Surfactants from Fatty Esters of Polyalkoxylated Polyol Glycosides

C.A. WILHAM, T.A. MCGUIRE, C.L. MEHLTRETTER and F.H. OTEY,
Northern Regional Research Laboratory,[1] Peoria, Illinois 61604

ABSTRACT

The glycoside raw materials used to prepare the surfactants were mixtures produced directly from low cost starch and the polyols by transglycosidation. After alkoxylation with ethylene oxide and propylene oxide, the glycosides were transesterified by the methyl esters of various fatty acids to yield the final products. Monolaurates of the polyalkoxylated glycosides containing a combination of 8 mol ethylene oxide and 4 mol propylene oxide per mole of glycoside showed detergency in an alkaline formulation comparable to two commercial detergents. An advantage in this application is the potential for complete biodegradation because of the fatty ester carbohydrate structures. The two monolaurates of glycerol glycoside polyethers containing 4.8 and 8 mol propylene oxide, in particular, produced oil-in-water emulsions of high stability.

INTRODUCTION

In 1946, Griffin (1) reacted glucose with propylene glycol to obtain a crude glucoside mixture. Polyethoxylation of the glucoside and esterification of the polyether by condensation with long chain fatty acids yielded products of value as emulsifying agents. Since then, Otey et al. (2) and Throckmorton et al. (3) used low cost corn starch as a starting material to prepare crude glycoside mixtures by transglycosidation with propylene glycol and glycerol. These investigators found that the reaction of propylene glycol glycoside (PGG) and glycerol glycoside (GG) mixtures with ethylene oxide (EO) and propylene oxide (PO), followed by transesterification with fatty acid methyl esters or by direct esterification with fatty acids, was an economically feasible procedure by which to make nonionic surfactants. Such products have potential in food processing and as biodegradable detergents. Previously we described the emulsifying properties of 24 such products in a simple French dressing (4).

This paper reports the surfactant properties of a series of fatty acid esters of polyethoxylated and polypropoxylated PGG and GG prepared by the procedure of Otey et al. (2). Comparative soil removal studies were made with a number of the nonionic surfactants in a detergent formulation containing an alkaline builder.

EXPERIMENTAL PROCEDURES

Forty-three fatty acid esters of polyethoxylated and polypropoxylated PGG and GG containing various ethoxyl and propoxyl contents and acyl substituents were synthesized by the three-step method of Otey et al. (2): (a) transglycosidation of starch with propylene glycol and glycerol, (b) alkoxylation with EO and PO and (c) transesterification with the methyl esters of long chain fatty acids. Extent of etherification was calculated from weight increase after addition of EO and PO to 1 mol glycoside mixture. Esterification of the products was determined indirectly by using the acetic anhydride-pyridine method (ASTM-D-1638-61T) for hydroxyl analysis before and after acylation. Substantially complete transesterification was indicated from the amount of methanol recovered.

[1]ARS, USDA.

RESULTS AND DISCUSSION

Standard tests (5) were chosen to evaluate the surfactant properties of the products. These included surface and interfacial tension, canvas disc wetting time, foam height and emulsion stability. In addition to the tests described by Harris (5), the detergency of nonionic products was determined in an alkaline formulation.

Table I records the surfactant properties of all the fatty ester polyalkoxylated glycosides prepared. Surface and interfacial tension values, as well as canvas disc wetting times, indicate that not all the products can be expected to be efficient surfactants.

Water Solubility

Almost all the esters produced either water clear or slightly opalescent aqueous solutions at 1% concentration. Milky dispersions resulted with ethoxylated (5 EO) PGG monostearate and monopalmitate and with the monolaurate of propoxylated GG (8 PO). Diesters containing less than 10 mol polyalkoxylation were also rather insoluble.

Emulsion Stability

Equal quantities (40 ml) of paraffin oil and aqueous surfactant (0.1% conc.) were shaken in 500 ml flasks for five cycles as described by Otey et al. (2) and each poured into 100 ml graduates. Time required for 10 and 20 ml of aqueous phase to separate was recorded.

Almost all products required from 10 to 15 min for 10 ml to separate. Exceptions were the propoxylated (5 and 8 PO) PGG monolaurate (17 and 19 min), and the propoxylated (5 and 8 PO) GG monolaurate esters (25 and 31 min). The mixed ethoxy-propoxy (8 EO, 4 PO) polyether of oleate GG and monolaurate PGG required 18 min. Approximately twice as much time was needed for 20 ml to separate. The monolaurate esters apparently have the necessary hydrophile-lipophile balance at the concentrations used to produce more satisfactory emulsification.

Surface and Interfacial Tension

Measurements were made with a Du Noüy interfacial tensiometer at 30 C. A light paraffin oil with Saybolt viscosity of 125-135 and a surface tension (air-oil) of 53 dynes/cm was used for (oil-aqueous solution) interfacial tension measurements.

Surface tension values for all products did not deviate from the 29-43 dynes/cm range even at the lowest concentration of 0.01%. However the mixed ethoxy-propoxy polyethers of the GG monolaurate ester series had the lowest values: 29-31 dynes/cm at both 1% and 0.1% concentration and 33 dynes/cm at 0.01% concentration. Surface tensions of the laurate esters of ethoxylated PGG and GG were 29-35 dynes/cm at 1% concentration, but values increased to 32-39 dynes/cm at 0.01% concentration. There was also a tendency for the surface tension to increase a few units as the moles of EO reacted increased from 5 to 20.

Interfacial tension (oil-aqueous solution) values for all products at concentrations of 0.1% and 1% were below 11

TABLE I

Properties of Fatty acid Ester Alkoxylated Glycosides

Glycoside	Surfactant composition, mol/mol glycoside			Acyl, %	Water solubility,[b] 25 C, 1% conc.	Emulsion stability, min	Interfacial tension, dynes/cm conc.,%		Canvas disc wetting time,[c] sec conc., %				Foam height, mm[d] Water			
													Distilled conc., %		300 ppm Hardness conc., %	
	Acyl	EO[a]	PO				1.0	0.1	1.0	0.5	0.2	0.1	0.5	0.1	0.5	0.1
Propylene glycol	Lauroyl															
	1	5	0	28.2	SO	10	2.6	3.7	13	22	88	c	135-120	70-60	125-100	60-35
	0.9	7.5	0	22.4	C	15	2.7	3.6	18	35	101	c	150-140	100-90	140-110	80-50
	1.1	10	0	24.0	C	15	3.0	3.4	28	36	133	c	135-110	85-70	130-100	70-50
	0.9	20		13.3	C	10	5.1	5.6	86	136	c	c	130-105	100-70	130-40	85-25
	0.9	5.5	1.8	21.6	C	12	3.0	3.6	18	24	74	c	140-90	85-55	110-20	25-15
	1	3.3	4	23.4	C	14	1.2	1.3	14	25	83	c	80-15	30-10	15-2	15-5
	0.9	8	4.5	16.7	C	18	---	3.1	14	27	82	c	100-70	55-20	40-5	30-10
	0.8	0	5	19.4	SO	17	2.3	1.9	---	---	93	c	35-15	20-5	5-0	5-0
	0.7	0	7.5	15.6	M	19	3.4	2.6	---	---	75	175	10-0	5-0	15-2	15-5
	1.9	5	0	44.2	M	3	2.8	7.5	---	62	c	c	30-15	15-5	5-0	10-0
	Palmitoyl															
	1	5	0	33.7	M	10	3.5	6.0	142	228	c	c		15-10		
	1	10	0	27.8	SO	11	4.7	6.5	209	c	c	c	100-80	45-30	90-45	50-30
	0.9	20	0	16.5	C	12	7.0	8.1	c	c	c	c	120-100	80-60	105-30	65-30
	Stearoyl															
	1	5	0	37.2	M	6	5.4	5.2	c	c	c	c	15-10	15-10	15-10	15-10
	0.9	10	0	26.8	SO	14	6.2	7.2	c	c	c	c	55-50	25-25	25-25	40-30
	0.9	20	0	18.3	C	14	9.3	9.9	c	c	c	c	65-20	50-40	50-40	50-35
Glycerol	Lauroyl															
	1	5.2	0	28.4	C	11	1.3	1.5	17	34	96	c	150-140	80-75	145-125	80-70
	0.8	7.5	0	19.2	C	10	1.7	1.5	44	55	104	c	160-150	110-100	150-140	110-100
	0.9	9.6	0	19.3	C	12	1.5	1.7	32	63	115	c	150-140	90-90	150-50	80-60
	0.7	14	0	17.8	C	12	1.9	1.9	36	66	184	c	150-60	105-80	150-50	100-60
	1	20	0	13.4	C	9	3.6	4.3	105	170	---	c	140-110	100-80	145-50	35-30
	1	5.3	2.2	22.9	C	9	1.7	1.5	11	24	102	c	145-125	95-70	135-115	25-15
	1	4	4	23.7	C	13	1.1	1.6	11	21	94	160	105-25	75-25	100-20	25-15
	1	8	4	17.8	C	16	2.4	3.5	11	32	111	c	115-25	85-45	120-15	55-35
	1.2	0	4.8	32.0	SO	25	1.2	1.5	20	34	79	c	100-20	65-30	0-0	15-10
	0.9	0	8	18.9	M	31	1.3	1.8	---	14	84	126	40-10	15-5	40-5	20-5
	Oleoyl															
	0.9	5.2	0	33.6	SO	13	3.2	4.3	126	187	c	c	15-15	15-10	25-15	15-12
	0.9	9.6	0	26.2	C	13	4.5	4.7	149	---	c	c	80-65	40-35	90-60	50-30
	0.9	14	0	20.7	C	11	4.4	5.8	138	210	c	c	100-80	60-55	120-20	40-30
	0.8	20	0	16.0	C	12	9.1	10.0	c	c	c	c	20-5	20-10	40-10	50-20
	0.9	8	4	23.0	C	18	6.5	7.2	93	133	232	c	65-40	40-30	60-30	40-25
	1.9	5.2	0	49.6	M	0.3	0.9	2.6	---	146	c	c	5-0	5-0	5-0	5-0
	1.7	9.6	0	38.4	M	9	7.5	10.8	82	160	c	c	15-15	10-10	15-10	15-10
	1.8	20	0	29.4	C	13	3.5	5.9	c	c	c	c	70-55	35-35	75-55	40-30
	1.9	8	4	36.7	M	4	7.0	9.3	73	133	c	c	25-20	15-10	5-0	15-10
	Palmitoyl															
	1	9.6	0	26.3	C	10	3.9	4.2	c	c	c	c	100-75	70-55	5-0	50-10
	1	20	0	17.5	C	9	3.3	3.6	c	c	c	c	140-120	90-70	130-20	60-40
	Stearoyl															
	1	5.2	0	36.2	---	13	3.2	4.3	126	187	c	c	15-15	15-10	25-15	15-12
	0.8	9.6	0	23.1	SO	13	3.5	4.7	149	---	c	c	80-65	40-35	90-60	50-30
	0.7	14	0	16.3	C	11	4.4	5.8	138	210	c	c	100-80	60-55	120-20	40-30

1	20	0	18.6	C	12	9.1	10.0	c	c	c	c	20-5	20-10	40-10	50-20
1	8	4	26.3	SO	11	6.5	6.8	c	c	c	c	65-45	40-40	55-40	50-30
1.9	20	0	30.3	SO	14	3.3	3.8	c	c	c	c	50-40	35-30	80-60	30-30

[a]EO = ethylene oxide; PO = propylene oxide.
[b]C = clear; SO = slightly opalescent; M = milky.
[c]Wetting time greater than 180 sec.
[d]Foam height, immediately and after 5 min.

dynes/cm, indicating good surfactant performance.

Canvas Disc Wetting Test

The wetting times of a 1 in. diameter no. 6 Mount Vernon canvas disc at concentrations of 0.1, 0.2, 0.5 and 1.0 g/100 ml of solution were used to compare efficiencies of these surface active agents. Almost all the products at 0.1% concentration required more than 180 sec to wet the disc. At 0.2% concentration, the two lower EO content monolaurate esters of PGG and GG required a maximum of 104 sec for wetting. As expected, increase in concentration of the products, in general, produced faster "wet-out," the lowest value being 11 sec at 1% concentration for the mixed alkoxylated monolauroyl GG.

Ross-Miles Foam Test

Foaming characteristics were evaluated in a Ross-Miles apparatus (6) at concentrations of 0.1% and 0.5% and 0 and 300 ppm water hardness at 50 C.

All products were low foamers; the monolaurates of most of the alkoxylated GG and PGG foamed better than the other fatty acid esters.

Initial foam heights in distilled water of the monolaurates of ethoxylated (5-20 EO) GG and PGG, ranged from 80 to 110 mm and from 130 to 160 mm at 0.1% and 0.5% concentrations, respectively. In water of 300 ppm hardness, initial foam height of these monolaurates, as well as foam height maintained after 5 min standing (foam stability), was not significantly lower than the distilled water values.

The propoxylated monolaurates of GG and PGG had reduced hydrophilic properties sufficiently, so that initial foam heights were much lower than their EO counterparts. Foam stability was poor with values on standing of 0-40 mm. Mixed alkoxylated GG and PGG fatty esters produced mixed results. The monolaurate of alkoxylated (5 EO, 2 PO) GG and PGG and the (4 EO, 4 PO) GG products had foam heights of 110-145 mm at 0.5% concentration in both hard and soft water. Foam stability was good only for the (5 EO, 2 PO) GG derivative.

Detergency

All surfactants prepared were evaluated for their soil removal efficiency in a detergent formulation consisting of sodium carbonate (1.1 g), sodium sulfate (0.28 g), sodium metasilicate (0.3 g), carboxymethyl cellulose (0.02 g) and surfactant (0.30 g). A 2.0 g sample of this formulation was used in 1 liter water of 150 ppm of hardness (Ca/Mg 2:1). Detergency was measured as the average increase in reflectance (ΔR) of six 4 x 4 in. swatches of U.S. Testing soiled cotton fabric after washing in a Terg-O-Tometer for 20 min at 49 C and 110 cycles per minute. After the swatches were rinsed in tap water and dried on steel plates at 80 C, their reflectance was determined with a Martin-Sweet automatic brightness tester. Percentage of soil removed was calculated from the equation (3):

$$\frac{R_W - R_S}{R_O - R_S} \times 100 = \%\ \text{soil removal}$$

R_W = reflectance after washing; R_S = reflectance of soiled fabric; R_O = reflectance of unsoiled fabric.

The monolaurate esters exhibited the best detergency, which generally was consistent with their surfactant properties. Soil removal values are recorded in Table II for only those values above 18%. None of the other esters reached 18% soil removal in the formulation used. The maximum percentage was 22.9 with the monolaurate of GG polyether containing 8 mol EO and 4 mol PO. This value compares well with those found for a commercial anionic detergent containing sodium tripolyphosphate builder and a commercial alkali-built, nonionic, heavy duty laundry detergent.

TABLE II

Detergency of Polyalkoxylated Glycoside Monolaurates

Mol/mol glycoside			
EO	PO	ΔR[a]	Soil removal, %
Propylene glycol glycoside			
5.5	1.8	10.9	18.0
8	4.5	13.6	22.4
0	5	12.1	20
7.5	0	11.1	18.3
Glycerol glycoside			
5.3	2.2	12.5	20.6
4	4	13.2	21.7
8	4	13.9	22.9
0	8	12.3	20.3
7.5	0	11.6	19.1
9.6	0	12.1	19.9
Commercial detergents			
Anionic		13.7	22.5
Nonionic		14.5	23.8

[a]ΔR is the change in reflectance of washed and unwashed cotton swatches. The least significant difference in ΔR between two means by analysis of variance at 95% probability was 0.75.

Biodegradability

The 5 day biochemical oxygen demand (BOD) test (7) was used with surfactants that showed significant detergency. The 20-29% BOD of theory obtained in 5 days (Table III) promises complete biodegradation of the products. Glucose, which is readily degraded biochemically, showed 66% theoretical degradation in the test.

TABLE III

Biochemical Oxygen Demand (BOD) of Polyalkoxylated Glycoside Monolaurates

Mol/mol glycoside			
EO	PO	BOD 5 days, mg O_2/mg	Per cent of theory[a]
Propylene glycol glycoside			
8	4.5	0.33	20
10	0	0.37	24
0	5	0.42	29
Glycerol glycoside			
4	4	0.41	28
8	4	0.33	23
5.3	2.2	0.36	25
9.6	0	0.34	23
0	8	0.35	25
Glucose (control)		0.70	66

[a]For complete degradation.

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REFERENCES

1. Griffin, W.C., Atlas Powders Co., U.S. Patents 2,407,001; 2,407,002; 2,407,003 (1946).
2. Otey, F.H., C.L. Mehltretter and C.E. Rist, JAOCS 40:76 (1963).
3. Throckmorton, P.E., D. Aelony, R.R. Egan and F.H. Otey, Tenside 10:1 (1973).
4. Wilham, C.A., T.A. McGuire, C.L. Mehltretter and H.H. Palmer, Food Prod. Develop. 7:59 (1973).
5. Harris, J.C., "Detergency and Testing," Interscience Publishers, New York, 1954, p. 41.
6. Ross, J., and G.D. Miles, Oil Soap 18:99 (1941).
7. "Standard Methods for the Evaluation of Water and Wastewater," 13th Edition, APHA, New York, 1971, p. 489 (first printing).

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