

## ✿ Synthesis of 2-Alkyloyl-1,4,3,6-Dianhydrosorbitol-5-Sulfates and Evaluation of the Surface Active Properties

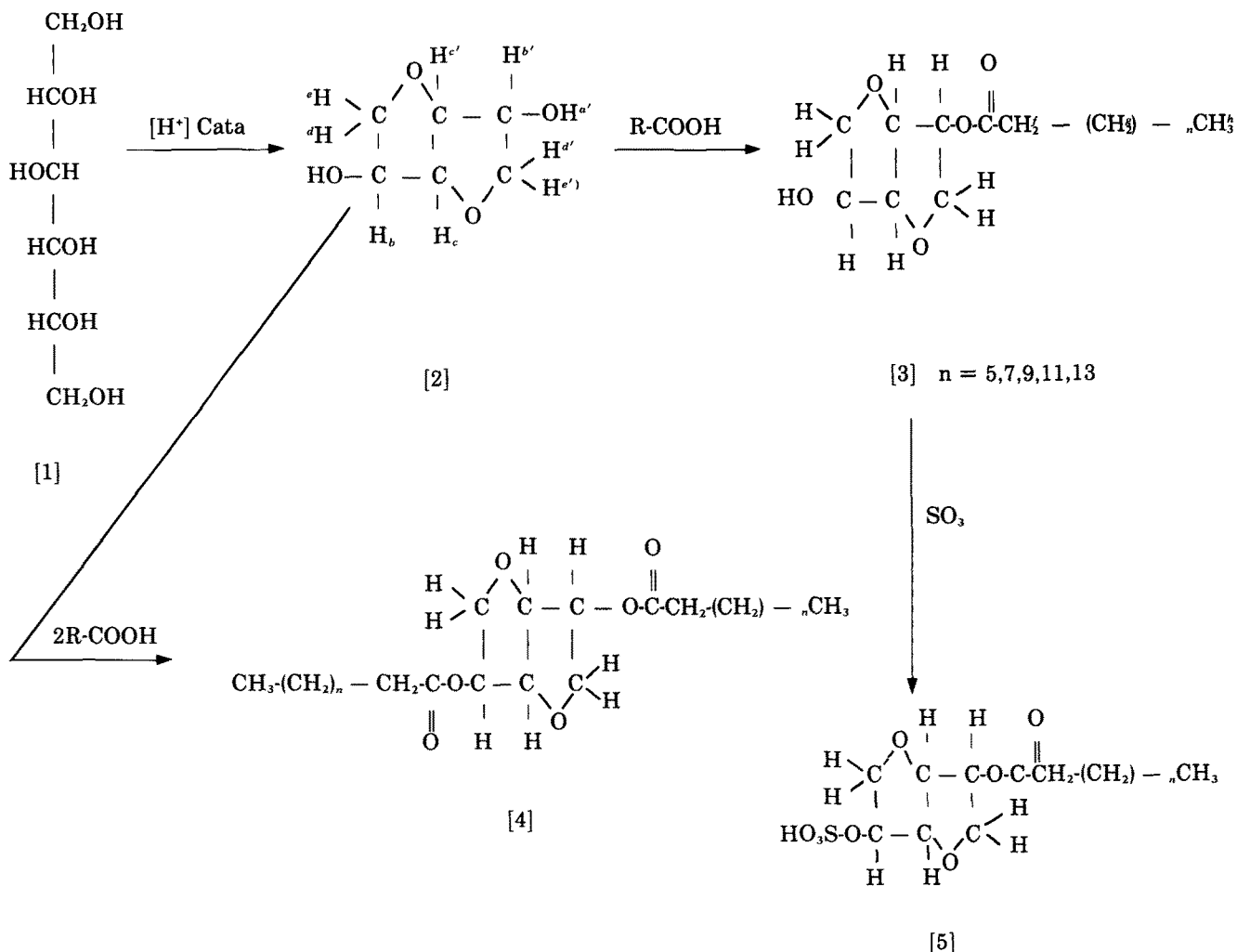
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New anionic surfactants 2-alkyloyl-1,4,3,6-dianhydrosorbitol-5-sulfates were synthesized by sulfation of 2-alkyloyl-1,4,3,6-dianhydrosorbitol. Studies on the surface active properties such as surface tension, dispersibility and emulsifiability of these surfactants were carried out. The results showed these surfactants are better dispersants and emulsifiers than Span 80 and Span 85.

This paper is a study of isosorbide derivatives. The formation, chemical properties and conformations of isosorbide (See [2], Scheme 1) were listed in Hockett (1), Montgomery (2,3,5), Soltzberg (4), Baker (6), Buck (7) and Brimacombe (8). <sup>1</sup>H-nmr studies for isosorbide and its diacetyl ester were performed by Inch (9), Abraham

(10), Hall (11) and Hopton (12). The well known Span series surfactants (Atlas Powder Co.) are fatty acid esters of anhydrosorbitols. These products are obtained commercially as a mixture of many components and have low solubility in water. A number of papers have been presented about these (14-23). In this paper, we prepare new anionic surfactants, monoalkyloyl-isosorbide-monosulfates as shown in Scheme 1. These compounds are obtained as pure products, as opposed to well known commercial products containing many components. As a result of studies on the surface active properties of each product, these compounds are found to be fit for use as surfactants. The alkyloyl group (Tables 1-5) is abbreviated as: n-capryloyl-(C8), n-caproyl-(C10), n-lauroyl-(C12), n-myristoyl-(C14) and n-palmitoyl-(C16).



Scheme 1. Synthetic scheme of 2-alkyloyl-1,4,3,6-dianhydrosorbitol-5-a, b, . . . , h: for NMR spectral assignment.

## EXPERIMENTAL

**General methods.** Infrared spectra (IR) were determined with a Hitachi grating spectrometer-215. Nuclear magnetic resonance spectra (NMR) were taken on a JEOL PMX 60 spectrometer using tetramethylsilane as an internal standard. Elemental analyses were performed by Yanaco MT-2 CHN corder. Thin layer chromatography (TLC) was performed on a silica-gel G 60 plate (Merk AG) with solvent systems of benzene-methanol-petroleum ether (15:1:1) for isosorbide and alkyloyl ester, n-butyl alcohol-water-acetic acid (4:1:2) for sulfated compound.

**Materials.** d-Sorbitol[1] (Wako Chemical Co., mp 110-112 C), Span 80, Span 85 (Atlas Powder Co.) were used without further purification. Commercial caprylic-, capric-, lauric-, myristic- and palmitic acids were purified by distillation under reduced pressure. Organic solvents such as xylene, 1,2-dichloroethane and 1,4-dioxane were dried over sodium or sodium sulfate and distilled before use. Other reagents were guaranteed grade. The water used in the measurements of surface active properties and the other tests was purified by distillation and passing through the ion exchange columns.

**Synthetic procedures.** 1,4,3,6-dianhydrosorbitol (Isosorbide) [2] was prepared in 70% yield by the methods of Hockett (1) and Montgomery (2,3), and recrystallized with ethyl acetate followed by vacuum distillation, bp. 160-162 C/10mm Hg. {160-165 C/10mm Hg(3)}, mp. 61-62 C, {61-63 C(2), 61.9-64 C(3,4)}. IR( $\text{cm}^{-1}$ ) ( $\text{CHCl}_3$ ) 3300-3400(S) ( $\nu_{\text{OH}}$ ), 1115 (s) ( $\nu_{\text{CO}}$ ), 1090(s) ( $\nu_{\text{C-O-C}}$ ). NMR ( $\text{DMSO-d}_6/\text{TMS}$ ) ( $\delta$  ppm) 4.77{m 2H (c), (c')}, 4.27{m 2H

(a), (b)}, 4.07{m 1H(b')}, 3.77{m 4H (a'), (d), (e), (e')}, 3.27{m 1H(d')}. Elemental Analysis: Found, C 49.30%, H 6.92%. Calcd. for  $\text{C}_{10}\text{H}_{10}\text{O}_4$ , C 49.31%, H 6.89%. These values agreed with those in the literature (1-13).

**Monoalkyloyl-isosorbide[3]:** Alkyloylations of isosorbide are inclined to introduce unfavorable compounds [4] due to the similar reactions of two OH groups in isosorbide. Therefore, the monoalkyloylation reaction was prepared under mild conditions. A typical synthetic procedure for [3] was as follows: 146 g of [2] (1.0 mol), 0.67 mol of a fatty acid (caprylic, capric, lauric, myristic and palmitic acid) and concentrated sulfuric acid (5.1 g) was dissolved in dry xylene (1500 ml) in a 2000-ml

TABLE 3

Critical Micelle Concentrations of Compound [5] Determined by Two Methods

Compound [5]	Cmc (mol/l) $\times 10^3$	
	Conductivity method	Surface tension method
C8-[5]	13.0	12.0
C10-[5]	6.5	5.7
C12-[5]	2.6	2.8
C14-[5]	1.1	0.8
C16-[5]	0.14	0.12

TABLE 4

Times Elapsed for Complete Sedimentation of  $\text{CaCO}_3$  in Sample Solution

Compound [5]	Conc (mol/l) $\times 10^4$	Complete sedimentation (min)
C8-[5]	200	2
C10-[5]	80	30
C12-[5]	40	60
C14-[5]	20	45
C16-[5]	2	1
Span 80	28	0.2
Span 85	13	0.2
Water	—	4

TABLE 1

Preparation of Compound [3]

Compound [3] Inner alkyloyl group	Yield (%)	Mp ( $^{\circ}\text{C}$ )	Rf value
C8-	27.5	61.5-62.3	0.24
C10-	25.5	66.8-67.9	0.43
C12-	32.0	73.0-74.0	0.44
C14-	26.7	80.1-81.2	0.46
C16-	30.5	85.5-86.0	0.49

TABLE 2

Preparation of Compound [5]

Compound[5] classified by alkyloyl chain length	Elemental analyses									
	C (%)		H (%)		N (%)		S (%)		Yield	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	(%)	value
C8-[5]	45.34	45.52	7.41	7.37	3.81	3.79	8.54	8.62	13	0.56
C10-[5]	48.47	48.35	7.90	7.86	3.56	3.52	7.94	8.07	21	0.59
C12-[5]	50.76	50.81	8.33	8.29	3.32	3.29	7.40	7.53	20	0.62
C14-[5]	52.81	52.98	8.75	8.67	3.21	3.09	6.92	7.07	36	0.63
C16-[5]	55.02	54.86	9.08	9.00	3.00	2.91	6.52	6.66	35	0.63

## SYNTHESIS OF DIANHYDROSORBITOLS

TABLE 5  
Emulsifiability (o/w) Tests

Compound [5]	Conc. (mol/l) $\times 10^4$	Vegetable oil						Liquid paraffin	
		Rapeseed		Soybean		Corn		(a)	(b)
		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
C8-[5]	200	0	2	0	2	0	2	0	4
	400	0	4	0	4	0	4	0	5
C10-[5]	40	3	>300	3	>300	3	>500	2	>300
	80	5	>300	5	>300	5	>500	2	>300
C12-[5]	20	3	>500	3	>500	3	>500	2	>500
	30	5	>500	5	>500	5	>500	3	>500
C14-[5]	20	5	>500	5	>500	5	>500	3	>500
	10	5	>500	5	>500	5	>500	3	>500
C16-[5]	1	3	3	5	7	4	5	3	10
	2	3	3	5	4	5	4	3	3
Span 80	10	1	90	1	90	1	120	1	90
Span 85	30	3	90	2	90	2	90	2	90

(a) Time required until appearance of oily phase (min).

(b) Finish time of demulsification (hr).

three-necked round-bottomed flask with a stirrer, thermometer and Deanstark reflux condenser connected with  $\text{CaCl}_2$  tube. The mixture was stirred for 12 hr at 135-140 C. After cooling to room temperature, the unreacted [2] was precipitated. The reaction mixture was filtered and washed twice in 300 ml of water. The xylene layer was evaporated under reduced pressure, leaving a waxy, black solid. The residue was recrystallized from methyl alcohol and n-hexane to give the white plate crystal of [3].

*Monoalkyloyl-isosorbide-5-sulfate* [5]. The typical sulfation procedure of [3] was as follows: A mixed solvent 100 ml (dioxane: 1,2-dichloroethane = 3:97) containing 0.167 mol of  $\text{SO}_3$  was cooled to -40 C in a 500-ml four-necked flask fitted with a stirrer, thermometer, dropping funnel and  $\text{CaCl}_2$  tube. 0.167 mol of [3] dissolved in 200 ml of dry chloroform was added drop by drop to the mixture at -40 C and stirred for 5 hr at the same temperature. The reaction mixture was neutralized with sodium hydroxide dissolved in methyl alcohol and allowed to warm to 10 C. The mixed solvent was evaporated under reduced pressure at 10 C, and the residue was extracted with chloroform to separate from unreacted [3]. The residual white precipitate [5] was dried in a vacuum desiccator over  $\text{P}_2\text{O}_5$  at room temperature.

*Surface activity.* The measurements of surface tension by the capillary method and electroconductivity by use of YANACO-model MY-7 conductivity FIT were performed at  $30 \pm 0.1$  C.

*Dispersibility.* Calcium carbonate (7g:sp. gr. 2.711, guaranteed reagent, Wako Chem. Co.) and 400 ml of aqueous solution of each sample ( $1 \times 10^{-2} \sim 1 \times 10^{-4}$  mol/l) was mixed in a cylindrical sedimentation glass vessel (7.0 cm in diameter, 12.0 cm in height). After 2 min of vigorous stirring, the sedimentation vessel was set in the sedimentation apparatus (Shimazu Manufacturing Co., Type SA 2) and the sedimentation immediately recorded. The sedimentation curve for each sample was obtained.

*Emulsifiability.* The aqueous solution of the sample (10 ml;  $4 \times 10^{-2} \sim 1 \times 10^{-4}$  mol/l) and an oil (10 ml) (liquid paraffin, rapeseed oil, soybean oil and corn oil) was mixed in a test tube (50 ml volume, 1.24 cm diameter). After being shaken 50 cm back and forth 20 times in 20 sec, the test tube was allowed to stand and its temperature adjusted to  $30 \pm 0.1$  C. The time necessary from the appearance of the oil phase to complete demulsification was observed.

## RESULTS AND DISCUSSION

*Synthesis of 2-alkyloyl-1,4,3,6-dianhydrosorbitol*[3]. The yield of [3] was generally poor due to the occurrence of the dialkyloylation reaction and required repeated recrystallization and extraction to obtain a pure compound. Data on the yield, mp and Rf value of TLC for preparation of [3] are given in Table 1. The IR and NMR data of C12-[3] are as follows: IR(KBr) ( $\text{cm}^{-1}$ ) 3400(s)( $\nu_{\text{CH}}$ ), 2900(s)( $\nu_{\text{CH}_2}$ ), 1725(s)( $\nu_{\text{C=O}}$ ), 115(s)( $\nu_{\text{C-O}}$ ), 1090(s)( $\nu_{\text{C-O-C}}$ ). NMR ( $\text{CDCl}_3/\text{TMS}$ ) ( $\delta$ ppm) 5.10{m 1H (a)}, 4.47{m 2H(b)(b')}, 4.00{m 2H(c)(c')}, 3.70{m 2H(e)(d)}, 3.27{m 2H(d')(e')}, 2.33{m 2H(f)}, 1.33{m 18H(g)}, 0.83{m 3H(h)}. Similar spectra for the other monoalkyloyl esters [3] were obtained and identified.

*Synthesis of 2-alkyloyl-1,4,3,6-dianhydrosorbitol-5-sulfates*[5]. Table 2 shows the results of elemental analyses, yields and Rf values of TLC for the ammonium salts. If decomposition from [3] to [2] can be suppressed during the work up to isolation of the compound [5], more favorable yields would be expected for the sulfation reaction. The IR data of lauroyl-[5] are as follows: IR(KBr) ( $\text{cm}^{-1}$ ) 3250(s)( $\nu_{\text{NH}^+}$ ), 1725(s)( $\nu_{\text{C=O}}$ ), 1240(s)( $\nu_{\text{S-O}}$ ), 1120(s)( $\nu_{\text{C-O}}$ ), 1095(s)( $\nu_{\text{C-O-C}}$ ). Similar data for the other samples of [5] were obtained. From data of elemental analyses, IR and TLC, all samples are identified.

*Surface tension.* Figure 1 shows the surface tension vs. concentration plot for the samples in distilled water. The solubility of C8-[5] decreased from 30 g/l to 0.2 g/l of C16-[5] as the alkyloyl chain length increased. As shown in Figure 1, C8-[5] depressed surface tension to 25.75 dyne/cm at  $4 \times 10^{-2}$  mol/l. For the other [5] compounds, the surface tension at higher concentration could not be measured due to their lower solubilities in water. From

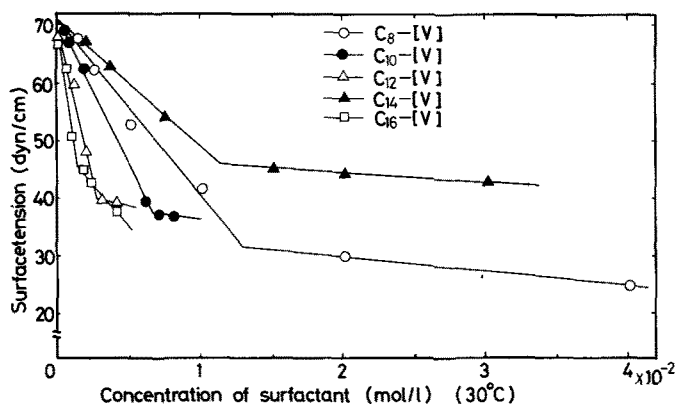


FIG. 1. Relationship between surface tension and concentration of the surfactants.

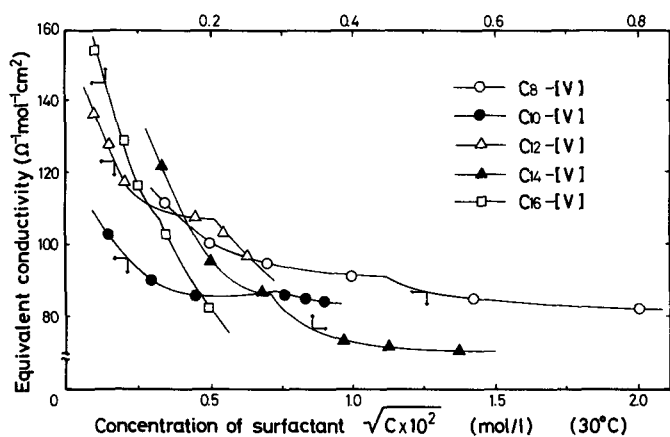


FIG. 2. Relationship between equivalent conductivity and concentration of the surfactants.

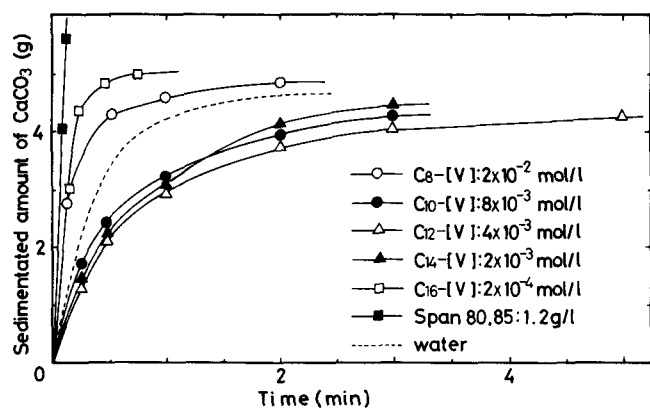


FIG. 3. Sedimental pattern of pigment ( $\text{CaCO}_3$ ) in water.

Figure 1, the critical micelle concentrations (CMC) of the samples were estimated to be  $12.0 \times 10^{-3}$ ,  $5.7 \times 10^{-3}$ ,  $2.8 \times 10^{-3}$ ,  $0.8 \times 10^{-3}$  and  $0.12 \times 10^{-3}$  mol/l for C8-, C10-, C12-, C14- and C16-[5], respectively (Table 3).

**Electroconductivity.** These data are also shown in Figure 2. The break points of conductivity vs concentration plot are shifted to lower concentration with decrease of alkyloyl chain length. From Figure 2, the CMCs of the samples can be graphically estimated; they are listed in Table 3. The values obtained from the two different methods compare favorably.

**Dispersibility.** Sedimentation curves of  $\text{CaCO}_3$  powder in water were presented in Figure 3. The pigment powder settled within 2 min in water without surfactant. As seen in Figure 3, C10-, C12- and C14-[5] showed good dispersibilities, while C8-, C16-[5] and the commercial surfactants Span 80 and Span 85 promoted the sedimentation of  $\text{CaCO}_3$  powder. The times required

for the complete sedimentation of  $\text{CaCO}_3$  in aqueous solution of the samples are summarized in Table 4, where the dispersibilities of C10-, C12- and C14-[5] were relatively good among the surfactants tested. No clear interpretation can be given for the rapid sedimentation which occurred in the case of C8- and C16-[5].

**Emulsifiability.** The results of the emulsifiability test are shown in Table 5. The emulsifiabilities of C10-, C12- and C14-[5] were superior to those of Span 80 and Span 85, while C8- and C16-[5] were inferior to the others. These results on the surface active properties of the samples [5] suggest that both the increased solubility in water by introduction of the sulfate group to the isosorbide skeleton and the proper HLB with monoalkyloylation of the OH group are responsible for the excellent emulsifying power. These sodium 2-alkyloyl-1, 4,3,6-dianhydrosorbitol-5-sulfates, especially C10-, C12- and C14-[5], seem to be promising for food and cosmetic additives due to their excellent emulsifiability and also their probable lack of deleterious effects on health.

#### ACKNOWLEDGMENTS

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