Polyoxyethylene Ethers of Some Polyol Glycosides and Their Fatty Esters[1]

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Abstract

Starch heated with a polyol, such as ethylene glycol, propylene glycol, or glycerol, in the presence of an acid catalyst undergoes transglycosidation and forms a mixture of polyol glycosides. This mixture is sufficiently heat-stable to permit polyetherification with ethylene oxide. The preparation and properties of a number of glycoside polyoxyethylene ethers are described.

Nonionic emulsifying agents were prepared by reacting glycoside polyethers with either saturated or unsaturated long-chain fatty acids and linseed oil. In general, the esterified glycoside polyethers exhibited good emulsifying action, and the unsaturated esters of the polyethers possessed film-forming properties.

Introduction

SORBITOL and methyl glucoside, derived from glucose, are sufficiently heat-stable to withstand direct esterification and polyetherification (170–250C). These polyols are useful raw materials for the preparation of surfactants (2,4,7). By reaction with the lower alcohols (1), starch may also be used to make heat-stable glucosides. However, little information is available on its reaction with higher boiling alcohols. This paper describes the reaction of starch with ethylene glycol and other alkyl polyols and subsequent polyoxyethylation followed by esterification.

Starch was reacted with alkyl polyols in the presence of an acid catalyst at elevated temperatures. Removal of unreacted alkyl polyols by vacuum distillation yielded optically active products essentially non-reducing to Fehling's solution. A mixture of substances was indicated by paper chromatography. Presumably transglycosidation occurred with the formation of polyol glycosides of mono-, di-, and oligosaccharides. In general the crude products are tan or brown solids. have low viscosities above 120C, and can be heated above 190C in the presence of an alkaline catalyst without appreciable decomposition. The use of glycols or glycerol, instead of ethanol or methanol, permits higher reaction temperatures at atmospheric pressure and yields products with higher hydroxyl content.

Attempts to esterify these polyol glycosides directly were unsuccessful. However, they react readily with ethylene oxide to produce polyethers that are easily esterified by the direct method and by transesterification. The esters have good emulsifying properties, and the unsaturated esters produce films upon drying at room temperature.

Experimental

Transglycosidation. Ethylene glycol (2 moles) and concentrated sulfuric acid (0.5 g) were heated under a blanket of nitrogen to 80C in a three-necked flask equipped with stirrer, thermometer, and Dean-Stark condenser. Starch (0.5 mole) was added with good stirring, and the slurry heated rapidly to 130C. Immediately a thick paste formed, which remained for about 10 min, then the mixture became a viscous solution. After this solution was held at 130C for 45 min, it was held under vacuum (water pump) at 120C for 15 min. The acid catalyst was neutralized with solid sodium bicarbonate after which the unreacted glycol was removed at 1-mm pressure as the temperature was slowly raised to 150C. The crude product was amber colored and slowly solidified upon cooling to about 60–70C. Weight increase in the final product indicated 0.74 mole of glycol per anhydroglucose unit (AGU). Analysis indicated 0.04 mole of this increase was unreacted ethylene glycol.

A number of glycoside preparations are listed in Table I. Runs were also made with equal molar quantities of starch and ethylene glycol, and the resulting product was etherified without removal of unreacted glycol. However, laboratory-scale preparations were more easily stirred when a 3-mole excess of glycol was used. Only a slight increase in the amount of ethylene glycol reacted was observed with either a longer reaction time or a larger excess of glycol. Propylene glycol and glycerol were reacted with starch by the same procedure described for ethylene glycol. Starch used in these reactions was air-dried and contained 11.3% water. Dry starch may also be used without any apparent change in the product.

Characterization of Ethylene Glycol Glycosides. Crude products obtained by reacting ethylene glycol with starch contained virtually no reducing sugars by the Somogyi (9) method of analysis. However dilute acid ($1.5N$ H_2SO_4) hydrolysis for 3 hr produced about 95% of the theoretical reducing sugar expressed as glucose. Lambert and Neish's (6) method of determining glycerol in the presence of glucose was used to analyze for unreacted residual ethylene glycol in the crude product. A sample of the product was diluted to 10 ml, acidified, and allowed to react 5 min with 5 ml of $0.1\ M$ sodium periodate. Formaldehyde was then determined by the color reaction with chromotropic acid. The crude product contained only 2–4% free ethylene glycol; however upon acid hydrolyses the ethylene glycol content was near theory.

TABLE I

Reaction of Starch With Some Alkyl Polyols

Ratio of Reactants—Moles polyol per mole AGU[a]	Cooking time,[b] hr	Polyol groups per AGU[c]	Free polyol groups per AGU[d]	Reducing sugar,[e] %
	Ethylene glycol			
4.0	1.0	0.74	0.04	0.06
4.0	1.3	0.77	......	......
4.0	2.0	0.78	0.05	0.03
5.4	1.0	0.83	0.08	0.07
5.4	2.3	0.83	0.07	0.05
	Propylene glycol			
3.0	1.3	0.66	......	......
3.4	2.0	0.60	......	......
	Glycerol			
4.0	1.0	0.75	......	......

[a] Catalyst was 0.4–0.5% sulfuric acid based on wt of starch.
[b] Approx heating time at 120–130C before neutralization with $NaHCO_3$.
[c] Based on wt of final product.
[d] Unreacted polyol by chromotropic acid analysis.
[e] By Somogyi analysis expressed as glucose.

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Paper chromatographic analysis of the crude product, using butanol-pyridine-water solvent and ammoniacal silver nitrate spray, showed at least three spots and also indicated high-molecular weight material near the origin. The spots had R_G values of approximately 1.7, 1.3, and 0.5 where R_G is the rate of travel of the unknowns per rate of travel of glucose. Compounds having R_G values of 1.3 and 0.5 were eluted from the paper, acid hydrolyzed, and analyzed for reducing sugar and ethylene glycol. Reducing monosaccharide obtained from the spot with an R_G of 1.3 was equivalent to 50 to 60% of the total carbohydrate. An equal molar amount of ethylene glycol was also obtained indicating that this spot was ethylene glycol glucoside. The spot with an R_G of 0.5 contained about 20% of the total carbohydrate and a half mole equivalent of ethylene glycol, indicating that it was ethylene glycol diglucoside. The third spot with an R_G value of 1.7 was small. The carbohydrate near the origin contained very little glycol and may consist of oligosaccharide glycosides. The acid hydrolyzed crude product gave only glucose and ethylene glycol spots.

Glucose reacted with ethylene glycol, according to the procedure of Griffin (5), gives a chromatogram similar to that observed for these starch products.

Results of the analyses show that the ethylene glycol is chemically combined with degraded starch. We have also shown that ethylene glycol and glucose are the products of mild hydrolysis, which is indicative of glycosidic linkages. Thus our data indicate that the reaction of starch and ethylene glycol gives glycol glycosides, principally of glucose with lesser amounts of oligosaccharide glycosides.

Polyoxyethylation of Polyol Glycosides. A mixture of polyol glycosides was heated in a three-necked flask fitted with nitrogen sparge tube, stirrer, thermometer, and an outlet tube (7,10). Either sodium bicarbonate or sodium hydroxide (0.1–0.5%) was added, and the nitrogen sparge was replaced with ethylene oxide. The initial reaction temperature was about 180–190C. As the reaction progressed however, its rate increased so rapidly that it was necessary to lower the temperature slowly to about 125–130C. The extent of etherification was determined by increase in weight. The amber product could then be either decolorized with carbon or bleached with hydrogen peroxide. In Table II a number of polyethers prepared by this method are listed in the order of increasing ethylene oxide content. Highest viscosities were observed for the polyethers of the propylene glycol glycosides. Experimental hydroxyl numbers for the ethylene glycol products indicate 4.4–4.6 hydroxyls per AGU.

TABLE II

Preparation and Properties of Polyoxyethylated Polyol Glycosides

Polyol glycoside,[a] moles AGU	Reaction time,[b] hr	C_2H_4O groups per AGU[c]	Hydroxyl number, exptl.	Viscosity,[d] cp	Color[e]
	Ethylene glycol glycosides				
1.1	4.5	4.6	626	69,000	7
1.1	5.0	5.9	527	27,000	9
1.1	8.0	6.7	526	14,100	11
1.1	7.0	8.3	451	7,850	9
1.1	9.5	9.7	407	4,700	6
0.2	8.0	15.0	339	1,408	11
0.5	11.5	20.0	......	1,296	13
	Propylene glycol glycosides				
0.5	6.0	6.6	......	32,000	......
0.6	8.0	7.1	......	14,500	12
0.2	6.0	13.0	395	2,600	14
	Glycerol glycoside				
0.2	8.5	11.0	......	3,260	......

[a] Same avg polyol content as products in Table I.

[b] Reactions were started at about 180C and slowly decreased to about 130C. Catalyst, 0.1–0.5% sodium hydroxide or sodium bicarbonate.

[c] Avg of ethylene oxide groups/anhydroglucose unit (AGU) based on increase in wt.

[d] Brookfield, Model LVF at 25C.

[e] Gardner (1933) color. Products with colors below 12 were treated with carbon (Darco G-60).

Esterification of Polyoxyethylated Polyol Glycosides. Procedures for esterification were essentially the same as those described previously for the preparation of methyl glucoside esters (3,7). To a 250-ml three-necked flask fitted with a gas-dispenser inlet, thermometer, magnetic stirrer, and a Dean-Stark trap with condenser were charged the polyoxyethylated ethylene glycol glycosides, fatty acids, litharge, and enough xylene to give a good reflux at 180C. The amount of fatty acid added depended upon the degree of esterification desired. The contents were heated rapidly, under a blanket of nitrogen, to 180C. Samples were removed at various intervals and titrated to determine the free acid content remaining. In general the monoesters and diesters required about 2 and 5 hr, respectively, at 180C to reduce the acid number to below 5. Xylene was then removed by increasing the temperature to about 200C *in vacuo*, and the lead was precipitated with adipic acid. The crude esters were amber colored and could be decolorized with either activated carbon or hydrogen peroxide. Properties of a number of polyether esters prepared by this procedure are listed in Table III.

Esters prepared from the glycerol and propylene glycol glycoside polyethers had about the same properties as those described for ethylene glycol products.

Transesterification with Linseed Oil. Into the previously described equipment was placed 26.2 g (0.03 mole) linseed oil, 50 ml xylene, and 33 g (0.03 mole)

TABLE III

Preparation and Properties of Fatty Acid Esters of Ethylene Glycol Glycoside Polyethers

Ester	Cooking time,[b] hr	C_2H_4O groups per AGU	Acid No.	Viscosity[c]	Color[d]	Surface tension 0.1% aq. conc. 25C	Water sol. 1%[e]	Emulsion stability[f]
Monooleate	2.0	16	....	V	14	40	S	20
Monooleate	2.0	20	4.0	T	14	38	S	16
Monostearate	2.5	20	1.0	Solid	Dark	42	S	21
Dilaurate	5.5	16	4.0	Q	Dark	33	S	23
Dilaurate	5.5	20	2.7	O	14	32	S	25
Dioleate	5.0	20	....	R	Dark	40	S	20
Distearate	5.5	20	....	Solid	Dark	44	D	16
Dilinolenate	6.0	16	5.0	N	15	39	D	16
Dilinolenate	4.5	20	5.8	N	15	39	S	19
Dilinseedate	5.0	15	1.4	R	12	39	D	7
Dilinseedate	3.0	20	....	N	14	41	S	26
Linseedate[g]	2.5	20	....	M	12	40	D	16

[a] 0.05 Mole (AGU) of the polyether was reacted with 0.05 or 0.1 mole of the fatty acid depending on the ester desired. Litharge catalyst (0.5% based on fatty acid).

[b] Temp: 180–190C.

[c] Gardner bubble viscometer.

[d] Gardner (1933) color; esters treated with carbon (Darco G-60).

[e] Stable milky dispersion = D; clear solution = S.

[f] Time in min for 10 cc of water to separate from a mineral-oil and water emulsion.

[g] Prepared by transesterification of equal molar quantities of linseed oil and the polyether.

TABLE IV

Properties of Films from the Unsaturated Esters

Ester	C_2H_4O groups per AGU	After 72 hr drying time	
		Type of film	Water test[a]
Dilinolenate	16	Slightly tacky	Failed
Dilinolenate	20	Tacky; soft	Failed
Dilinseedate	15	Slightly tacky	Good
Dilinseedate	20	Tacky	Good
Linseedate	20	Slightly tacky	Good

[a] Good, no apparent change in film; failed, film washed off but did not dissolve.

of an ethylene glycol glycoside containing 20 mole equivalents of ethylene oxide. No additional catalyst was added since there was sufficient alkaline catalyst in the polyether from the etherification reaction. The reactants were heated under nitrogen with stirring at 150C for 1.75 hr, during which time a solution was formed. The solution was then slowly heated to 260C for 45 min (2). Properties of this linseedate are listed in Table III.

Physical Characteristics of the Esters

Emulsifying Properties. Forty milliliters of 0.1% aqueous solution of the polyether esters were mixed with 40 ml of light paraffin oil, N.F., in a 500-ml glass-stoppered Erlenmeyer flask and manually shaken in five cycles. Each cycle consisted of five violent downward motions and 1 min of standing. The emulsion was then poured into a 100-ml graduate cylinder, and the time required for 10 ml of the aqueous phase to separate was recorded (10). Values for these esters, reported in Table III, are comparable to those reported for methyl glucoside polyether esters (7).

Film-Forming Properties. Polyether unsaturated esters (3 g) were mixed with enough naphthenate drier to give a mixture containing 0.42% lead and 0.042% cobalt. The esters were then drawn into films with a doctor blade at a wet thickness of 0.005 in. on glass plates. After drying 72 hr at room temperature, the films were characterized as reported in Table IV. An additional 48 hr of drying did not appreciably change film properties. A "water test" was made by allowing 5.2 liters of water, at 27C, to run from a spigot onto the films (8). The water-soluble esters, which form relatively insoluble films upon drying, have potential utility as emulsifiers in water-base paints.

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A Study of the Biodegradation of Anionic Synthetic Detergents

A New Laboratory Test

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Abstract

The biodegradation of anionic synthetic detergents is studied by means of a new laboratory test. The bacterial source used in this test is activated sludge from the Sewage Works at Amsterdam. Important differences in biological "softness" were found between various detergents with this test, which gives results similar to those found in pilot plant experiments.

Introduction

MANY PUBLICATIONS, especially from the United Kingdom, have dealt with troublesome foam in Sewage Works and rivers which is caused by the presence of non-degraded anionic synthetic detergents in effluent.

From the work done so far it is clear that a certain type of synthetic detergent viz. the alkylbenzene sulfonate based on propylene tetramer (DOBS PT) is the main offender because the heavily branched structure of this product is attacked more slowly and to a lesser extent by the bacteria in the Sewage purification process than e.g., primary alcohol sulfates or other synthetic detergents with straighter chains.

In this laboratory the biodegradation of syndets has been studied by means of a test using water from the river IJ as the source of bacteria for the degradation and also by means of activated-sludge pilot-plant experiments (1).

The river-water test, which can be considered representative for biodegradation of anionic detergents in open water, is carried out by making a solution of the anionic detergent in the water and storing this solution without aeration. The amount of detergent degraded by the bacteria present in the water is determined at suitable intervals by the method of Longwell and Maniece (2,3,4).

As the IJ-water test gives a very slow degradation we set out to develop a laboratory test which was likely to provide conditions nearer to those prevailing in actual Sewage Works.

Description of the Test

To a solution of various inorganic salts in distilled water activated sludge from the Sewage Works in Amsterdam and a small amount (10 ppm) of an anionic detergent are added. The mixture is aerated at room temp. Every day homogeneous samples containing the activated sludge are taken from the test liquor and the amount of detergent left is determined according to the method of Longwell and Maniece. The test lasts for seven days after which in general the ultimate hard residue is reached. As activated sludge usually contains material that interferes in the determination of the amount of detergent, this must first be removed. For this purpose the activated sludge suspension is washed with distilled water by centrifugation, resuspended, and aerated before use.