

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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.