components in the proportions determined by the GLC study for the top (benzene-ethanol-water 41:7:1) and the bottom (5:28:18) phases of the BEW system. The flasks were shaken and the solvent systems used immediately for the development of another set of plates. No difference could be detected in the resolution or clarity of the aflatoxins on the plates prepared using this instant BEW preparation from that obtained with BEW systems using overnight equilibration.

Because ethanol is the most costly reagent in this solvent system and the bottom layer contains four times as much ethanol as the top layer, it is worthwhile to use the bottom layer repeatedly. This is possible because the bottom layer of solvent is in the bottom of the developing tank and does not come in contact with the TLC plate. Thereby the cost of using the BEW system is substantially reduced.

The instantly prepared BEW system containing benzene-ethanol-water 41:7:1 in the top layer and 5:28:18 in the bottom layer was used in our laboratory almost exclusively for over a year with repeatedly excellent resolution. The bottom layer (50 ml) was not replaced or supplemented during an entire week's operation, which ranged between 5 and 20 plates, while 25 ml of the top layer was pipetted into a clean trough for each run. However, after various laboratories around the country that had been asked to evaluate the system reported mixed success, apparently related to climatic conditions, a study was made to determine the effect of minor moisture differences on the system. Separate TLC plates were prepared using solutions containing the proportions indicated in Table I for set 1 and set 2, as well as the top layer of set 1 with the bottom layer of set 2, and the top layer of set 2 with the bottom layer of set 1. Improved separation of the aflatoxins was obtained in proportion to the amount of water in the system, with the best plate being the one prepared with the top layer of set 1 and the bottom layer of set 2. Additional plates were prepared varying the component proportions of the solution in the indicated direction until the optimal resolution, size and position of the aflatoxins on the plate were established. This system is composed of solutions of 40:6:3 for the top layer or trough solution and 4:27:20 for the bottom layer (% v/v benzene-ethanol-water, respectively). While the top layer preparation had a cloudy appearance after shaking and frequently separated into two phases with time, no adverse effect was found if the solution was thoroughly shaken just prior to use.

Evaluation of this system by six laboratories over the past year has shown it to be consistently superior to the previous BEW solvent system and less affected by climatic conditions. Optimum results are obtained by placement of the developing chamber in a constant temperature cabinet at 68-70 F.

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Ethoxylated Glycerol and Propylene Glycol Glycoside Palmitates from Lactose

ABSTRACT

Polyoxyethylene polyol glycoside palmitates were prepared by the following successive reactions: transglycosylation of lactose by glycerol and propylene glycol to yield crude mixtures of the polyol glucosides and galactosides; alkoxylation with ethylene oxide; and tranesterfication by methyl palmitate. Almost all the solid waxy products exhibited low surface and interfacial tensions and good emulsion stability; they are expected to be effective food emulsifiers, cosmetic surfactants and biodegradable industrial surfactants.

Lactose is a crystalline sugar isolated from cheese whey (1). The potential supply of this sugar is estimated to be more than a billion pounds annually, based on the availability of whey solids in 1968 (2). Recovery and fractionation of whey are among the more encouraging proposals for the solution of pollution problems associated with whey disposal (3). An aspect of this approach would be the development of new industrial uses for lactose.

Lactose is a disaccharide composed of D-glucose and D-galactose in 1,4-linkage and certain of its derivatives, like those of glucose, (4-6) may have potential for use as food additives. Polyoxyethylene ethers derived from carbohydrates and long chain fatty acids, such as sorbitan polyoxyethylene monostearate, have been approved by the FDA for addition to food products in small amounts. Presumedly polyoxyethylene ethers of glycosides prepared from lactose and glycerol or propylene glycol would also be of interest for similar addition to foods. Proof of nontoxicity would be required, however, for FDA approval of such products for food additive use. We therefore prepared a series of polyoxyethylene glycerol and propylene glycol glycoside palmitates from lactose as the base sugar. Lactose was reacted separately with glycerol and propylene glycol by transglycosylation to yield predominantly mixtures of the corresponding glucosides and galactosides, as shown below:

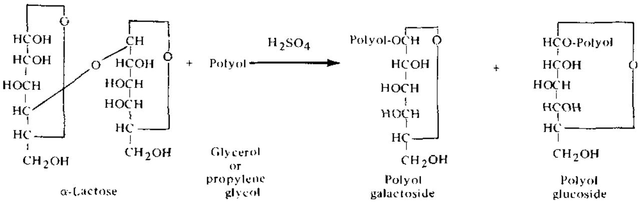

TABLE I

Surfactant Properties of Ethoxylated Polyol Glycoside Palmitates

Product composition, mol/mol glycoside			Emulsion stability,[b] min	Interfacial tension,[c] dynes/cm conc., %	
Palmitoyl	Polyol	EO[a]		1.0	0.1
Glycerol glycoside					
1.0	0.9	2.5	9.5	4.5	5.5
2.0	0.9	2.5	3.5	4.0	8.5
1.2	0.9	5.0	13.0	4.9	6.8
1.7	0.9	5.0	1.4	4.4	5.9
Propylene glycol glycoside					
0.9	0.6	3.9	11.8	9.3	10.0
1.9	0.6	3.9	11.8	5.6	5.9
1.0[d]	0.6	6.3	11.8	7.0	7.3
1.9	0.6	6.3	4.0	6.3	10.8

[a] EO = ethylene oxide.
[b] Time for 10 ml water to separate
[c] Between light paraffin oil and water.
[d] Liquid product.

The polyol glycosides are probably mixtures of the alpha and beta configurations. Byproduct glycosides present could include polyol lactosides and possibly glycosides obtained from reversion products of glucose and galactose. The crude mixture obtained by transglycosylation was next etherified with varying amounts of ethylene oxide, followed by transesterfication with methyl palmitate to afford the ethoxylated polyol glycoside palmitates.

In a typical preparation by the general methods of Otey et al. (5) and Throckmorton et al. (7), a mixture of 4.0 mol anhydrous glycerol, 0.52 mol lactose (Difco Laboratories) and 0.76 ml concentrated sulfuric acid was heated in a nitrogen atmosphere at 100 C and 35 mm pressure of Hg for 30 min, and at 130 C for 30 min to complete the transglycosylation reaction. After neutralization with barium carbonate, excess glycerol was removed by vacuum distillation. The amount of glycerol that had reacted was determined by weight increase of the mixture. The product was dissolved in water, decolorized with carbon (Darco G-60) and then concentrated in vacuo (water pump) on a steam bath and finally at a reduced pressure of 1 mm Hg for 3 hr.

The dried product was heated with 1.5 g potassium hydroxide in a nitrogen atmosphere for 1 hr at 125-130 C. The temperature was then raised to 160-185 C and ethylene oxide introduced. Almost 4 hr was required to add 2.5 mol ethylene oxide. The product was dissolved in water, decolorized with carbon, adjusted to pH 6-7 and concentrated to dryness in vacuo. A portion of the ethoxylated glycerol glycoside (0.28 mol) was dried at 125 C for 1 hr at 1 mm Hg pressure under nitrogen. Methyl palmitate (0.28 mol) preheated with 0.9 g potassium carbonate to 170 C was reacted with the glycoside at 185-190 C with quantitative methanol recovery. The transesterification was complete in ca. 7 min, but the reaction was continued for 30 min more to disproportionate any di- and triesters to the monoester. The final product was bleached with a few grams of 50% hydrogen peroxide and neutralized to pH 7 with concentrated hydrochloric acid.

All final products were tan-colored waxy solids except one of the propylene glycol glycoside polyether palmitates, which was a liquid. They formed turbid solutions at 1% concentration in water.

The amount of glycerol reacted with lactose indicated that extensive transglycosylation occurred with predominant formation of monoglycosides. In contrast, propylene glycol appeared to produce more of the higher glycosides, such as diglycosides, than did glycerol, as only 0.6 mol of the glycol had reacted per mole of monosaccharide.

Table I shows the composition of the products, together with emulsion stability and interfacial tension values determined as described by Wilham et al. (8). Doubling of the palmitoyl substitution in the glycerol glycoside polyether (2.5 EO), on one hand, significantly reduced emulsion stability without much effect on the interfacial tension values at 1% concentration. On the other hand, a similar change in palmitoyl content of the propylene glycol glycoside polyether (3.9 EO) did not modify emulsion stability but greatly lowered the interfacial surface tension. Surface tension values for all products were between 31 and 35 dynes/cm at 1% concentration in water and between 36 and 44 dynes/cm at 0.01% concentration.

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