

# Hexitol and Sucrose Esters of $\alpha$ -Sulfo Fatty Acids<sup>1</sup>

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## Abstract

Use of the  $\alpha$ -sulfo acid, the acid chloride and the methyl ester was explored in the preparation of mannitol, sorbitol and sucrose esters of  $\alpha$ -sulfopalmitic and  $\alpha$ -sulfostearic acids. The products were difficult to purify because of solubilization of reactants. The  $\alpha$ -sulfo esters are more soluble and more resistant to hydrolysis than hexitol and sucrose palmitates and stearates.

## Introduction

Since the  $\alpha$ -sulfo fatty acids are convenient, versatile intermediates a number of different types of esters have been prepared and examined for surface active properties in relation to structure. These include esters of linear and branched chain primary and secondary alcohols, allyl alcohol, sodium isethionate, benzyl alcohol, phenol and cyclohexanol (3). The present paper is a continuation, with polyhydroxy alcohols, selecting hexitols and sucrose because of availability and their established use as surface active intermediates. Recent articles and reviews have discussed sucrose esters and related nonionic surface active agents and developments in production and utilization (1,2,4,6).

Hexitol monoesters of tallow fatty acids are not water soluble and only the monoester of sucrose is soluble enough to have useful surface active properties. The presence of an  $\alpha$ -sulfo group in the fatty acid chain could in each case make mono-, di- or polyesters more water soluble and considerably more resistant to acid or alkaline hydrolysis. Since all of the esters could be water soluble at least in some degree, separation of the mono- from the di- and polyesters might not be necessary. The presence of an  $\alpha$ -sulfo group may have considerable effect on properties, of course, because it changes the ester from a nonionic to an anionic surface active agent, and the product is like an ether alcohol sulfate in that it may have both anionic and nonionic characteristics.

Three methods were investigated: (a) direct esterification in which the  $\alpha$ -sulfo acid acts as its own esterification catalyst, with azeotropic removal of water; (b) acylation of the hydroxyl group with the acid chloride of the  $\alpha$ -sulfo acid; and (c) alkali-catalyzed alcoholysis of the sodium salt of the methyl ester with the hexitol or sucrose.

## Experimental Procedures

### Direct Esterification: Hexitol Diesters

Direct esterification of sucrose with  $\alpha$ -sulfostearic acid in chloroform, benzene or toluene gave a charred product with no indication of ester formation. This method was successful only with the hexitols and is illustrated in the case of mannitol.

A mixture of 0.15 mole of D-mannitol (reagent grade), 0.06 mole of  $\alpha$ -sulfostearic acid and 200 ml of benzene was refluxed 4 hr with azeotropic removal

TABLE I  
Hexitol and Sucrose Esters of  $\alpha$ -Sulfo Acids

No.	Esters	Esterification method	Elemental analysis, %			
			C	H	Na	S
<b>Monoester</b>						
1	Sorbitol $\alpha$ -sulfopalmitate	Acid chloride	50.54	8.88	4.43	6.31
2	Mannitol $\alpha$ -sulfopalmitate	Alcoholysis	50.38	8.63	4.32	6.14
3	Sorbitol $\alpha$ -sulfopalmitate	Alcoholysis	49.86	8.62	4.69	6.00
4	Mannitol $\alpha$ -sulfostearate	Alcoholysis	51.24	8.77	4.06	5.83
5	Sorbitol $\alpha$ -sulfostearate	Alcoholysis	52.08	8.75	4.28	5.75
6	Sucrose $\alpha$ -sulfopalmitate	Acid chloride	48.65	7.94	3.53	5.00
7	Sucrose $\alpha$ -sulfopalmitate	Alcoholysis	48.53	7.85	3.45	4.69
8	Sucrose $\alpha$ -sulfostearate	Acid chloride	49.65	8.15	3.25	4.47
9	Sucrose $\alpha$ -sulfostearate	Alcoholysis	49.30	7.91	3.59	4.47
<b>Diester</b>						
10	Mannitol $\alpha$ -sulfopalmitate	Direct	53.06	8.28	5.35	7.90
11	Sorbitol $\alpha$ -sulfopalmitate	Direct	53.32	8.21	5.19	7.75
12	Mannitol $\alpha$ -sulfostearate	Direct	54.50	8.47	4.59	6.62
13	Sorbitol $\alpha$ -sulfostearate	Direct	53.98	8.24	4.74	6.96
<b>Theoretical values</b>						
Calculated for hexitol mono $\alpha$ -sulfopalmitate $C_{22}H_{42}NaO_{10}S$			50.56	8.29	4.40	6.14
Calculated for hexitol mono $\alpha$ -sulfostearate $C_{22}H_{42}NaO_{10}S$			52.34	8.60	4.18	5.82
Calculated for sucrose mono $\alpha$ -sulfopalmitate $C_{22}H_{42}NaO_{15}S$			49.25	7.53	3.37	4.47
Calculated for sucrose mono $\alpha$ -sulfostearate $C_{20}H_{38}NaO_{15}S$			50.69	7.80	3.24	4.51
Calculated for hexitol di ( $\alpha$ -sulfopalmitate) $C_{38}H_{72}Na_2O_{14}S_2$			52.63	8.37	5.77	7.40
Calculated for hexitol di ( $\alpha$ -sulfostearate) $C_{42}H_{80}Na_2O_{14}S_2$			54.88	8.77	5.00	6.98
Calculated for sucrose di ( $\alpha$ -sulfopalmitate) $C_{44}H_{80}Na_2O_{19}S_2$			51.65	7.88	4.50	6.27
Calculated for sucrose di ( $\alpha$ -sulfostearate) $C_{48}H_{88}Na_2O_{19}S_2$			53.41	8.22	4.26	5.94

of water. After cooling, 100 ml of 95% ethanol was added and the mixture was neutralized with 18 N NaOH. Unreacted mannitol and disodium  $\alpha$ -sulfostearate were removed by filtration. The filtrate was evaporated and crystallized from absolute ethanol at  $-30^\circ\text{C}$  to give a 60% yield of product with an elemental analysis in agreement with that for a diester. Products prepared in this way are shown in Table I.

### Acid Chloride Method

This method, described previously (3), is applicable to both hexitols and sucrose and is illustrated for sodium sucrose  $\alpha$ -sulfopalmitate.

Sucrose (10-X, 0.25 mole) was dissolved in a mixture of 335 ml of dimethylformamide and 44 ml of pyridine and heated to  $70^\circ\text{C}$ .  $\alpha$ -Sulfopalmitoyl chloride (0.25 mole) dissolved in 500 ml carbon tetrachloride was added dropwise over an hour. After cooling, 50% aqueous ethanol was added followed by neutralization with 18 N NaOH. The monoester, yield 36%, was isolated from the aqueous ethanol phase after systematic extraction with carbon tetrachloride to remove di- and polyesters.

Sucrose  $\alpha$ -sulfostearate and sorbitol  $\alpha$ -sulfopalmitate, essentially monoesters, were prepared in the same way with the elemental analyses shown in Table I.

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TABLE III  
Surface Active Properties

No.	$\alpha$ -Sulfo ester <sup>a</sup>	Esterification method	Solubility <sup>b</sup> 25 C	Ca <sup>++</sup> stability ppm CaCO <sub>3</sub>	Lime soap dispersing power %	Foam height <sup>c</sup> 60 C mm	Detergency <sup>c</sup> 60 C $\Delta R$
1	Sorbitol $\alpha$ -sulfopalmitate	Acid chloride	20%	630	14	170	31
2	Mannitol $\alpha$ -sulfostearate	Alcoholysis	20%	1500	10	170	32
3	Sorbitol $\alpha$ -sulfostearate	Alcoholysis	20%	650	14	180	31
4	Mannitol $\alpha$ -sulfostearate	Direct	20%	>1800	10	120	27
5	Sorbitol $\alpha$ -sulfostearate	Direct	20%	>>1800	10	170	27
6	Sucrose $\alpha$ -sulfopalmitate	Acid chloride	20%	>>1800	9	160	28
7	Sucrose $\alpha$ -sulfostearate	Alcoholysis	20%	>>1800	10	180	31
	Sodium methyl $\alpha$ -sulfostearate		0.2%	>1800	9	180	35
	Sucrose monopalmitate <sup>d</sup>		0.5%		9	50	30

<sup>a</sup> Essentially monoesters except for No. 4 and 5 which are diesters.

<sup>b</sup> The 20% solutions were clear and maximum solubility may be significantly greater than 20%.

<sup>c</sup> Foam height and detergency were measured on 0.25% built solutions (0.05% active ingredient + 0.20% builder) in hard water of 300 ppm.

<sup>d</sup> Commercial sample.

<sup>e</sup> Too turbid for the test method.

### Alcoholysis

The alcoholysis method for sucrose monostearate (7,8) was applied with some modification to hexitol and sucrose monoesters of  $\alpha$ -sulfo acids, and is illustrated for sodium sucrose  $\alpha$ -sulfostearate.

Sucrose (10-X, 0.14 moles) and sodium methyl  $\alpha$ -sulfostearate (0.13 moles), dried at 100 C at 1 mm pressure, were dissolved in 100 ml of dimethylformamide. Grade 10-X was used because of more rapid solubility and low moisture content. Sodium methoxide catalyst (0.5 g) was added and the mixture was heated and stirred 6 hr at 100 C, removing methanol. Dimethylformamide was removed by distillation at reduced pressure. The glassy product was dissolved in absolute ethanol and insoluble matter, mainly sucrose, was filtered off. Crystallization from absolute ethanol at -30 C gave 75% yield of a product which was essentially the monoester, containing through solubilization significant amounts of sucrose, sodium methyl  $\alpha$ -sulfostearate, and disodium  $\alpha$ -sulfostearate. Elemental analyses for hexitol and sucrose monoesters prepared in this way are listed in Table I.

### Analysis of Esters

In some cases, particularly with the alcoholysis method, it was difficult to remove small amounts of the starting materials from the reaction product. The following scheme was developed in the analysis for suspected impurities.

**Disodium Salt.** A plot was made of the infrared absorbancy ratio  $C=O/COO^-$  against composition ester-salt for known mixtures of the methyl ester  $RCH(SO_3Na)CO_2CH_3$  and the disodium salt  $RCH(SO_3Na)CO_2Na$ . Comparing absorbance at 5.7  $\mu$  (carboxylic ester) with absorbance at 6.3  $\mu$  (ionized carboxyl) the amount of disodium salt in a hexitol or sucrose ester preparation was determined.

**Methyl Ester:**  $RCH(SO_3Na)CO_2CH_3$ . The hexitol and sucrose ester prepared by alcoholysis was saponified with an excess of 0.7 N NaOH and the

methanol-water distillate was collected. By reference to density tables for aqueous methanol the amount of unreacted methyl ester was determined.

**Total Sugar.** The optical rotation of a 5% aqueous solution of a sucrose ester preparation showed the total amount of sucrose present, both free and in combination as sucrose mono-( $\alpha$ -sulfopalmitate) or stearate. Because of low specific rotation hexitols could not be determined this way.

**Sodium Analysis.** Total sodium was determined by ignition to sodium sulfate. Total sodium minus sodium present as the disodium salt minus sodium present as the sodium salt of the methyl ester = sodium present as the salt of the  $\alpha$ -sulfo ester of hexitol or sucrose.

**Elemental Analysis.** Composition was confirmed by analysis for C, H and S.

Esters from the different methods were analyzed by the appropriate methods shown above. Analyses for some esters from the alcoholysis reaction are shown in Table II.

### Surface Active Properties

Krafft point, Ca<sup>++</sup> stability, lime soap dispersion power, foam height and detergency were measured on representative preparations by methods used in previous publications (3). The results are shown in Table III.

## Results and Discussion

### Composition

From the symmetry of D-mannitol there are 3 possible monoesters and 9 possible diesters; for sorbitol there are 6 monoesters and 15 diesters. For sucrose there are 8 monoesters and 28 diesters (calculated from  $\frac{n(n-1)}{2}$ ). In the absence of directing

forces or blocking groups it would therefore be very difficult to isolate one chemical individual from an esterification product.

Because of the greater reactivity of primary alcohol groups (9) and the limited solubility of mannitol and sorbitol in benzene the direct method gave a product which was essentially the 1,6-diester  $[RCH(SO_3Na)CO_2CH_2(CHOH)_2]_2$  with possibly small amounts of a monoester, triester and disodium salt present. The acid chloride method gave a product which was essentially a monoester, presumably a mixture composed primarily of the 1- and 6-monoesters. The alcoholysis method gave a product of about 85% purity as a monoester, as shown in Table II. The mannitol ester from alcoholysis is

TABLE II  
Analysis of Esters From the Alcoholysis Reaction

Preparation	Sodium methyl $\alpha$ -sulfostearate %	Disodium $\alpha$ -sulfostearate %	Hexitol or sucrose %	Monoester of hexitol or sucrose %
Sodium mannitol $\alpha$ -sulfostearate	4	2	6	88
Sodium sorbitol $\alpha$ -sulfostearate	12	3	7	78
Sodium sucrose $\alpha$ -sulfostearate	10	5	15	70

probably primarily the 1-monoester and the sorbitol monoester primarily a mixture of the 1- and 6-monoesters.

The sucrose esters from the acid chloride method appear to be essentially monoesters, principally of the primary alcohol groups, containing perhaps small amounts of sucrose, diesters and the disodium salt.

The sucrose esters from the alcoholysis reaction are primarily monoesters with impurities resulting from solubilized reactants as shown in Table II. As in the case of sucrose monomyristate (5) esterification may be expected to take place principally at the primary alcohols 6' and 6.

#### Properties

In Table III the products are essentially monoesters except for the mannitol and sorbitol diesters obtained by direct esterification (No. 4 and 5). All are easily soluble and most of them have excellent calcium stability. They are fairly good lime soap dispersing agents and have moderate foaming properties. Detergency lies between that for sodium

methyl  $\alpha$ -sulfostearate and sucrose monotalloate.

Improvements in esterification and further investigation of properties may show greater possibilities for utilization. Of the methods employed the direct esterification which led to the preparation of hexitol diesters in a fairly pure state is the most attractive.

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#### REFERENCES

1. Ames, G. R., *Chem. Rev.* **60**, 541-553 (1960).
2. Anonymous, *Chem. Eng.* **75**, 56-58 (1968).
3. Bistline, R. G., Jr., and A. J. Stirton, *JAACS* **45**, 78-79 (1968).
4. Gaertner, V. R., *Ibid.* **33**, 410-418 (1961).
5. Lemieux, R. U., and A. G. McInnes, *Can. J. Chem.* **40**, 2394-2401 (1962).
6. Osipow, L., and W. Rosenblatt, *JAACS* **44**, 307-309 (1967).
7. Osipow, L., F. D. Snell, W. C. York and A. Finchler, *Ind. Eng. Chem.* **48**, 1459-1462 (1956).
8. Osipow, L., F. D. Snell, D. Marra and W. C. York, *Ibid.* **1462-1464**.
9. Reinefeld, E., and G. Klauenberg, *Tenside* **5**, 266-270 (1968).

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