Biodegradable Surfactants Derived from Corn Starch

PETER E. THROCKMORTON, RICHARD R. EGAN, and **DAVID AELONY**[1], Ashland Chemical Company, Columbus, Ohio 43216, **GAYLE K. MULBERRY,** Hill Top Research, Inc., Miamiville, Ohio 45147, and **FELIX H. OTEY,** Northern Regional Research Laboratory[2], Peoria, Illinois 61604

ABSTRACT

Polyol glucosides, prepared by reacting corn starch with ethylene glycol or glycerol, were used to make biodegradable surfactants. The hydroxyl sites of the glycosides were first partially polyalkoxylated with ethylene oxide or a mixture of ethylene and propylene oxides. The resulting derivatives then were reacted with various long chain epoxides or fatty esters. A good hydrophilic-lipophilic balance in these products was achieved by controlling the number of alkoxide and aliphatic groups/anhydroglucose unit. Surface active properties of these products were destroyed rapidly by the bacteria of an activated sludge. This excellent biodegradability property was attributed to the presence of the glycoside unit.

INTRODUCTION

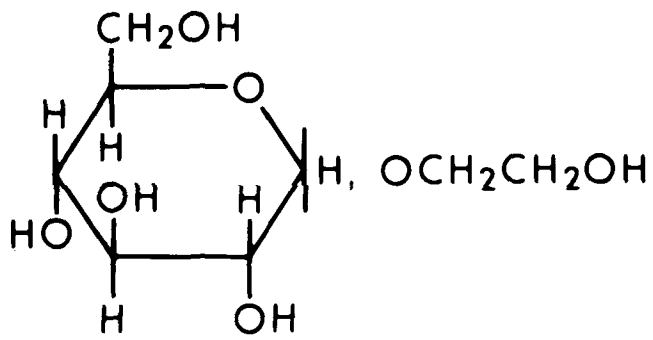
A series of new biodegradable surfactants has been prepared by reacting starch derived glycol and glycerol glycosides with ethylene oxide or mixed ethylene oxide-propylene oixde and long chain lipophilic materials. The economics and preparation, in part, as well as detailed surface-active and detergency properties, of these biodegradable surfactants have been reported (1). In this paper, we complete the account of product compositions by showing results of a biodegradability study and, also, typical molecular size distributions by gel permeation chromatography. Detergency and surface-active properties are summarized for ready comparison.

Transglycosylation of corn starch to yield starch glycosides was first reported on a laboratory scale by Otey, et al. (2). McKillip, et al., (3) and Leitheiser, et al., (4) demonstrated pilot plant-scale manufacture of starch glycosides. We reported that starch derived surfactants could provide economically feasible detergents based upon a projected manufacturing cost of $0.17/lb (1). Our estimate was based upon production of 100 million lb/year of an ether glycoside surfactant (product 25, Table I) using pilot plant data.

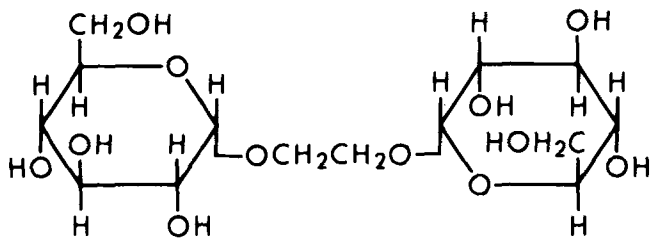
During transglycosylation, starch is broken down to give a mixture of polyol glycosides, which provide the starting materials for further synthesis to make surfactants. Otey and associates (5) showed that glycosides derived by the action of ethylene glycol on corn starch are 62-72% monomer (I) and 17-23% dimer (II) and contain small amounts of oligosaccharides.

A plurality of hydroxyl sites are available in the glycoside material. Either ethylene glycol or glycerol glycoside was reacted at one or more of the hydroxyl sites with ethylene oxide or mixtures of ethylene and propylene oxides. The materials so obtained were either ethoxylated (III, x = 0) or mixed random alkoxylated glycosides (III). In structure III only one of the hydroxyl sites is shown reacted.

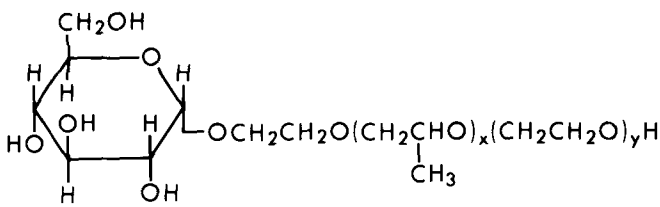
These polyalkoxylated glycosides then were reacted with fatty esters to yield ester surfactants or with long chain epoxides to yield ether surfactants. Conceptual structures IV of the ester and V of the ether surfactants are shown



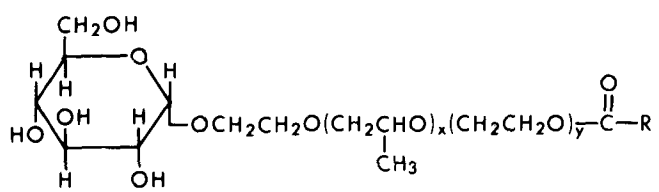
I



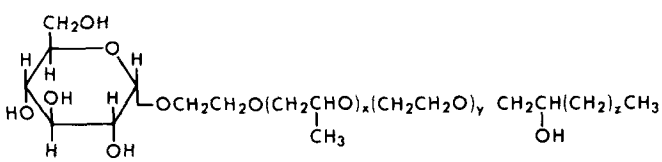
II



III



IV



V

with only one available hydroxyl reacted. Obviously, each structure shown represents only one of many possible isomers since ethylene and propylene oxides could be attached at any or all of the glycoside hydroxyls and the lypophilic material at a glycoside hydroxyl or at the end of any alkoxide chain. The glycoside or carbohydrate moiety in such surfactants was considered to provide a likely site

[1]Present address: Makhteshim Chemical Works, Ltd., Beer-Sheva, Israel.

[2]ARS, USDA.

TABLE I

Surfactant and Detergent Properties of Fatty Alkoxylated Polyol Glycosides

Product no.	Surfactant[c] composition/AGU (C_n/EO/PO/SO_4)	Surfactant properties[a]						Canvas disc[d] wet-out time, sec	Detergent properties[b]			
		Surface tension, dynes/cm		Interfacial tension, dynes/cm		Ross-Miles foam ht, mm[d]			Change in reflectancy, ΔR[e]		Soil removed, %[e]	
		0.1%	1.0%	0.1%	1.0%	Initial	After 5 min		0 ppm Ca/Mg	300 ppm Ca/Mg	0 ppm Ca/Mg	300 ppm Ca/Mg
					Fatty ethers of alkoxylated glycol glycosides							
1	0/10.6/0/0	---	---	---	---	---	---	---	5.7	5.9	9.2	9.5
42	0/10/5/0	---	---	---	---	---	---	---	---	7.3[f]	---	11.7[f]
9	$2C_{14-16}$/10/0/0	36.5	36.5	6.4	4.5	30	15	180	13.2	15.0[f]	21.1	24.1[f]
16	$2C_{12}$/8/4/1	36.9	33.7	14.5	11.2	---	---	180	---	---	18.0	14.9
22	$1.2C_{12}$/10.6/0/0	35.3	31.9	10.3	2.4	---	---	86	18.9	18.6	30.1	29.8
24	$1.6C_{12}$/10.6/0/0	---	32.6	---	3.4	---	---	78	19.4	---	31.1	---
25	$1.8C_{12}$/10.6/0/0	34.2	32.9	9.1	7.4	---	---	51	21.0	17.3	33.7	27.7
26	$2C_{12}$/10.6/0/0	33.6	31.6	10.1	8.4	---	---	58	---	17.8	---	28.5
27	$2C_{10}$/10.6/0/0	31.5	32.5	6.4	7.7	20	15	---	---	17.5[f]	---	28.1[f]
29	$1.3C_{12}$/8/4/0	29.4	28.6	4.3	1.6	---	---	30	21.0	---	34.0	---
43	$1C_{10}$/8/4/0	30.1	29.6	4.4	3.3	---	---	24	18.1	---	29.1	---
45	$2.3C_{12}$/10/5/0	32.7	30.2	5.4	2.7	---	---	30	20.6	10.5	33.0	16.8
47	$3.2C_{12}$/10/5/0	33.4	29.3	6.4	3.5	---	---	63	20.7	10.8	33.2	17.3
49	$1.7C_{14-16}$/11.3/5.6/0	38.2	36.5	12.8	9.2	---	---	180	17.9	17.2	28.7	27.6
50	$2C_{14-16}$/8.8/0/0	37.9	32.8	11.4	7.8	---	---	---	21.2	13.6	34.0	21.8
					Fatty ethers of alkoxylated glycerol glycosides							
30	0/10/0/0	---	---	---	---	---	---	---	7.5	5.7	12.1	9.2
37	$2C_{12}$/10/0/0	33.7	30.0	11.5	8.7	43	33	---	19.1	17.9	30.6	28.2
					Fatty esters of alkoxylated glycol glycosides		gly					
6	$1C_{18}$/0/0/0	---	---	---	---	---	---	---	7.3	6.6	11.7	10.5
7	$2C_{18}$/10/0/0	42.1	38.0	13.5	9.5	26	23	---	6.3	---	10.0	---
10	$0.72C_{16-18}$/10.6/0/0	37.7	38.8	14.8	13.0	26	18	180	13.0	10.9	20.8	17.5
48	$1C_{18}$/20/0/0	---	---	---	---	k	---	---	---	11.3[f]	---	18.2[f]
					Fatty ester of alkoxylated glycerol glycoside							
35	$1C_{18}$/10/0/0	41.6	39.7	14.9	13.1	23	18	---	9.7	---	15.6	---
					Controls							
Polyalkoxylated tallow alcohol		34.7[g]	---	7.2[g]	---	---	---	---	20.9	---	33.5	---
Ionic detergent		---	---	---	---	---	---	---	16.0	---	25.7	---

[a]Tests conducted on pure surfactant solutions.

[b]Tests conducted at 55 C with 0.25% solution of built formulations.

[c]Example: Product 16 was obtained by reacting 2 moles dodecane-1-oxide, 8 moles ethylene oxide (EO), 4 moles propylene oxide (PO), and 1 mole chlorosulfonic acid with each mole of glycoside or anhydroglucose unit (AGU).

[d]Procedure of reference 8.

[e]Procedure of reference 8. U.S. Testing Co. Standard Soiled cotton fabric washed in a Terg-O-Tometer. Lot no. 604. $R_O = 86.5$; $R_S = 24.1$ after soiling. Soil removed, $\% = \Delta R/R_O\text{-}R_S\ (100)$, where $\Delta R = R\text{-}R_S$.

[f]Conducted at 38 C and 100 ppm Ca/Mg hardness.

[g]At 0.05% concentration.

TABLE II

Biodegradability of Alkoxylated Polyol Glycosides and Derivatives

Product no.	Surfactant[a] composition/AGU (C_n/EO/PO/SO_4)	Time, hr	Concentration, ppm: Initial (C_o)	Concentration, ppm: LAS[b] (C)	Foam ht, ml: Initial	Foam ht, ml: 60 sec	Foam ht, ml: 180 sec	Surface tension (γ) (dynes/cm)	Percent biodegradability[c]: (by LAS[b] conc.)	Percent biodegradability[c]: D (by γ_t)	Bacterial count (average/ml x 10^{-3})	Blank[d] ($\gamma_{b,t}$) (dynes/cm)
				Fatty ethers of alkoxylated glycol glycosides								
1	0/10.6/0/0	0	500		170	110	102	46.0			195	
		96			192			48.5			1267	
		264			170	108	102	55.0		68		59.2
		384			170	108	106	54.5			162	
16	$2C_{12}$/8/4/1	0	50	23.0				41.5			3435	
		48		23.0				54.0		89		56.0
		72		5.9				50.0				
		144		2.3				50.5				
		168		1.9				52.2	92		1260	
20	$2C_{14-16}$/20/0/1.3	0	50	27.0				43.5			3435	
		24		25.0				54.5		86		57.0
		48		5.8				53.5				
		168		1.8				48.5	93		1260	
25	$1.8C_{12}$/10.6/0/0	0	500		190	190	180	32.5			195	
		96			170	170	165	36.8			865	
		264			170	168	160	37.0				
		384			160	150	150	42.5		38	1340	59.2
		0	50					40.5			885	
		48						43.5			1305	
		120						54.0		80		57.5
		168						52.2			21	
				Fatty ether of alkoxylated glycerol glycoside								
38	$1C_{12}$/8/4/0	0	500		210	210	210	33.2			195	
		96			190	180	175	36.0			1340	
		144			190	180	170	46.0				
		264			180	170	160	47.5			1220	
		384			180	170	160	51.0		69		59.2
				Fatty ester of alkoxylated glycol glycoside								
10	$0.72C_{16-18}$/10.6/0/0	0	500		140	130	130	39.5			195	
		48			112	112	110	43.5				
		96			110	108	108	54.0		81	385	57.5
		144			110	108	108	53.5				
		312			110	108	106	49.5			1370	
		0	50					42.0			885	
		48						51.0			76	
		120						52.2				
		168						65.0		100	15	61.0
				Controls								
Ethoxylated octyl phenol		0	50					36.8			885	
		12						41.5		20		60.0
		48						39.2			370	
		120						38.5				
		192						40.5			282	
Sodium lauryl sulfate		0	50	53.5				43.0			3,435	
		6		52.0				48.5				
		48		4.6				63.7		100		56.0
		168		1.2				53.0	98			
		192						55.9			10,500	

[a]Example: Product 16 was obtained by reacting 2 moles dodecane-1-oxide, 8 moles ethylene oxide (EO), 4 moles propylene oxide (PO), and 1 mole chlorosulfonic acid with each mole of glycoside. AGU = anhydroglucose unit.

[b]Concentration (conc.) equivalent to linear alkyl benzene sulfonate (LAS) as found by the methylene blue test (reference 12).

[c]By fraction of initial LAS (equivalent) concentration diminished, or by surface tension (γ) increase, calculated as percent degraded, $D = \frac{\gamma_t - \gamma_o}{\gamma_{b,t} - \gamma_o} \times 100$.

[d]Nutrients and active sludge but no surfactant.

TABLE III

Gel Permeation and Mol Wt[a] of Ethoxylated Glycol Glycoside (Product 1)

Elution counts (5 ml vol)	Cumulative wt, %	Peak ht ($H_i = M_iN_i$)	Chain length[b] ($A_i = M_i/Q$)	Number of particles ($N_iQ = H_i/A_i$)
29	100	43	69	0.623
30	85	144	46	3.130
31	34	72	34	2.105
32	9	13	22	0.599
33	4.2	8	15	0.533
34	1.4	4	10	0.388
			$\Sigma H_i = 284$	$\Sigma N_iQ = 7.380$

[a] $\bar{M}_n = 38.5Q = 626$ (assume Q = 16).

[b] $\bar{A} = \Sigma H_i/\Sigma N_iQ = 38.5$ Å average chain.

for rapid bacterial cleavage. Once the glycoside was cleaved, we believed the surface-active effect of such a fatty glycoside surfactant would be lost. Our object was to synthesize a number of such corn starch derived surfactants, test their surface activity in water, and examine their detergency performance in a built detergent formula. Finally, we tested their biodegradability in a medium containing an activated sludge.

EXPERIMENTAL PROCEDURES

Selected examples of the 52 starch glycoside derivatives prepared are listed in Tables I and II. (Additional examples are available on request to Ashland Chemical Company, Columbus, Ohio 43216.) Typical procedures are described below for preparing the glycosides (ethylene glycol glycoside and glycerol glycoside), the ester- and ether-alkoxylated glycosides and the built detergents.

Synthesis and Detergent Formulation Procedures

2-Hydroxyethyl-α,β-D-glucopyranoside (ethylene glycol glycoside) (structure I) (pilot plant run): The transglycosylation of corn starch after McKillip, et al., (3) was done on a pilot plant scale in a 30 gal stainless steel reactor to which was charged 133 lb ethylene glycol and 0.64 lb sulfuric acid. Laboratory-scale preparations have been described elsewhere (1,2,5,6). The mixture was heated to 120 C with good stirring and kept under a nitrogen blanket. One hundred lbs (87 lb, dry basis) of pearl corn starch was added over a 40 min period while maintaining a temperature of 120 C. When addition was complete, the pressure was reduced to 40 mm Hg, and heating and stirring were continued for 30 min. The mixture was cooled and neutralized with 0.65 lb calcium carbonate. The reactor was sealed and the unreacted ethylene glycol removed at 5-10 mm Hg as the temperature was raised slowly to ca. 140 C. After stripping was complete, the glycoside was dissolved in 100 lb water, decolorized with 5 lb charcoal, filtered, and finally adjusted to a concentration of 70-80% solids in water.

The product (71.5% solution) tested: Gardner color, 1; acid value, 0.2; and hydroxyl value (OHV), 1175 mg KOH/g. By gas liquid chromatography, (GLC) after Otey, et al. (5), the product (100% solids basis) contained 40.9% 2-hydroxyethyl-α-D-glucopyranoside and 22.0% 2-hydroxyethyl-β-D-glucopyranoside (total 62.9% monomer [I] ethylene glycol glycoside); the balance (37.1%) was mostly dimer glycoside (II) and higher glycol oligosaccharides. The product contained an average of 4.6 hydroxyl groups/anhydroglucose unit (AGU). On the basis of a determined OHV of 1175, the average mol wt of the product was 219.

Ethylene-bis-1,2(glucopyranoside) (II): The bis(glucopyranoside) or dimer (II) formed in preparation of I was not isolated. Gel permeation analysis of a liquid chromatographic sample of I, free of higher oligosaccharides, showed a minor fraction eluted at 22.5 counts (5 ml elution count volume) in tetrahydrofuran (THF) through 4-Styragel (polystrene) permeation columns in series (100, 100, 60, and 60 Å pore size). A major fraction was assigned as 2-hydroxyethyl-α, β-D-glucopyranoside, which eluted at 23.8 counts. The minor fraction was believed to be II.

Poly(ethyleneoxy)-α,β-D-glucopyranoside (polyethoxylated ethylene glycol glucoside) (III, x = 0, y = 10.6) (product 1) (pilot plant run): A 71.5% aqueous solution (92.6 lb) of ethylene glycol glycoside (OHV of solids was 1175 mg KOH/g, $\bar{M}$ = 219; number OH groups = 4.6/AGU) was charged to a stainless steel autoclave and fitted with heating and cooling coils and motor driven stirrer. With agitation, full steam jet vacuum and 0.1 cfm nitrogen sparge, 26 lb water was distilled off. To the anhydrous residue (66.6 lb) was added a mixture of 0.133 lb anhydrous sodium acetate in 0.529 lb glacial acetic acid. Ethylene oxide (EO) from a cylinder then was fed continuously at a rate of 5 lb/hr to the reactor at 157 C, 50 psig. The rate was increased to 37 lb/hr at 177 C and 35 psig as the reaction proceeded. Temperature of the mass during the addition of EO was maintained at 177 C by an automatic cooling device. A total of 133.8 lb EO was consumed over a 6 hr addition period. The reaction then was shut down by first cooling to 110 C and then venting to the vacuum line with a nitrogen sparge rate of 0.5 cfm. The product (200.3 lb) was a liquid with Gardner color 13, viscosity 45.8 Stokes, and OHV 375 mg KOH/g, which corresponds to 10.6 moles EO/AGU. A 1 lb portion was bleached at 71-88 C for 1 hr with 0.7% of 70% hydrogen peroxide and then vacuum stripped at 93 C. The bleached product had a Gardner color of 6-7 and a OHV of 388 mg KOH/g.

Gel permeation chromatography (GPC) analysis of the ethoxylated ethylene glycol glycoside in THF solution through 4 Styragel columns in series (10^5, 10^4, 10^3, and 60 Å pore size) showed that particles were 38.5 Å number average chain length for constant index of refraction (Table III). This corresponds to a number average molt wt ($\bar{M}_n$) of 616, assuming a factor Q = 16 for this carbohydrate. Calculated mol wt is 685. Based upon GPC peak ht the ethoxylated glycol glycoside comprised 15% of 46-69 Å, 51% of 34-46 Å, 25% of 22-34 Å, and 5% of 15-22 Å particles. The latter was believed to be lower ethoxylates. There was 1% of less than 10 Å and 2% of 10-15 Å particles which were believed to be unethoxylated glycosides. Continuous ethyl ether extraction (48 hr) in a separate experiment yielded 6.5% extract, which was believed to be polyethylene oxides.

Hydrogenated tallowate of ethyoxylated ethylene glycol glycoside (IV, x = 0, y = 10.6, R = ∿$C_{17}H_{35}$) (product 10) (pilot plant run): To a stainless steel pressure reactor

TABLE IV

Gel Permeation and Mol Wt[a] of Hydrogenated Tallowate Ester of Ethoxylated Glycol Glycoside (Product 10)

Elution counts (5 ml vol)	Cumulative wt, %	Peak ht ($H_i = M_iN_i$)	Chain length[b] ($A_i = M_i/Q$)	Number of particles ($N_iQ = H_i/A_i$)
18	100	25	111	0.225
19	88	80	73	1.096
20	58	72	56	1.293
21	29	40	44	0.917
22	13	20	36	0.563
23	5.2	6	29	0.205
24	2.8	3	25	0.122
25	1.6	1	21	0.048
26	1.2	2	18	0.112
27	0.4	1	15	0.065
		$\Sigma H_i = 250$		$\Sigma N_iQ = 4.647$

[a] $\bar{M}_n = 53.8Q = 836$ (assume Q = 15.5).

[b] $\bar{A}_n = \Sigma H_i/\Sigma N_iQ = 53.8$ Å average chain.

equipped with automatic temperature and pressure regulation and two stage distillate condensers was charged 190 lb (0.277 mole) of polyethoxylated ethylene glycol glycoside, which analyzed OHV 375 mg KOH/g or 10.6 EO/AGU, along with 59 lb of (0.20 mole) hydrogenated tallow split of average mol wt 288-295 comprising 69% methyl stearate, 28% methyl palmitate, and 3% methyl myristate, 302 lb dimethyl formamide (DMF) and 3.96 lb of anhydrous potassium carbonate. The mixture was stirred and heated 12-1/2 hr at 105-115 mm Hg and 99-102 C under total reflux. Then the volatiles were distilled at 100 mm Hg. The distillate was condensed in a two stage condenser arranged to provide partial reflux in the first stage (27 C) and removal of methanol-DMF in the second stage (7 C). The distillation was followed by recording the index of refraction of the condensate mixture from the second stage condenser. When a composition of 100% DMF was reached, the remaining DMF was removed under 29 in. of vacuum and 93 C temperature. The mixture was allowed to cool to room temperature, and 5 lb potassium carbonate slurry was drained from the base of the reactor. Inert filter aid (6 lb) was added and the product filtered at 93 C to yield 218 lb (96% of theory) ester. Then 7 lb 50% aqueous hydrogen peroxide was added for bleaching, while the product was held at 38 C for 1 hr. The solid product had a melting range of 70-80 C, gave a Gardner color of 5 when liquid and formed a cloudy solution at 1% in water. It showed a typical strong absorption of ester carbonyl in the IR at 1735 cm^{-1}.

Properties of product 10 were as follows: $[\alpha]_D^{23} + 28.7°$ (c, 1 in $CHCl_3$); saponification value (SV) of 51.6 mg KOH/g (calculated for 0.723 mole tallowate ester of ethoxylated glycoside is 46.4 mg KOH/g); OHV of 239 (calculated, 251); 0.2% ash; 0% reducing sugar; and a $\bar{M}_n$ of 894 by vapor phase osmometry (calculated $\bar{M}$ is 873).

GPC analysis in THF solution through four Styragel columns (100, 100, 60, and 60 Å pore size) showed that particles were 53.8 Å number average chain length for constant index of refraction (Table IV). This corresponds to a $\bar{M}_n$ of 836 assuming Q = 15.5 ($\bar{M}$ calculated is 873 for a tallowate/AGU of 0.723). The ethoxylated glucoside tallow ester product comprised 12% of 73-111 Å, 30% of 56-73 Å, 53% of 29-56 Å, and 4.8% of particles in the lower range 15-29 Å.

2'-Hydroxydodecyl-1'-ether of ethoxylated ethylene glycol glycoside (V, x = 0, y = 10.6, z = 9) (product 26) (pilot plant run): To a 30 gal stainless steel reactor equipped with stirrer and automatic temperature control was charged 101.4 lb (0.15 mole) of ethoxylated ethylene glycol glycoside (OHV = 382 mg KOH/g; $\bar{M}$ = 676; EO/AGU = 10.6), 51.6 lb (0.30 mole) of a technical grade dodecane-1-oxide, which by GLC analyzed 93.8% dodecane-1-oxide, 4.4% unknown oxides, a trace of tetradecane-1-oxide and 0.0% decane-1-oxide, and 22.8 lb 1,2-dimethoxyethane solvent. The mixture was agitated with temperature control set to hold 91 C.

A catalyst solution composed of 1.52 lb boron trifluoride etherate and 7.6 lb 1,2-dimethoxyethane then was added portionwise. At first, 1.6 lb catalyst solution was added to the stirred mixture. The temperature in the reactor immediately began to rise rapidly and reached 104 C despite the automatic control. Auxiliary manual cooling then was used to control the reaction at 104 C. The initially insoluble mixture in the reactor becomes homogeneous as the reaction ensued. After 10 min, the addition of 1.1 lb more of the catalyst solution caused another rapid temperature rise. Control at 99 C was achieved quickly using full cooling capacity. As the temperature in the reactor dropped below 99 C and with full cooling still on, a third, 1.2 lb portion of catalyst solution was added. With this catalyst portion, however, the exotherm was not sufficient to raise the temperature above 91 C set by the cooling water capacity, and automatic control was regained. Finally, two additional catalyst solution portions of 0.5 lb each were added in succession to make a total of 4.9 lb catalyst solution added over a 30 min period. Although the reaction appeared to be complete at this time, the remaining 4.2 lb catalyst solution was added, and the mixture was heated for an additional 3-1/2 hr at 91 C to ensure that the reaction was complete.

After the mixture stood at room temperature overnight, the 1,2-dimethoxyethane solvent was stripped out at 104 C and 40-20 mm Hg with the aid of nitrogen sparging at 0.5 cfm. Then at 71 C, 1.5 lb 70% aqueous H_2O_2 was added to the residue with stirring. After the reactor temperature was raised to 104 C, another 1.5 lb H_2O_2 was added, and heating was continued for 1/2 hr until the product had a Gardner 6 color. Additional heating did not improve the color, so the reactor was evacuated to 25 mm Hg for 20 min at 104 C to decompose any remaining H_2O_2. There was obtained 153 lb (100%) viscous liquid (product 26).

The product had the following properties: OHV, 228 mg KOH/g (calculated for 2.0 C_{12}/10.6 EO/AGU was 249); 0% reducing sugar; specific rotation $[\alpha]_D^{21} + 21.9°$ (c, 1 in $CHCl_3$); specific gravity, 1.0831; and viscosity (Stokes), 22.8 (100%), 6.3 (50.1% aqueous solution), 1.4 (26.1% aqueous solution), and 0.10 (9.3% aqueous solution).

GPC analysis of a similar laboratory sample (product 25) in THF solution through four Styragel columns, (10^5, 10^4, 10^3, and 60 Å pore size) showed that particles were, for

TABLE V

Gel Permeation and Mol Wt[a] of Hydroxydodecyl Ether of Ethoxylated Glycol Glycoside (Product 25)

Elution counts (5 ml vols)	Cumulative wt, %	Peak ht ($H_i = M_iN_i$)	Chain length[b] ($A_i = M_i/Q$)	Number of particles ($N_iQ = H_i/A_i$)
27	100	13	158	0.082
28	95.3	66	103	0.641
29	71.5	106	69	1.536
30	33.2	57	46	1.239
31	12.6	20	34	0.585
32	5.4	9	22	0.415
33	2.2	4	15	0.267
34	0.7	2	10	0.194
		$\Sigma H_i = 277$		$\Sigma N_iQ = 4.959$

[a] $\bar{M}_n = 55.9Q = 867$ (assume Q = 15.5).

[b] $\bar{A}_n = \Sigma H_i/\Sigma N_iQ = 55.9$ Å average chain.

constant index of refraction, of 55.9 Å number average chain length (Table V). This corresponds to a $\bar{M}_n$ of 867 assuming Q = 15.5. $\bar{M}$ calculated for the composition as dodecyl ether of ethoxylated glycol glycoside of molar proportions 1.8 C_{12}/10.6 EO/AGU is 1016. This ethoxylated glycoside dodecyl ether comprised 28% of 69-158 Å particles, 38% of 46-69 Å particles, 20% of particles in the range 34-46 Å, and 12% in the lower range 10-34 Å. The detailed GPC analysis is given in Table V.

2'-Hydroxydodecyl-1'-ether of mixed, random polyalkoxylated ethylene glycol glycoside (V, x = 5, y = 10, z = 9) (product 45): Ethylene glycol glycoside (305.5 g; 0.325 mole), which had been polyalkoxylated by the procedure of Egan and Smiens (7) using 10 moles EO and 5 moles propylene oxide (PO)/AGU (calculated OHV, 272; found OHV, 276 mg KOH/g), was added to 138 g (0.750 mole) dodecane-1-oxide dissolved in 110 g 1,2-dimethoxyethane solvent. Even though the mixture was agitated rapidly, it did not form a complete solution. When 4.5 g boron trifluoride etherate, dissolved in 20 g 1,2-dimethoxyethane, was added to the mixture over a period of 15 min, the temperature rose to 60 C, and ca. 10 min later the mixture became a homogeneous, dark solution. After solution was heated at 90 C for 1.5 hr, it was allowed to stand overnight. When 1 g additional boron trifluroide etherate in 5 ml ethyl ether was added, no additional rise in temperature indicated that the reaction was complete. The solvent was removed from the reaction solution in a rotary vacuum evaporator at 90 C, and 4.5 ml 70% hydrogen peroxide was added which in 1 hr bleached the dark product to a light color. However, upon stripping at 100 C to remove excess H_2O_2, the product slowly darkened to a final color of Gardner 7-8. The yield was 442.7 g (theory, 443.5 g). The product formed a clear solution in water at concentrations above and below 0.1% but was cloudy at 0.1%. The product had an OHV of 173 (calculated for molar proportions 2.3 C_{12}/10 EO/5 PO/AGU is 189) and an $[\alpha]_D$ +18.4° (c, 1 in $CHCl_3$).

2,3-Dihydroxypropyl-α, β-D-glucopyranoside (glycerol glycoside): To 460 g (5.0 moles) glycerol containing 5 g concentrated sulfuric acid at 110-115 C was added, with vigorous stirring over 1.5 hr, 810 g (5.0 moles, dry basis) corn starch slurried in 300 ml toluene. With reflux condenser and Dean-Stark trap in place, the mixture was stirred continuously under reflux for 3-1/4 hr, during which time the free water contained in the corn starch was removed azeotropically and collected in the trap. The mixture then was neutralized with 5 g $CaCO_3$. Then, the reflux condenser was replaced with one arranged for downward distillation, and the toluene was distilled off. Stirring was continued, and the temperature was maintained at 115 C as the pressure on the system was lowered gradually to facilitate continued removal of the toluene. After all toluene was distilled off, a liter water was stirred gradually in and 100 g Nuchar decolorizing carbon was added. The mixture was stirred and refluxed for 3 hr and immediately filtered hot to remove the Nuchar and then filtered again cold to remove insolubles. The clear filtrate was Gardner color 8, which was considered too dark. The decolorization procedure was repeated with Nuchar, and the filtrate concentrated by rotary vacuum evaporation to 58.4% solids aqueous solution with a Gardner color of 2.

The solution contained 936 g anhydrous glycerol glycoside (74.0% yield based upon 2,3-dihydroxypropyl-α, β-D-glucopyranoside). Analysis on the concentrated product gave: OHV, 1143 (calculated, 1327); 0.2% reducing sugar; 3.3% H_2O; 0.2% ash; and an $[\alpha]_D^{20}$ + 78.2°.

Using three Porasil columns of 400XF, 250XF, and 60XF treated to reduce the captive sites on the silica polymer backbone and distilled water eluent, GPC showed only a single rather broad peak in the mol wt range 300-400. ($\bar{M}$ calculated for glycerol glycoside monomer, 256). Because the sample eluted in the area of poor resolution of the column, the composition of this product was not determined further.

Stearate ester of polyethoxylated glycerol glycoside (product 35): An aqueous solution of glycerol glycoside (686.0 g; 446 g nonvolatile; 1.84 moles) was concentrated to dryness in a Parr bomb by heating under vacuum. Then, 0.9 g glacial acetic acid, and 3.3 g sodium acetate was added. EO (811 g; 18.4 moles) was added over 10 hr at a reaction temperature of 177 C. A drop in pressure accompanied the complete uptake of the EO. The dark product amounted to 1181 g (93% of theory). Analysis revealed: OHV, 442 (calculated OHV for $\bar{M}$ = 690 and 5.6 hydroxyls/AGU is 454); 0.4% ash; and 0.00% reducing sugar.

The above polyethoxylated glycerol glycoside (354.0 g; 0.531 mole), 156.0 g (0.531 mole) Ashland Chemical's 95% methyl stearate, 10.0 g of potassium carbonate and 500 ml DMF were charged to a flask fitted with a thermometer, stirring shaft, and an 18 in. length of 6 plate bubble column. As the transesterification reaction proceeded, methanol was collected in a dry ice-acetone trap. The reaction was run under a pressure of 100-140 mm Hg. After 4 hr of heting at 124-140 C, the theoretical amount of methanol was collected. The reaction mixture was filtered to remove the potassium carbonate catalyst, combined with 40 g Nuchar decolorizing carbon, heated on the steam batch for 1 hr, and filtered. The solution then was vacuum stripped of DMF, and the residue product amounted to 420.9 g (85% of theory). It had a Gardner color of 15, an OHV of 247 (calculated, 274) and an SV of 67.8 (calculated, 64.5).

Sulfate of 2'-hydroxydodecyl-1'-ether of polyethoxylated ethylene glycol glycoside (product 16): To 218 g (0.183 mole) 2'-hydroxydodecyl polyethoxylated glycoside (V, x = 4, y = 8, z = 9) was added 100 g chloroform. A solution of 42.7 g (0.368 mole) chlorosulfonic acid (CSA) in 85 g diethyl ether was fed dropwise into the flask containing the glycoside solution. The exothermic reaction was maintained at a temperature of 20 ± 5 C by an external ice bath. After addition of the CSA was complete (ca. 20 min), the mixture was allowed to cool before neutralizing to pH 8 with 28.5 g sodium hydroxide as quickly as control of the exothermic heating would permit. The water and chloroform solvents were removed by a rotary vacuum evaporator. Titration of the sulfated residue product with diisobutyl phenoxyethoxyethyl dimethylbenzyl ammonium chloride (Hyamine 1622) showed the presence of 0.95 mole sufate/AGU.

Built detergent heavy duty formula: A blend of 3.06 lb 2'-hydroxydodecyl polyethoxylated ethylene glycol glycoside ether (product 26) and 15.28 lb light density sodium tripolyphosphate was prepared by stirring and kneading the initially heterogeneous mixture until there were no more lumps. Then, the mixture was rolled for 20 min in a 5 gal cylinder mounted horizontally on power rolls. A fully homogeneous and free flowing dry powder resulted.

A subblend of 8.25 lb anhydrous sodium sulfate mixed with a one-half portion of a mixture of 1.02 lb carboxymethyl cellulose (CMC, Hercules Inc., Wilmington, Del., medium viscosity) and 0.031 lb Tinopal RT-37 (optical brightener) was prepared. Another subblend was prepared consisting of 3.06 lb sodium metasilicate pentahydrate mixed with the one-half portion remaining of the CMC and Tinopal. The two homogeneous subblends then were simultaneously stirred into the glycoside-tripolyphosphate blend to form the basic detergent mixture, which was made into a fully homogeneous, dry powder by rotating 20 min on the power rolls. The free flowing powder weighed 30 lb. At 300 ppm hardness in water at 38 C, it removed 28.7% and at 100 ppm hardness and at 55 C, 31.7% of the soil from standard cloth washed by the standard procedure (8).

Surface-Active and Detergency Tests

The surface-active and detergency tests were air-water and mineral oil-water surface tensions, washing, and wet-out after Harris (8). The findings are summarized in Table I. Surface tension (air-water) lowering to 30 dynes/cm at 0.1% and interfacial tension (oil-water) lowering to 4 dynes/cm at 0.1% were found. Wet-out was as low as 24 sec (canvas disc wet-out time) and up to 34% soil removal occurred at 55 C in 0 ppm hardness water for 0.025% surfactant concentrations with builders (vs 26-34% same test with commercial controls).

Biodegradability Tests

Samples of the products were evaluated by a modification of the Borstlap and Kooijman (9) activated sludge procedure.

Activated sludge suspension: A fresh suspension, containing ca. 1% evaporation residue, came from a sewage purification pilot plant located in the Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio. It had a combined domestic and industrial sewage influent. This suspension was stored at 0 C.

Salt solution: The solution contained the following salts in specified quantities: $FeCl_3 \cdot 6H_2O$, 0.1 ppm; $CaCl_2$, 27 ppm; $MgSO_4 \cdot 7H_2O$, 25 ppm; and $(NH_4)_2SO_4$, 2 ppm. It further contained 0.125% of a phosphate buffer prepared by dissolving 3.4 g analytical reagent grade KH_2PO_4 in 50 ml distilled water, adding ca. 17.5 ml 1 N NaOH solution to pH 7.2 and making up to 100 ml.

Washing out of sludege suspension: Four 250 ml centrifuge tubes with 25 ml homogeneous activated sludge suspension were centrifuged for 15 min at 2600 rpm, and the upper water layer was discarded. The remaining solid material was mixed thoroughly with 150 ml distilled water and again centrifuged. This process was repeated 10 times. The solid material from each tube then was suspended separately in 25 ml salt solution and aerated at 25 C through a sintered glass filter with a maximum pore size of 40-60 μ for 16 hr at an aeration rate of ca. 1 liter/hr. The solution was stirred slowly throughout the aeration period.

Degradation: The test medium consisted of 940 ml salt solution, 10 ml aqueous solution at the concentration required of the compound being tested, and 50 ml washed-out activated sludge suspension. This mixture was placed in a 2 qt jar and stirred and aerated as described during the entire test period.

Analysis of Degradation Results

Nonionic surfactants: A loss of the surface tension lowering and a loss of foaming properties are considered valid indices of the biodegradation of nonionic surfactants (10). These parameters were measured to determine the degree of degradation of the nonionic surfactants. Also, since an increase in the microbial population may provide further evidence of biodegradation, bacterial counts were made at various intervals by a standard method (11). Initial and successive bacterial counts over the test period are reported/milliliter x 10^{-3} (Table II).

Foamability: The foamability of the nonionics during the degradation test was determined at intervals by pouring 100 ml portions of the filtered test medium into a 200 ml glass stoppered graduated cylinder. The cylinder then was shaken until maximum foam ht was obtained. A reading in milliliter foam ht was made immediately of the amount of foam present. The amount of foam was read again 60 and 180 sec after the initial reading. The number of hr required to attain minimum observed foam ht is reported in Table II.

Foam readings were not made on all samples; but, since the products are low foamers, the percent biodegradation was calculated from surface tension and methylene blue linear alkyl benzene sulfonate (LAS) data.

Surface tension: Samples taken daily, or even more frequently, were filtered through no. 1 Whatman filter paper before measuring the surface tension. Surface tension measurements were made periodically on each sample during the degradation test period on a Central Scientific Co. Tensiometer, catalog no. 70520, calibrated over the range γ = 18.4-γ = 74 dynes/cm. Percent biodegradation (D) (Table II) was calculated from the maximum observed surface tension at the time (γ_t), the initial surface tension (γ_o), and that of a blank consisting of the aerated sludge and nutrients but no surfactant and taken at the same time ($\gamma_{b,t}$):

$$D = \frac{\gamma_t - \gamma_o}{\gamma_{b,t} - \gamma_o} \times 100$$

Ionic surfactants: The percent biodegradation of the ionic surfactants (sulfates) was determined (Table II) by the methylene blue method (12). Degradation was calculated as percent decrease in LAS concentration.

Surface tension and bacterial population changes were measured also for the ionic surfactants according to the same procedure used for the nonionic surfactants.

RESULTS AND DISCUSSION

Synthesis and Structure

Compositions synthesized from alkoxylated starch glycosides to yield the esters and ethers studied are shown

in Tables I and II, along with their properties.

Glycoside esters: Following the general method of Osipow, et al. (13), polyol glycosides can be transesterified readily using fatty methyl esters. Reaction of methyl stearate with unalkoxylated ethylene glycol glycoside in our hands produced a stearated glycoside in fair yield. However, the water solubility of this stearated glycoside proved to be inadequate for aqueous detergency application. Transesterification reactions with polyethoxylated or mixed polyalkoxylated glycoside gave a more water-soluble product in good yields. These glycoside fatty esters were prepared generally from methyl stearate or tallowate and the alkoxylated glycoside in boiling DMF solvent by slowly distilling the DMF with the methanol formed. Alternatively, they were made by a solvent-free procedure (1). Methyl stearate and methyl hydrogenated tallowate esters of ethoxylated and mixed ethoxylated-propoxylated ethylene glycol or glycerol glycosides were produced with one or two C_{18} or $C_{16\text{-}18}$ groupings/AGU. The compositions were optimum to impart the desired solubility and surfactancy properties.

We made no attempt to determine the position or configuration of the fatty group attachments to the glycoside unit. The attachment could occur conceivably by any random combination using any or all the 4.6 average available hydroxyl sites in the alkoxylated glycoside (III). The ester surfactant structure (IV) shows the fatty group attached at the primary hydroxyl site of an alkoxylated chain. This structure is believed to represent a typical species of these ester glycosides.

GPC of a glycoside ester (Table IV) shows that there are many mol wt species present. For comparison, GPC of the starting alkoxylated glycoside is shown (Table III). The higher species, if less soluble, might be undesirable surfactants, but this effect was not explored. Any hydroxyl site of the polyol glucosides could serve to attach polyalkoxy chains, and any of these chains could be terminated either with fatty ester, fatty ether, or hydroxyl groupings. Selected alkoxylated fatty glycoside ester derivatives are reported in Tables I and II.

Glycoside ethers: Surface properties (Table I) were improved further by attaching the lipophilic group to the alkoxylated glycoside through a β-hydroxy ether linkage. In the presence of certain catalysts, epoxy compounds are opened readily by alcohols (14). Our study revealed that hydroxyl sites in an alkoxylated polyol glycoside also can open a terminal epoxy grouping in a reactant fatty molecule to yield a glycoside β-hydroxy fatty ether derivative like type V. The alkyleneoxy chains, as in the ester derivatives above, could be attached by any random combination to the polyol glycosides. In the ether derivative shown (V), the fatty group is at the most distant primary hydroxyl site. Any of the polyalkyleneoxy chains could be terminated by either a fatty hydroxy ether grouping or by a hydroxyl grouping. Fatty epoxides with 10, 12, and 14-16 carbons were reacted with either alkoxylated glycol or glycerol glycosides in glyme solvent or in emulsion and no solvent. The compositions were optimum to impart the desired solubility and surfactancy properties.

GPC of α-glycoside ether product is shown in Table V. Selected alkoxylated fatty glycoside ether derivatives are reported in Tables I and II.

Surface-Active and Detergency Properties

Even though surface-active and detergency properties of many of the alkoxylated polyol glycosides prepared already have been reported (1), a summary of selected examples is given in Table I for ready reference. Products 1 and 42 lead the table for comparison; they are polyalkoxylated glycol glycosides and show low detergency.

Glycoside ethers: The fatty ethers generally showed excellent surface-active and detergency properties. The best products were mixed alkoxylated ethers, such as products 29, 43, and 45, as demonstrated by their lowering of the surface and interfacial tensions of water, low canvas disc wet-out times and as much as 34% soil removal. The straight ethoxylated fatty ethers, such as product 25, also demonstrated good soil removal, but they generally gave slightly higher interfacial tensions and longer wet-out times than the mixed ethers. Product 16 is representative of the sulfate derivatives of this class. The sulfates prepared had inferior properties compared to the corresponding nonsulfated product; however, the optimum ratio of glycoside to alkylene oxide was not necessarily obtained. Glycerol glycoside-based product (37) appears to have properties equivalent to those based upon ethylene glycol.

Glycoside esters: When the lipophilic portion of the molecule was introduced through esterification, the product were inferior in surface-active and detergency properties to the corresponding fatty ether derivatives. Of those evaluated, product 10 which is a monotallowate of ethoxylated glycol glycoside, gave the best detergency properties. The addition of sulfate groups to the esters or the use of glycerol glycoside (product 35) as the base polyol did not improve their properties. Apparently a more extensive study is needed to ascertain the optimum composition for these ester derivatives.

Biodegradability

By all the criteria employed—foam collapse, surface tension, equivalent LAS concentration decrease, and multiplication of bacteria—several glycoside derivatives showed excellent percent biodegradability (D) when tested at initial concentrations (C_0) of 50 and 500 ppm in the presence of activated sludge (Table II). As anticipated, the straight ethoxylated glycol glycoside (product 1), which was the starting material for many of these products, was highly biodegradable even at the high C_0 of 500 ppm (D = 68% in 264 hr).

At C_0 of 50 ppm, the fatty ethers showed 80-89% degradability, while at 500 ppm the glycerol glycoside based ether (product 38) was 69% degraded.

The fatty esters gave even better biodegradability than the ethers. At C_0 of 50 ppm, product 10 was 100% degraded in 7 days and at C_0 of 500 ppm, it was 81% degraded in 4 days. Both the ethers and esters had a much higher rate of degradation than the commercial ethoxylated phenol, which had a maximum D of 20% during the 8 day test. Sodium lauryl sulfate surfactant gave the highest rate of degradation of any product studied.

Although the glycoside products are low foamers, evidence of biodegradability is seen from loss of foam ht. For example, product 38 with an initial foam ht of 210 ml produced only 160 ml (180 sec) after 11 days in the activated sludge.

An increase in bacterial population also indicates biodegradation. This was particularly true when the initial bacterial count was at the lower level of 195 x 10^3/milliliter. Note that the ester (product 10), which is the most degradable of new products tested, sustained the highest bacterial increase (1370 x 10^3/milliliter after 13 days) when evaluated at C_0 of 500 ppm.

ACKNOWLEDGMENTS

Analyses were by W.E. Link and coworkers of Ashland Chemical Co. Gel permeation chromatography was by M.R. Hallwachs also of Ashland Chemical Co. Projected manufacturing costs and, published earlier, the economics for producing 100 million lb/year glycoside fatty ether surfactant were by J. Lee (1). This work was conducted by Ashland Chemical Co. under Contract 12-14-100-9510(71) from the ARS, USDA. The contract was supervised by the Northern Regional Research Laboratory, Peoria, Ill.

REFERENCES

1. Throckmorton, P.E., D. Aelony, R.R. Egan, and F.H. Otey, Tenside Deterg. 10:1 (1973).
2. Otey, F.H., C.L. Mehltretter, and C.E. Rist, JAOCS 40:76 (1963).
3. McKillip, W.J., J.N. Kellen, C.N. Impola, R.W. Buckney, and F.H. Otey, J. Paint Technol. 42:312 (1970).
4. Leitheiser, R.H., C.N. Impola, R.J. Reid, and F.H. Otey, Ind. Eng. Chem. Prod. Res. Develop. 5:276 (1966).
5. Otey, F.H., B.L. Zagoren, F.L. Bennett, and C.L. Mehltretter, Ibid. 4:224 (1965).
6. Otey, F.H., B.L. Zagoren, and C.L. Mehltretter, Ibid. 2:256 (1963).
7. Egan, R.R., and L.D. Smiens, U.S. Pat. 3,382,285 (1968).
8. Harris, J.C., "Detergency Evaluation and Testing," Interscience Publishing, New York, N.Y., 1954.
9. Borstlap, C., and R.P. Kooijman, JAOCS 40:78 (1963).
10. Huddleston, R.L., and R.C. Allred, Ibid. 42:983 (1965).
11. American Public Health Association, "Standard Methods for the Examination of Water and Wastewater," Twelfth Edition, American Public Health Association, New York, N.Y., 1965, p. 592.
12. American Public Health Association, Ibid., p. 297.
13. Osipow, L., F.D. Snell, W.C. York, and A. Finchler, Ind. Eng. Chem. 48:1459 (1956).
14. Weissberger, A., "Heterocyclic Compounds with Three- and Four-Membered Rings," Part I, Interscience Publishers, New York, N.Y., 1964, p. 289.

[Received March 6, 1974]