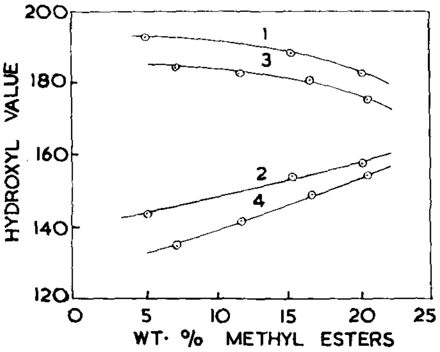

FIG. 4. Change of hydroxyl value for castor oil methyl esters, nitromethane-hexane system.
1. Esters from nitromethane phase at 59.6% nitromethane
2. Esters from hexane phase at 59.6% nitromethane
3. Esters from nitromethane phase at 15% hexane
4. Esters from hexane phase at 15% hexane

esters at a constant concentration of polar or nonpolar solvent was also determined. Figure 3 shows the effect on hydroxyl values of esters fractionated at 25% furfural and 35% hexane for the system, methyl esters-furfural-hexane. Figure 4 shows a similar effect for the system, nitromethane-methyl esters-hexane, at 59–60% nitromethane and 15% of hexane. It is observed that the hydroxyl values of esters from the polar solvent phase decrease with a higher concentration of esters. It may also be seen that the increase of hydroxyl values of esters in the polar solvent is accompanied by a decrease in the hydroxyl values of the esters obtained from the nonpolar solvent phase.

Conclusion

The phase equilibrium data are presented for methyl esters-furfural-hexane and methyl esters-nitromethane-hexane at 30°C.

The hydroxyl values of ester samples obtained from the furfural and nitromethane phases indicate that furfural and nitromethane can be used as solvents for fractionating hydroxy esters from the mixed esters obtained by the methanolysis of castor oil.

Acknowledgment

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Synthesis of Polyoxyethylene Derivatives of Diesters of Sucrose with Long-Chain Fatty Acids

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A NUMBER of publications concerning the long-chain fatty acid monoesters of sucrose have appeared since the synthesis of the sucrose monoesters was first reported in 1956 by Osipow and co-workers (1). The method of preparation (2,3,4), properties (5,6,7), and uses (8,9) have been investigated in detail.

Sucrose monoesters are said to be inexpensive as compared with other nonionic surfactants and have many desirable properties as solubilizing (8) or emulsifying agents for food or cosmetics. However, in the manufacture of sucrose monoesters, sucrose diesters are inevitable by-products responsible for a lowered surface-activity because of the poor solubility of the diesters in water. For certain purposes the sucrose monoesters can be separated and purified by recrystallizing the mixture from acetone or ethanol (1,6,10), but this method is difficult and costly, and from an industrial standpoint it is more desirable to use the mixture of mono- and diesters without further refining.

Although sucrose diesters can be simply prepared by alcoholysis by using a 2:1 molar ratio of the methyl ester to sucrose (11), sucrose diesters of acids of chain length greater than myristic acid are practically insoluble in water, and their use as emulsifying agents is limited to the formation of water in oil emulsions.

Accordingly since it is important to find new uses for sucrose esters, we have attempted to increase the solubility in water of palmitic and stearic acid esters by reaction with ethylene oxide in order to make use of them as solubilizing or emulsifying agents. Sucrose esters resemble sorbitan monoesters in properties, and it can be expected that solubilizing properties similar to those of the "Tweens" (12,13) could be obtained by the introduction of polyoxyethylene radicals.

The reaction of sucrose with ethylene oxide has been reported by DeGroote (14,15,16), by the use of xylene as the solvent, and by sodium methylate as the catalyst in an autoclave at 150–170°.

In the present research sucrose diesters were chosen as the starting materials. Pure sucrose dimyristate, dipalmitate, distearate, dioleate, and dierucate were prepared by interesterification between sucrose and the methyl esters, using formylmorpholine as the solvent, and the properties of the diesters were studied. The diesters were then caused to react with ethylene oxide in an autoclave, with an alkaline catalyst such as sodium hydroxide, potassium hydroxide, or tertiary amines (17).

The polyoxyethylene derivatives of diesters of sucrose with long-chain fatty acids were found to be oily or waxy products soluble in water; the surface activities of the aqueous solutions were very similar to those of the "Tweens."

Since the toxicity of the products to mice was quite low and the production cost may be expected to be small in comparison to the Tweens because the hydrogenation step is omitted, the polyoxyethylene derivatives of sucrose esters can be expected to be useful in the food and cosmetic industries.

Sucrose Diesters

The methyl esters of myristic, palmitic, stearic, and oleic acids were prepared by esterification with methanol at the reflux temperature, in the presence of toluenesulfonic acid, and refined by vacuum distillation. Methyl erucate was prepared by the methanolysis of rapeseed oil. Properties of the esters are shown in Table I.

TABLE I
Properties of Methyl Esters

Ester	B.P./mm.	M.P.	Saponification value	Iodine value
Methyl laurate	122–4°/7	4.5°	259.5	......
Methyl myristate	134°/3	18.5–20°	226.1	......
Methyl palmitate	168–9°/5	29.0–30.5°	208.1	......
Methyl stearate	132–3°/1	38.9–40.3°	187.9	......
Methyl oleate	149–51°/3	......	189.0	88.2
Methyl erucate	187–90°/0.1	......	160.7	72.1

Formylmorpholine was prepared by the direct reaction of morpholine with formic acid in aqueous solution, refined by distillation, and found to have a pH of 6.5 and b.p. 84.5–86° at 2 mm.

Sucrose was crushed in a ball mill and dehydrated by refluxing with benzene.

Reaction Rate. We have shown previously (2), in the preparation of sucrose monoesters with a large ratio of sucrose to the methyl ester, that the methyl ester is consumed within 2 hrs. at 100° and 35 mm. A slower reaction is to be expected in the preparation of sucrose diesters with a mole ratio of methyl ester to sucrose of 1:1 or greater. Methyl laurate was caused to react with sucrose in formylmorpholine at 100° and 30 mm., with potassium carbonate as catalyst. At definite time-intervals the weight of methyl laurate remaining unreacted was estimated by a method previously described (2). As can be seen from Figure 1, the reaction should be continued for more than 5 hrs. to obtain pure sucrose diesters.

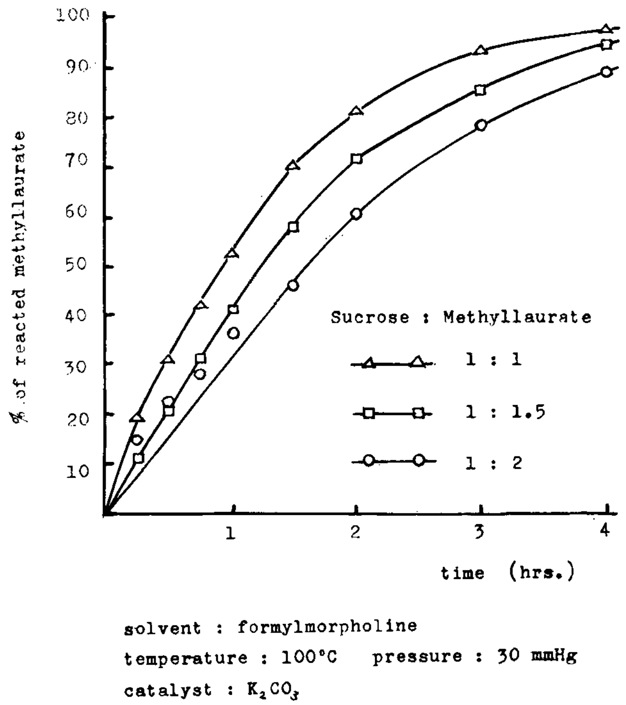

FIG. 1. Reaction rate of interesterification of sucrose with methyl laurate.

Synthesis and Purification. Methyl myristate, palmitate, stearate, oleate, and erucate were converted to the corresponding sucrose diesters by alcoholysis with sucrose at 100° and a reduced pressure of 30 mm. In all cases the mole ratio of methyl ester to sucrose was 2:1; the solvent was formylmorpholine and the catalyst, potassium carbonate.

The reaction conditions and products are shown in Table II and the method of purification in Figure 2. The reaction tube containing methyl ester, sucrose, and formylmorpholine was heated to 100° with agitation under a reduced pressure of 30 mm. until the sucrose was entirely in solution. The indicated amount of potassium carbonate was added, and the reaction was continued for 2, 3.5, or 6 hrs. at constant temperature and pressure.

At the end of the reaction time the solution was neutralized and filtered; the solvent was removed by distillation at 1 mm. Extraction with n-hexane has no

TABLE II
Synthesis of Sucrose Diesters
(Temperature 100°, Reduced Pressure 30 mm., Mole Ratio Methyl Ester/Sucrose 2:1)

Sucrose diester	Products								
	Reaction conditions	Unreacted sucrose. g.	Unreacted methyl ester, g.	Acetone extract [e]			Butanol extract [f]		
				Weight, g.	Yield, %	Sapon. value	Weight, g.	Yield, %	Sapon. value
Dimyristate	a	9.8	15.5	26.2	49.0	150.7	....	....	....
Dipalmitate	b	7.2	13.5	28.3	56.0	128.0	1.2	2.2	73.3
Distearate	b	6.0	10.7	35.0	66.6	129.3	2.6	4.8	100.8
Dioleate	b	6.0	11.0	34.5	66.1	139.1	....	....	....
Dipalmitate	c	1.7	2.9	18.2	74.4	138.7	0.3	1.2	94.5
Distearate	c	1.0	2.5	19.3	80.4	129.6	1.2	5.0	77.6
Dioleate	c	2.5	4.1	18.6	71.5	133.9	....	....	....
Dierucate	c	2.8	4.0	20.7	70.2	117.1	....	....	....
Dimyristate	d	0.6	2.5	41.0	89.5	143.9	1.2	2.6	100.9
Dipalmitate	d	0.4	2.0	45.5	92.5	135.3	1.2	2.4	90.3
Distearate	d	1.0	2.8	46.4	88.6	127.1	0.7	1.3	86.5
Dioleate	d	8.7	2.2	48.3	94.6	131.4	0.5	1.0	78.9
Dierucate	d	0.7	3.0	52.0	88.6	111.2	....	....	....

a = Time 2 hrs., mole ratio 0.14/0.07, 150 g. formylmorpholine, 0.5 g. K_2CO_3.
b = Time 2 hrs., mole ratio 0.12/0.06, 170 g. formylmorpholine, 0.5 g. K_2CO_3.
c = Time 3.5 hrs., mole ratio 0.06/0.03, 100 g. formylmorpholine, 0.2 g. K_2CO_3.
d = Time 6.0 hrs., mole ratio 0.12/0.06, 170 g. formylmorpholine, 0.7 g. K_2CO_3.

[e] Mainly sucrose diester, see II of Figure 2.

[f] Mainly sucrose monoester, see IV of Figure 2.

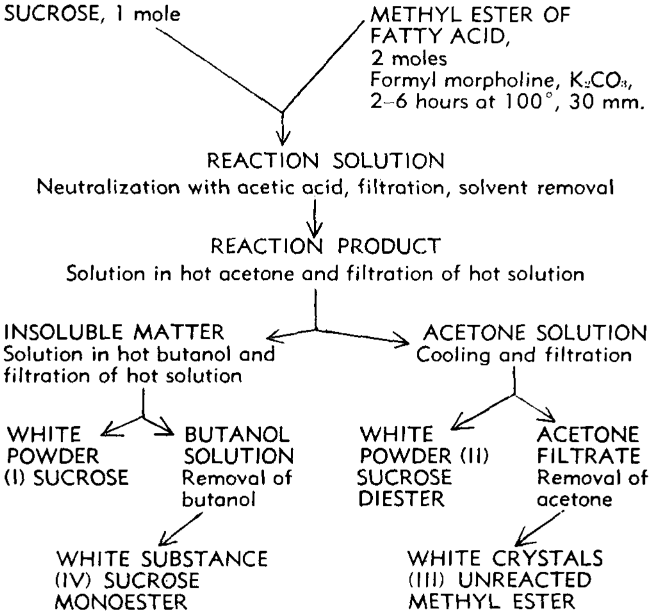

FIG. 2. General procedure for synthesizing and refining sucrose diester.

advantage at this point because the sucrose diester would be extracted along with unreacted methyl ester. Accordingly the reaction product, from methyl palmitate, for example, contains at this point sucrose dipalmitate, sucrose monopalmitate, unreacted sucrose, methyl palmitate, and potassium palmitate. The solid residue was crushed and treated with twenty times the volume of hot acetone; the insoluble material was separated by hot filtration. Extraction of the acetone-insoluble material with butanol gave products considered to be sucrose (I) and sucrose monoester (IV) (Figure 2). The acetone solution was concentrated to one-half the volume, cooled and filtered, and the evaporated acetone filtrate gave products considered to be sucrose diester (II) and unreacted methyl ester (III).

The saponification value of the white powder crystallized from the acetone extract (Table II) was generally in fair agreement with the calculated value for the diester (theoretical values 147.1, 137.0, 128.2, 128.8, and 114.1 for the dimyristate, dipalmitate, distearate, dioleate, and dierucate, respectively), but as the products appeared to contain impurities, they were refined by repeated crystallization from acetone. The sucrose diesters of the saturated acids were white powders, but those of the unsaturated acids were resinous solids. The properties of the purified diesters are recorded in Table III.

TABLE III

Properties of Sucrose Diesters[a]

Sucrose diester	Saponification value	Specific rotation $[\alpha]^{20/D}$	Softening point	Properties
Dimyristate	144.1 (147.0)	+31.23[b]	73–5°	white, odorless, tasteless solid, slightly soluble in water
Dipalmitate	138.5 (137.0)	+29.16[b]	69–71°	white, odorless, tasteless solid, hardly soluble in water
Distearate	129.6 (128.1)	+25.29[b] (+16.8)	64– 7° (55– 8°)	white, odorless, tasteless solid, hardly soluble in water
Dioleate	133.9 (128.8)	+27.12[c] (+16.4)	65–70° (108–12°)	yellow resinous solid, odorless and tasteless insoluble in cold water
Dierucate	117.1 (114.1)	+29.79[c]	63–72°	yellow resinous solid, odorless and tasteless, insoluble in water

[a] Values in parentheses are theoretical or literature values.
[b] Measured in chloroform solution.
[c] Measured in ethanol solution.

Polyoxyethylene Derivatives of Sucrose Diesters

Synthesis. A small autoclave was charged with the sucrose diester, an excess of ethylene oxide, and a catalyst and was heated slowly with shaking, after the method of polyoxyethylene derivatives of sorbitan monoesters. The reaction was also found to proceed in the presence of solvents by first dissolving the ethylene oxide in an organic solvent such as benzene, toluene, xylene, dimethylformamide, or formylmorpholine; most of the experiments of Table IV were carried out in this manner. The catalysts were potassium hydroxide, sodium hydroxide, sodium methylate, also such tertiary amines as methylmorpholine and dimethylbenzylamine, the catalytic activity of which in the reaction of ethylene oxide with hydroxy compounds has been previously reported by Komori (17).

TABLE IV

Synthesis of Polyoxyethylene Derivatives of Sucrose Diesters

Sucrose diester	Reaction conditions							
	Ratio C_2H_4O/diester, g.	Solvent,[a] g.	Catalyst,[a] g.	Temperature	Gauge pressure, kg./cm.^{2}	Saponification value	C_2H_4O[b] groups/mole	Properties
Dimyristate	18:5	none	.03 KOH	125–41°	27.0–8	35.2	60	light yellow liquid
Dimyristate	10:3	none	.05 MM	103–16°	14.8–6	55.9	30	yellow liquid
Dipalmitate	20:2	20 FM	.10 NaOH	124–31°	15.6–6	21.2	100	yellow wax
Dipalmitate	10:3	none	.05 MM	115–26°	19.0–4	37.6	50	orange wax $[\alpha]^{20/D}$ + 4.58
Dipalmitate	9:3	none	.05 DBA	110–23°	14.9–5.2	44.0	40	orange wax
Dipalmitate	10:2	20 FM	.05 KOH	123–7°	9.5–4.3	51.3	30	orange wax
Dipalmitate	10:5	15 Tol.	.05 KOH	124–120°	9.7–3	58.5	25	yellow wax, aq. soln. not clear
Distearate	21:3	19 DMF	.03 KOH	135–160°	22.0–8	27.2	75	light brown wax
Distearate	10:3	20 FM	.20 KOH	117–34°	9.7–3.5	30.7	65	orange wax$[\alpha]^{20/D}$ + 3.82
Distearate	9:4	20 FM	.10 NaOMe	125–32°	12.5–6.2	47.4	35	orange wax
Dioleate	20:3.3	15 DMF	.03 KOH	122–7°	14.5–4.2	20.0	105	orange wax
Dioleate	19:3	20 Benz.	.05 NaOH	132–5°	11.1–6.7	23.9	85	light yellow wax $[\alpha]^{20/D}$+5.87
Dioleate	14:4	20 FM	.10 KOH	122–38°	11.0–4.9	37.0	50	yellow liquid
Dioleate	18:5	25 FM	.05 NaOH	128–33°	16.1–12	50.0	30	orange liquid
Dioleate	10:4	20 FM	.05 NaOH	122–33°	11.1–8	57.9	25	orange liquid
Dierucate	18:2	15 Tol.	.05 KOH	130–4°	16.0–4.5	11.9	190	yellow wax $[\alpha]^{20/D}$ + 2.15
Dierucate	19:3	15 FM	.05 KOH	137–67°	21.0–7	20.0	105	brown wax
Dierucate	13:5	15 Benz.	.05 KOH	127–9°	13.7–6	35.0	50	yellow liquid

[a] Abbreviations: Benz. = benzene, DBA = dimethylbenzylamine, DMF = dimethylforamide, FM = formylmorpholine, MM = methylmorpholine, Tol. = toluene.
[b] Number of C_2H_4O groups/mole, a rounded-off average number based on saponification value.

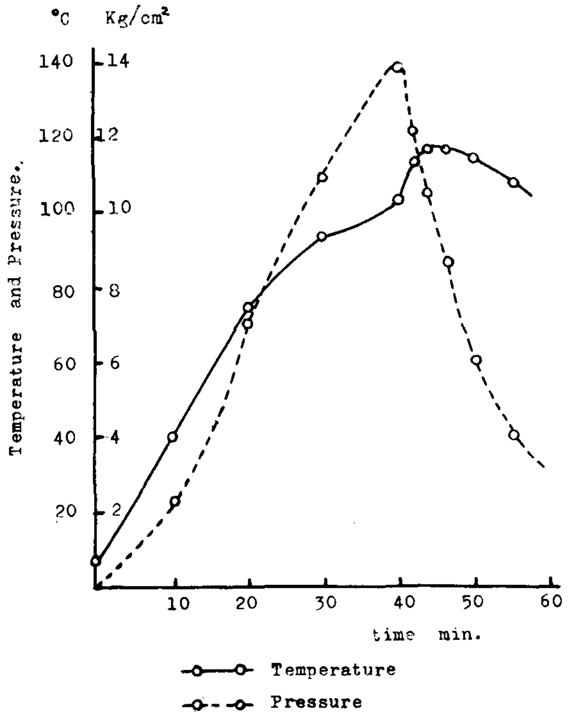

FIG. 3. Changes in temperature and pressure during the reaction of sucrosediester and ethylene oxide, sucrosedimyristate; 3.0 g.: ethylene oxide; 10 g.: catalyst; methylmorpholine 0.05 g., without solvent.

The reaction usually began between 100–120°, and the pressure decreased rapidly as the reaction proceeded. Changes in temperature and pressure during the reaction are shown in Figures 3 and 4.

On completion of the reaction the solution was filtered and neutralized with acetic acid; the solvent was removed under reduced pressure. In the absence of solvent the product, generally a viscous liquid, was dissolved in acetone or ethanol and neutralized, and the solvent was removed.

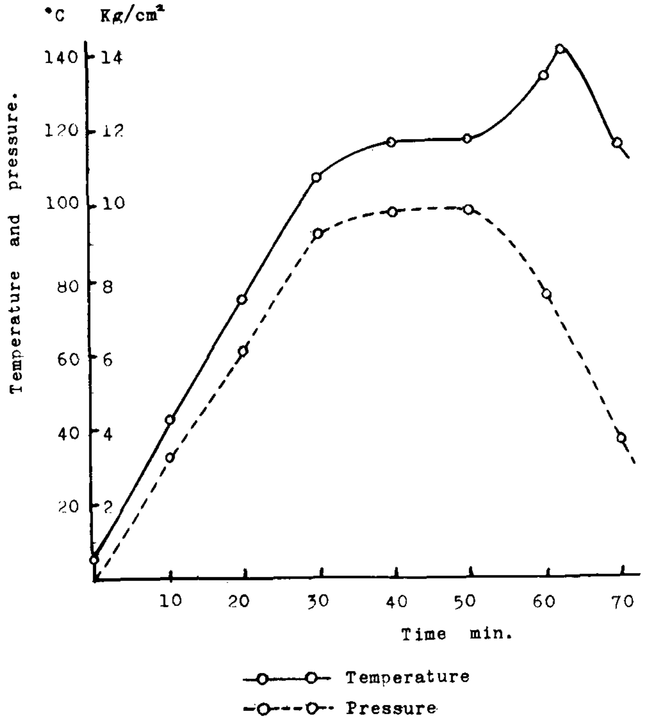

FIG. 4. Changes in temperature and pressure during the reaction of sucrose diester and ethylene oxide; sucrose distearate 3.0 g.; ethylene oxide 10 g.; catalyst KOH; solvent; formylmorpholine 20 g.

The products of Table IV were analyzed by determination of the saponification value from which n, the average number of oxyethyl groups per mole, was calculated. Estimation of the number of oxyethyl groups by increase in weight is less accurate in this case. The HLB or hydrophile-lipophile balance, calculated from the expression HLB = 20(1-S/A), where S is the saponification value of the product and A the acid value of the fatty acid, ranged from 14.2 (polyoxyethylated sucrose dioleate, n = 25) to 18.6 (polyoxyethylated sucrose dierucate, n = 190).

Properties. The polyoxyethylene derivatives of sucrose diesters were generally yellow or orange oils or waxes with a somewhat bitter taste, with melting points in the range of 10–40°, soluble in water to give clear solutions except at values of n of about 25 or less.

The surface tension of aqueous solutions and the interfacial tension of aqueous solutions against kerosene were measured by the duNoüy tensiometer at 25° and are shown in Figures 5 and 6. Aqueous solutions lowered surface tension to about the same extent as a polyoxyethylene derivative of sorbitan mono-oleate (Tween 80).

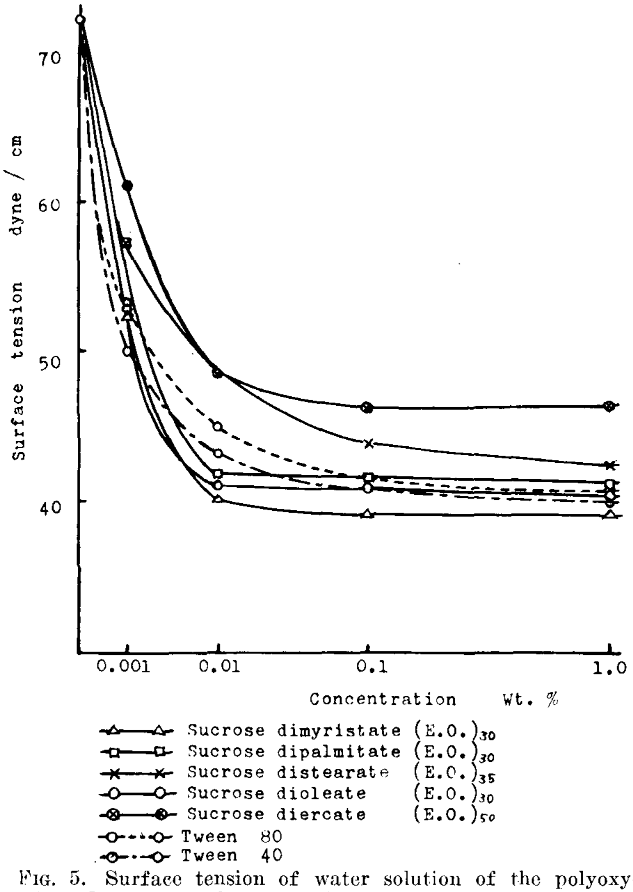

FIG. 5. Surface tension of water solution of the polyoxyethylene derivatives of sucrose diesters.

Foaming properties of aqueous solutions of the polyoxyethylene derivatives of sucrose diesters, measured by the Ross-Miles method at 25° and 40°, are shown in Table V.

Toxicity. The polyoxyethylene derivatives of sucrose diesters have good surface-active properties and

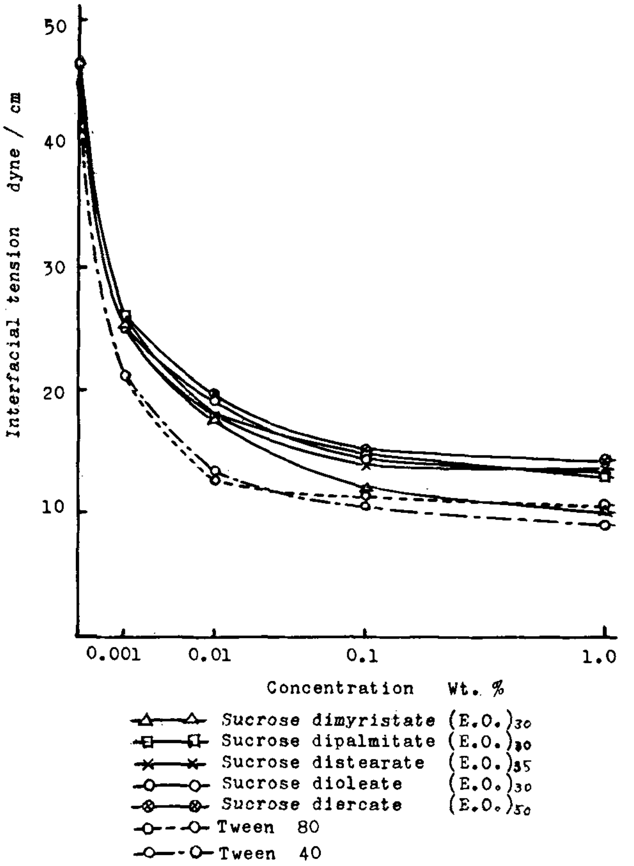

FIG. 6. Interfacial tension of water solution of the polyoxyethylene derivatives of sucrose diesters.

therefore can be used as emulsifying or solubilizing agents. However, for utlization in the food and cosmetic industries, toxicity is a very important problem.

Accordingly the lethal dose (LD_{50}) of the polyoxyethylene derivative of sucrose dioleate to mice, by intravenous injection, was investigated, with the following results:

Polyoxyethylene derivative of	LD_{50}, mg./kg.
sucrose dioleate	7,500
sorbitan monoleate	5,800
sorbitan monolaurate	3,700

From these results the toxicity may be considered quite low and the product suitable for use in the food industries.

Discussion

The alcoholysis of methyl esters by sucrose proceeded slowly at 2:1 molar ratio of methyl esters to sucrose, as shown in Figure 1. Experiments on the effect of reaction time showed that the yield of diesters increased from 50–60% at 2 hrs. to about 90% at 6 hrs. without the occurrence of undesirable side reactions and with good agreement between the reaction rate of the methyl esters and the yield of sucrose esters. Sucrose diesters were synthesized in good yield by heating 2 moles of methyl ester and 1 mole of sucrose for 6 hrs. at 100° at 30 mm., in the presence of potassium carbonate (Table II).

The reaction products appeared to be chiefly diesters, the yield of monoester did not exceed 5%, refining was rather simple, and pure sucrose diesters could be readily obtained. However, when unsaturated methyl esters were employed and unreacted methyl esters remained, crystallization of the product from acetone was quite difficult. In such a case the acetone solution was cooled to −10°, and a highly viscous liquid assumed to be diester was separated from the solution.

TABLE V

Foaming Properties of Polyoxyethylene Derivatives of Sucrose Diesters, % Concentratiion

Sucrose diester	Oxyethyl groups per mole	Foam height, mm.			
		25°		40°	
		Initial	At 30 min.	Initial	At 30 min.
Dimyristate	60	51	39	50	19
Dimyristate	30	38	26	36	15
Dipalmitate	100	39	23	45	28
Dipalmitate	30	26	15	46	32
Distearate	80	32	16	34	6
Distearate	35	15	10	25	13
Dioleate	85	36	24	45	7
Dioleate	25	40	24	50	19
Dierucate	105	24	16	28	10
Dierucate	50	27	22	33	20

The specific rotation of the sucrose diesters estimated in ethanol or chloroform solution gave higher values than those reported by Osipow (1) and Mihara (11).

The use of such solvents as formylmorpholine or dimethylformamide in the reaction of sucrose diesters with ethylene oxide would have industrial importance because the sucrose diesters could then be used immediately after the alcoholysis reaction, and the time and trouble required to refine the diesters would be prevented. However the reaction proceeded rather violently when such solvents were employed, and degeneration of the product occurred in consequence of a rapid rise in temperature. It was therefore concluded from the results of Table IV that the reaction should be carried out without solvent in the usual method. The tertiary amines were found to be excellent catalysts because the reaction began at a low temperature and proceeded moderately.

The polyoxyethylene derivatives of sucrose diesters were investigated by determination of the weight increase, the specific rotation, and the saponification value. However, as the products were expected to include polyethylene glycol and the like and as they are themselves mixtures of products having various molecular weights, the analysis was rather difficult and entirely satisfactory results could not be obtained. Accordingly the average number of moles of ethylene oxide condensed in the reaction product was calculated roughly from the saponification value as shown in Table IV.

As the surface-active properties of aqueous solutions of the polyoxyethylene derivatives were found to equal the "Tweens" from the results of Figures 5 and 6 and Table V, and moreover as they can be said to be almost nontoxic when taken by mouth, their use in food, for example, as a solubilizer of oil-soluble vitamins in water will undoubtedly be expected in the future.

Summary

Since the long-chain fatty acid sucrose diesters inevitably produced in the synthesis of monoesters are only slightly soluble in water, no important use can be found for them at the present time except as oil-soluble emulsifying agents.

In order to exploit new uses we have attempted to improve their solubility in water by introducing oxyethylene radicals into the molecule.

The addition reaction of ethylene oxide with the sucrose diesters was carried out in an autoclave in the presence of alkaline catalysts. With the reaction temperature maintained between 100–130° the pressure decreased as the reaction proceeded, and one to two hours were required to consume the ethylene oxide used.

The addition products are yellow or orange oily materials soluble in water. Aqueous solutions showed good surface-active properties.

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Hydrogenation of Fatty Oils with Palladium Catalysts. V. Products of the Tall Oil Industry

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Conditions were found for reducing tall oil distillate to an iodine number of 22 with a sufficiently small amount of palladium catalyst to make the process commercially feasible. The operating conditions were 200°C. and 2,600 psi.

Tall oil fatty acids were reduced with palladium and the concentration of linoleic acid, *cis*-oleic acid, saturated acid, and *trans* isomers were determined as a function of iodine number. The five-platinum group metals (Pt, Pd, Ir, Rh, Ru) were compared as to activity, selectivity of partial hydrogenation, and tendency to form *trans*-isomers.

HYDROGENATION of tall oil products results in materials with new properties and of increased value and utility. The hydrogenation of good prerefined whole tall oil to 95 to 100 I.V. with nickel or nickel-copper catalysts (1) is fairly easy even at low pressure, although a relatively large amount of catalyst is needed (2). Hydrogenation to a low iodine number is considerably more difficult. Even refined tall oil products still contain catalyst poisons, mostly sulfur compounds of unsaponifiables. Distilled products contain less poisons, but distillation isomerizes the rosin acids to a more difficult form to hydrogenate (3). Various methods for the removal of poisons have been published and patented (4–7). Treatment with spent catalyst before hydrogenation is frequently suggested (8). In the case of rosin acids this procedure removes poisons, but complicates hydrogenation by promoting isomerization to compounds more difficult to reduce.

Commercial hydrogenations of tall oil are done exclusively with nickel. Platinum metals have received so far no attention commercially and only scant mention in the literature. One excellent study of hydrogenation of tall oil rosin acid with catalysts of the platinum metal group has been made (3). One patent has been issued on hydrogenation of rosin with rhodium, ruthenium, and palladium catalysts (9), two other patents mention platinum and palladium catalysts (10) and platinum oxide (11).

Two specific aspects of the tall oil hydrogenation problem are examined in this paper. One is the hydrogenation of a tall oil distillate to a low iodine number, yielding a commercially interesting product, stable to oxidation; the other is the hydrogenation of tall oil fatty acids with the aim of producing the maximum amount of the valuable *cis*-oleic acid in a suitable mixture of other products. This means that reduction should be directed toward removing linoleic acid selectively, and minimizing formation of trans-isomers and saturated acids.

Experimental

Four different hydrogenation units were used in these experiments. At atmospheric pressure and room temperature a one-liter glass flask shaken at 280 strokes per minute was used. At pressure up to about 50 psig. and room or elevated temperature and with a high degree of agitation, a one-gallon stainless steel autoclave with a stirrer, cooling coil, and electrical heater controlled by a thermocouple was employed. High-pressure hydrogenation with a low degree of agitation was done in a Parr shaking bomb of 100-ml. capacity. A higher degree of agitation at high pressure was achieved by use of a 500-ml. Magne Dash autoclave.

The tall oil distillate used in these experiments had the analysis: fatty acids, 53%; rosin acids, 45%; unsaponifiable, 2%; acid number, 187; iodine number, 138. The fatty acids were 42% linoleic acid, 55% oleic acid, 3% saturated acids. Tall oil fatty acids had the analysis: fatty acids, 97%; rosin acids, 1.0%; unsaponifiable, 2%; acid number, 195; iodine number, 130. The composition of the fatty acids was: linoleic acid, 38%; oleic acid, 51%; conjugated dienoid acids, 6%; palmitic acid, 3%; stearic acid, 2%.

Analyses of the products obtained in this work were made according to official methods of the American