Lactose-Derived Surfactants: II. Fatty Esters of Lactitol[1]

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ABSTRACT

Lactitol, prepared by reduction of lactose, was transesterified successfully with a series of fatty methyl esters with the aid of alkaline catalysts at 90 C. This was in marked contrast to previous experiences with lactose. Lactitol laurate, palmitate, stearate, and tallowate were prepared in this manner. Their surface-active properties, such as detergency, emulsification time, and lime soap dispersant requirement, were comparable to those of corresponding lactose derivatives. Addition of ethylene oxide to the esters was accomplished under conditions of alkaline catalysis and elevated temperatures. Surface-active properties of the oxyethylated derivatives were compared with those of the unoxyethylated esters described above. The improvement in surface-active properties is ascribed primarily to an increase in water solubility. Biodegradation studies under aerobic conditions showed that the rate of degradation of lactitol and lactose palmitates equalled or exceeded that of sodium hexadecyl sulfate.

INTRODUCTION

Lactose obtained from whey is potentially an inexpensive raw material for the preparation of biodegradable surfactants. As previously discussed (1), the chemical structure of lactose is well suited to serve as the hydrophilic portion of a nonionic, surface-active agent. Accordingly, several fatty acid esters of lactose were prepared and evaluated with respect to their detergency behavior, emulsification time, and lime soap dispersant requirement (LSDR) (1). At that time, it was noted that, unlike fatty esters of sucrose (2), esters of lactose are formed with difficulty. For example, no reaction could be obtained when the transesterification of lactose with fatty acid esters was attempted. The lack of reactivity was ascribed to steric factors caused by the close proximity of the two primary hydroxyl groups of lactose in contrast to the lack of blockage afforded to the three primary hydroxyls of sucrose. Also, lactose, a reducing sugar, is markedly sensitive to alkaline agents used as transesterification catalysts. Our past experience demonstrated the necessity of recourse to the more effective acyl halide reagents.

Lactitol, obtained by reduction of lactose, was not expected to give the difficulties experienced with lactose. The more commercially feasible transesterification process, it was anticipated, would take place more readily. This approach had been taken by Taniguchi and coworkers in 1964 (3). However, these workers reported no detergency data, although they did study properties, such as surface tension, emulsification power and foaming power of lactitol laurate, palmitate, stearate, and linoleate. The presently reported work describes the preparation and surface-active properties (detergency, emulsification time, and LSDR) of lactitol laurate, palmitate, stearate, and tallowate, as well as of their oxyethylated derivatives, together with a cursory biodegradation study of the palmitate esters.

EXPERIMENTAL PROCEDURES

Materials

α-Lactose monohydrate was obtained from Sigma Chemical Company, St. Louis, Mo.

Methyl laurate, methyl palmitate, and methyl stearate were prepared from the appropriate purified fatty acids by esterification with methyl alcohol and subsequent distillation. Each of the esters was over 99.3% pure as shown by gas liquid chromatography (GLC). Methyl tallowate was obtained from Procter and Gamble, Cincinnati, Ohio, as no. 1618 methyl ester, analysis: C_{18} esters (68.1%), C_{16} esters (28.8%), and C_{14} esters (3.1%).

Procedures

Lactitol: To a solution of 54.0 g lactose monohydrate (0.150 mole) in 450 cc water was added a solution of 6.3 g sodium borohydride (0.165 mole) in 150 cc water, dropwise with stirring over 15 min, while maintaining the temperature at 5-7 C. The solution was allowed to warm to room temperature and after an additional 2 hr, Amberlite IR-120 (H^+ form) was added slowly with stirring until gas evolution ceased. An additional 150 cc resin were added and stirring was continued for 15 min. The resin was

TABLE I

Lactitol Esters Detergency Data $(\Delta R)^a$

Compounds and concentrations	Testfabrics		EMPA		U.S. Testing	
	300 ppm H_2O	50 ppm H_2O	300 ppm H_2O	50 ppm H_2O	300 ppm H_2O	50 ppm H_2O
Laurate (0.1%)	18.5	17.0	11.0	12.2	8.9	8.8
Laurate (0.02%)	5.5	3.7	4.3	7.5	1.7	3.2
Palmitate (0.1%)	20.0	19.9	6.5	11.2	10.2	10.0
Palmitate (0.02%)	15.2	16.1	8.1	13.3	9.5	8.3
Stearate (0.1%)	21.3	20.6	7.3	11.0	11.2	10.3
Stearate (0.02%)	14.1	18.1	7.2	12.3	8.4	8.7
Tallowate (0.1%)	21.4	19.6	6.2	12.0	10.2	9.5
Tallowate (0.02%)	16.1	17.6	9.0	13.1	8.3	8.4
Control^b (0.1%)	25.3	26.0	8.8	11.3	9.2	10.9
Control (0.02%)	15.5	18.1	7.5	12.6	7.6	8.8

$^a\Delta R$ = increase in reflectance after washing.
^{b}Triton X-100.

TABLE II

Ethoxylated Lactitol Esters Detergency Data (ΔR)[a]

Compounds and concentrations	Testfabrics		EMPA		U.S. Testing	
	300 ppm H_2O	50 ppm H_2O	300 ppm H_2O	50 ppm H_2O	300 ppm H_2O	50 ppm H_2O
Laurate (0.1%)	15.1	14.6	10.2	13.4	8.1	9.3
Laurate (0.02%)	3.0	4.7	4.1	5.9	2.2	3.3
Palmitate (0.1%)	19.4	17.2	5.6	10.7	9.2	10.0
Palmitate (0.02%)	17.7	15.1	8.0	13.6	8.7	8.8
Stearate (0.1%)	19.1	19.1	8.0	13.2	9.9	10.2
Stearate (0.02%)	15.7	14.5	7.7	12.4	9.0	8.1
Tallowate (0.1%)	19.4	18.4	5.9	12.5	9.0	10.9
Tallowate (0.02%)	16.2	15.5	8.8	12.7	8.7	9.0
Control[b] (0.1%)	25.3	26.0	8.8	11.3	9.2	10.9
Control (0.02%)	15.5	18.1	7.5	12.6	7.6	8.8

[a]ΔR = increase in reflectance after washing.

[b]Triton X-100.

removed by filtration, and the filtrate was evaporated to dryness in vacuo. The residue was dissolved in methanol and then the mixture was reevaporated at reduced pressure. This process was repeated four times to remove boric acid as methyl borate. The final product was a noncrystalline solid (yield 85-90%) and contained no reducing sugar.

Fatty acid esters of lactitol: To a solution of 0.15 mole lactitol in 300 ml dimethylformamide (DMF) was added 0.05 mole fatty acid methyl ester and 0.80 g potassium tertiary butoxide catalyst. The reaction flask was equipped with a distilling head and condenser, and its system was maintained at 90-95 C under reduced pressure (140-160 mm) while stirring for 16 hr. The solution was cooled to room temperature and extracted several times with petroleum ether to remove unreacted methyl ester. The DMF solution was evaporated to dryness in vacuo, and the residue was dissolved in 200 ml chloroform and 50 ml water and transferred to a separatory funnel. The aqueous phase was extracted with a second portion of chloroform. The combined chloroform extracts were dried and evaporated in vacuo to obtain the crude product. The IR spectrum of the latter showed a strong ester peak at 1735 cm^{-1}, as well as hydroxyl absorption at 3350 cm^{-1}. Thin layer chromatography (TLC) (n-BuOH-AcOH-Et$_2$O-H$_2$O; 9-6-3-1) showed one major component (monoester) and two minor components (higher esters). Crude yields (assuming monoesters) of 30 and 39% were obtained for the laurate and palmitate, respectively, and were 40 and 55% for the stearate and tallowate. To ascertain the degree of esterification, a saponification number determination was carried out with the lactitol laurate. Saponification number calculated for lactitol monolaurate: 106.5. Found: 120.0.

Oxyethylations: These reactions were affected as described previously (1) by alkali-catalyzed addition of 6 moles ethylene oxide to lactitol esters dissolved in t-butanol. Once again the reactions were carried out in a stainless steel autoclave at 80 C with magnetic stirring. The absorption of ca. 6 moles ethylene oxide was confirmed by wt gain and by elemental analysis. However, the products are undoubtedly mixtures formed by random addition of the oxide to any or all of the seven hydroxyl groups afforded by the lactitol ester. No attempt was made to separate the mixture into its components.

Surface-active properties: Detergency measurements were carried out as previously described (1) in a Tergotometer operated at 120 F for 20 min at 110 cycles/min. EMPA (cotton), Testfabrics (cotton-polyester with permanent press finish), and U.S. Testing (cotton) cloths were washed with 0.10 and 0.02% concentrations of the esters. No additives were present. The detergencies of the esters and their oxyethylated products were compared at two water

TABLE III

Lactitol Esters Surface-Active Properties

	Atlab emulsification time (sec)	LSDR[a] (%)
Laurate	14	19
Laurate + EO[b]	23	18
Palmitate	113	18
Palmitate + EO	234	16
Stearate	66	19
Stearate + EO	272	14
Tallowate	67	11
Tallowate + EO	250	9
Control[c]	52	4

[a]LSDR = lime soap dispersant requirement.

[b]EO = ethylene oxide.

[c]Triton X-100.

TABLE IV

Biodegradation of Lactitol and Lactose Esters of Palmitic Acid Compared with Sodium Hexadecyl Sulfate

Compound	Percent carbon reduction after elapsed time (days)			
	2	5	9	22
Sodium hexadecyl sulfate	59	77	83	90
Lactitol palmitate	58	85	85	92
Lactitol palmitate + EO[a]	66	84	84	91
Lactose palmitate + EO	37	65	73	85
Lactose palmitate	42	70	76	91

[a]EO = ethylene oxide.

hardnesses (50 and 300 ppm). Triton X-100 (Rohm and Haas Co., Philadelphia, Pa.) was used as a control. Detergency was determined by means of reflectance measurements, and the results, compiled in Tables I and II, are given in terms of difference in reflectance (ΔR) before and after washing.

Emulsion stabilities were measured in an Atlab Emulsion Test Apparatus using standard procedures (1), and LSDR were determined according to the Borghetty and Bergman method (4). Results are summarized in Table III and discussed below.

Biodegradation: Biodegradability was determined in replicate runs under aerobic conditions at 25 C by the Esso controlled nutrient procedure (5) in which the test detergent at 40 ppm was the sole source of carbon and energy. Activated sludge from a local sewage treatment plant was

TABLE V

Biodegradation Surface Tension Values for Lactitol and Lactose
Esters of Palmitic Acid and Sodium Hexadecyl Sulfate

Compound	Time (Days)			
	0	1	2	3
Sodium hexadecyl sulfate	37.1	63.8	66.5	69.0
Lactitol palmitate	36.6	71.8	---	---
Lactitol palmitate + EO[a]	32.6	71.8	---	---
Lactose palmitate + EO	36.0	73.1	---	---
Lactose palmitate	38.2	69.1	---	---

[a]EO = ethylene oxide.

used as the source of inoculum. The course of biodegradation was followed by the measurement of loss of carbon and by the increase in surface tension (5). The extent of biodegradation was expressed as percent carbon reduction calculated from $\frac{\text{carbon content found}}{\text{initial carbon content}}$ x 100. Tables IV and V list the averages of replicate experiments.

DISCUSSION

Lactitol can be prepared by reduction of lactose with sodium borohydride (equation I).

(I)
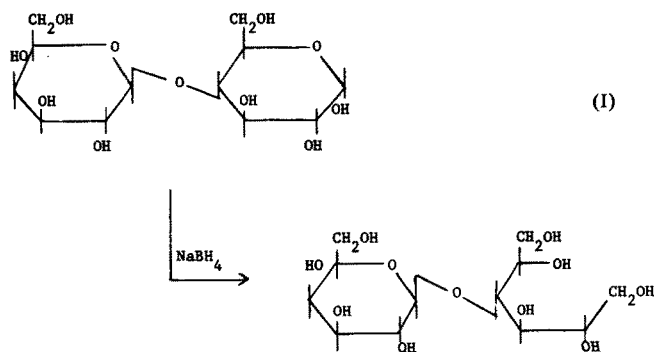
In contrast with lactose, lactitol has three primary hydroxyl groups, two of which are less rigidly bound and presumably more readily accessible for transesterification. The steric problem associated with the primary hydroxyls of lactose has been discussed above and can explain their apparent unreactivity. Transesterification reaction conditions that failed with lactose were found to succeed when applied to lactitol. Lactitol laurate, palmitate, stearate, and tallowate were prepared. Monoesters were the principal products formed, and this was confirmed by TLC and by saponification number.

Tables I and II summarize the detergency data obtained by use of our lactitol esters and their ethoxylated derivatives. The compounds were used at concentrations of 0.1 and 0.02%. As might be expected, better ΔR results were

obtained at the higher concentration. Comparison of ΔR values from tests in 50 and 300 ppm hard water showed no great difference with Testfabrics (cotton-polyester) or UST (cotton) cloths, but differences were greater with EMPA (cotton) swatches. Similarly, a comparison of Table I with Table II reveals no improvement in detergency stemming from the addition of ethylene oxide to the lactitol esters, even though the adducts were more water soluble. The control detergent (Triton X-100) appeared to perform better than the lactitol derivatives in washing of Testfabrics but was not superior with EMPA or UST cloths.

The data in Table III reveal that the oxyethylated lactitol esters possess greater emulsifying power (as exhibited by longer emulsification times) than the esters that were not oxyethylated. This was contrary to the results reported for our lactose esters and their ethylene oxide adducts. On the other hand, LSDR were only slightly improved by addition of ethylene oxide.

With respect to biodegradation studies, Table IV shows the percent carbon removal for the lactitol and lactose esters compared to a sodium hexadecyl sulfate control, which has been established as readily biodegradable (6). There is virtually no difference between the lactitol palmitate and its oxyethylated derivative, which degrades at about the same rate as sodium hexadecyl sulfate. Lactose palmitate appears to have a slower rate of degradation, but, after 22 days, the amount of carbon removed equals that of the lactitol esters. Oxyethylation of lactose palmitate causes a reduction in the rate of biodegradation. Apparently, the opening of the glucose moiety of lactose to form lactitol and its esters results in a somewhat more linear structure aiding in their metabolism by the sewage microorganisms. Table V shows the complete loss of surface activity which occurred in 1 or 2 days with all of the test compounds.

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