Lactose-Derived Surfactants (I) Fatty Esters of Lactose[1]

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ABSTRACT

Lactose, the principal solid component of whey, is a potentially inexpensive and abundantly available raw material. Its chemical structure is well suited to serve as the hydrophilic portion of a nonionic surfactant molecule. Accordingly, a series of esters of lactose was prepared by reaction of fatty acid chlorides with anhydrous lactose in N-methyl-2-pyrrolidinone. Monoesters of lauric, myristic, palmitic, stearic, oleic, and tallow fatty acids were obtained in this manner. Other methods of synthesis of the products were investigated but were unsuccessful. The lactose esters and their oxyethylated products were evaluated for detergency behavior, emulsification time, and lime soap dispersant requirement. The results indicate that their surfactant properties are comparable to those exhibited by analogous sucrose derivatives.

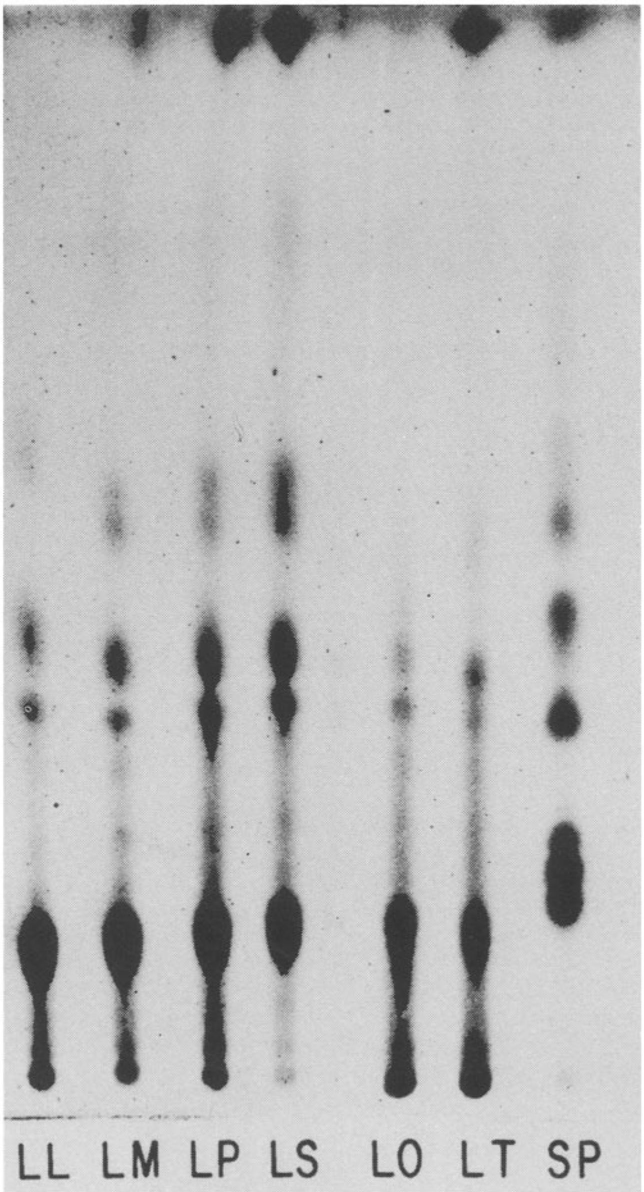


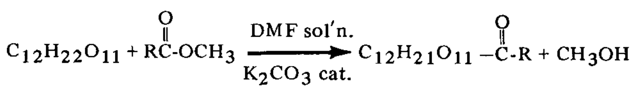
FIG. 1. Thin layer chromagram of esters. LL = lactose laurate, LM = lactose myristate, LP = lactose palmitate, LS = lactose stearate, LO = lactose oleate, LT = lactose tallowate, and SP = sucrose palmitate.

INTRODUCTION

The disposal of whey, the principal by-product of cheese production, has become a major problem in pollution from agricultural products. For every lb cheese produced there are ca. 8-9 lb liquid whey formed. Recent (1970) U.S. Department of Agriculture statistics show that ca. 22 billion lb of fluid whey are produced annually, of which ca. a third is used in food or as a supplement to animal feeds. The remaining two-thirds, ca. 14.8 billion lb, lacks an industrial outlet and is disposed of as sewage.

Liquid whey is essentially a dilute (5.0-5.5%) solution of lactose. The lactose concentration varies with the composition of the original milk, the extent of fermentation, and the method used to expel the whey during the production of cheese. Liquid whey contains ca. 7% solids. The composition of whey solids is typically: 72% lactose, 13% protein, 8% ash (salts), 4% water, 2% lactic acid, and 1% fat. Lactose from whey is potentially an inexpensive industrial chemical raw material if an area for its utilization can be developed.

The chemical structure of lactose indicates that it would be suitable as the hydrophilic moiety in a surfactant molecule. Furthermore, presumably the sugar-based surfactant would be biodegradable, probably more so than the nonionic polyglycol ethers used as surface-active agents and derived from petroleum-based C_{12}-C_{18} alcohols. A variety of surfactants has been prepared from another disaccharide, sucrose; and it was assumed that lactose derivatives would possess similar activity. Sucrose esters of long chain fatty acids, such as sucrose laurate, myristate, palmitate, and stearate, were prepared in 1956 by Osipow, et al., (1) by transesterification of the appropriate fatty ester with sucrose using potassium carbonate as catalyst.



$$C_{12}H_{22}O_{11} + R\overset{O}{\overset{\|}{C}}\text{-}OCH_3 \xrightarrow[K_2CO_3\ cat.]{DMF\ sol'n.} C_{12}H_{21}O_{11}-\overset{O}{\overset{\|}{C}}\text{-}R + CH_3OH$$

When a 3:1 molar ratio of sucrose to methyl esters is used, the product has been reported to contain 85% monoester + 15% diester. Other methods for preparation of sucrose esters have been developed, including interesterification of sucrose with fatty esters in propylene glycol solutions containing ca. 50% sodium soap (2) and interesterification of molten sucrose and fatty acid esters (3), as well as reaction of sucrose with α-sulfo fatty acids (4).

To obtain maximum surface activity in sugar esters, the presence of monoesters, rather than di- or polyesters, is preferred, not only for optimum detergency, but also for improved water solubility. Structurally, lactose possesses some advantages over sucrose, since it has but two primary hydroxyl groups vs. three in sucrose. Because primary hydroxyl groups are more reactive, it was anticipated that monoester formation from lactose would be easier than from sucrose. Also, the two primary hydroxyls of lactose are of unequal chemical reactivity so that bromine-water oxidizes the primary hydroxyl of the glucose moiety, while

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TABLE I

Detergency Data (0.1% Concentration)

	ΔR^a Values					
	Testfabrics		EMPA		U.S. Testing	
Compounds	300 ppm H_2O	50 ppm H_2O	300 ppm H_2O	50 ppm H_2O	300 ppm H_2O	50 ppm H_2O
Lactose laurate	19.6	17.5	8.9	12.6	8.3	8.4
Lactose laurate +E.O.[b]	20.6	18.6	9.5	14.8	7.7	8.6
Lactose myristate	19.9	18.2	8.6	15.0	8.7	9.0
Lactose myristate +E.O.	19.3	19.2	9.4	15.1	8.0	8.8
Lactose palmitate	13.4	14.7	5.0	13.9	8.8	8.0
Lactose palmitate +E.O.	16.8	16.9	7.1	15.7	7.6	6.1
Lactose stearate	13.9	11.2	5.6	11.6	7.2	7.6
Lactose stearate +E.O.	16.2	13.7	8.6	12.6	6.9	8.2
Lactose oleate	14.7	16.1	4.4	10.4	8.7	7.4
Lactose oleate +E.O.	14.9	13.2	8.0	13.3	5.0	7.5
Lactose tallowate	14.4	16.1	7.6	13.7	7.3	7.0
Lactose tallowate +E.O.	12.5	12.5	7.4	11.4	6.3	6.4
Sucrose palmitate	17.6	17.2	5.9	13.4	7.2	7.6
Sucrose palmitate +E.O.	6.8	5.4	6.3	8.6	3.8	4.5
Control	25.8	25.3	7.3	11.7	9.3	10.0

[a] ΔR, increase in reflectance after washing.

[b] E.O. is ethylene oxide.

that of the galactose remains intact (5). Under properly chosen conditions, it was expected that fairly clean monoacyl derivatives of lactose could be prepared with good surface-active properties.

EXPERIMENTAL PROCEDURES

Materials

α-Lactose was obtained from commercial sources as the monohydrate and was dried azeotropically as described below. All the fatty acids (except the tallow fatty acids) were purified by standard distillation and crystallization procedures and were found to have a purity in excess of 99% by gas liquid chromatography (GLC). The tallow fatty acids were obtained from Acme Hardesty, Jenkintown, Pa., and were composed of oleic 41.4%, stearic 21.0%, linoleic 3.2%, palmitic 29.3%, palmitoleic 2.8%, and myristic 2.3% acids.

Procedures

Preparation of lactose esters: The following general procedures was found to be the most satisfactory for preparation of the esters.

A solution of 72.0 g (0.20 mole) α-lactose monohydrate in 500 ml N-methyl-2-pyrrolidinone was heated with 100 ml benzene and allowed to reflux until all water present in the system was removed with the aid of a Dean-Stark tube. The benzene then was removed by distillation, and the mixture was cooled to room temperature. Ca. 20.0 ml pyridine was added to the dried lactose solution, and a solution containing 0.067 mole fatty acyl halide in 50 ml N-methyl-2-pyrrolidinone then was added dropwise with stirring at room temperature. (The acyl halide was prepared preferably from the fatty acid and oxalyl chloride or obtained by redistillation of commercially available materials.) After 5 hr of stirring at room temperature, 500 ml water was added, and the mixture was extracted with several portions of carbon tetrachloride. After the extract had been dried over anhydrous magnesium sulfate, solvents were evaporated under reduced pressure and the residue recrystallized usually from acetone or methyl ethyl ketone. This method was used to prepare lactose esters of lauric, myristic, palmitic, stearic, oleic, and tallow fatty acids. It should be noted that the lactose tallowate was not recrystallized after preparation to avoid fractionation of the product. Crude yields of 88-95% were obtained in all cases.

Analysis of the esters proved to be difficult because of their hygroscopicity and the known nonstoichiometric reaction of lactose and its derivatives with base (6). Thin layer chromatography (TLC) was useful in showing that the product consisted of a mixture of esters, with the monoester predominating. This was confirmed by elemental analyses of the purified esters. Although quantitative estimation of sucrose esters has been achieved via densitometer measurements of spots on TLC plates (7), this method was not used at this time.

TLC of lactose esters: Commercial (Analtech Uniplates) TLC plates of silica gel (250 μ thickness) were prewashed with a solvent system of 80% chloroform, 10% methyl alcohol, 8% acetic acid, and 2% water. After air-drying, the plates were spotted from left to right with 3 microliters of a 1% solution of the ester in chloroform. The plate was air-dried for 10 min and developed in the aforementioned solvent system. After air-drying for 30 min, the plate was sprayed with bichromate-sulfuric acid reagent and charred in a heating oven. Figure 1 illustrates the behavior of lactose esters on TLC. For comparison, a sample of sucrose palmitate prepared by the standard interesterification technique in dimethyl formamide (DMF) was also spotted on the same plate. In contrast to the sucrose palmitate, each lactose ester had one principal spot, believed to be the monoester, close to the origin. The sucrose palmitate seemed to afford three readily defined spots containing esters which were somewhat less polar than those from lactose.

Oxyethylations: A solution of 0.02 mole sugar ester (100% monoester was assumed) in 100 ml t-butanol and 0.10 g potassium hydroxide were placed in a 200 ml stainless steel autoclave. The later was evacuated and flushed with nitrogen. Ethylene oxide (0.12 mole) was distilled into the reaction vessel which then was sealed and heated at 80 C for 2 hr with magnetic stirring. The autoclave then was cooled to room temperature, and the solvent was removed by heating in a rotary evaporator at 60 C under less than 1 mm pressure. The addition of 6 moles of ethylene oxide was confirmed by wt gain and by elemental analyses.

Surface active properties: Detergency measurements were carried out in a Tergotometer operated at 120 F for 20 min at 110 cycles/min. Five 4 in circles of EMPA (cotton), Testfabrics (cotton-polyester) with permanent press finish, and U.S. Testing (cotton) cloth were washed

TABLE II

Detergency Data (0.02% Concentration)

	ΔR^a Values					
	Testfabrics		EMPA		U.S. Testing	
Compounds	300 ppm H_2O	50 ppm H_2O	300 ppm H_2O	50 ppm H_2O	300 ppm H_2O	50 ppm H_2O
Lactose laurate	14.0	11.8	7.2	11.5	6.9	6.3
Lactose laurate +E.O.[b]	12.7	11.3	9.6	12.4	6.9	6.8
Lactose myristate	13.9	13.4	7.4	11.7	6.7	6.5
Lactose myristate +E.O.	14.4	13.6	10.6	11.4	7.7	7.0
Lactose palmitate	10.6	10.4	5.7	10.3	5.6	5.8
Lactose palmitate +E.O.	12.2	12.2	9.0	11.0	6.3	6.6
Lactose stearate	7.9	10.5	5.7	8.6	4.9	5.0
Lactose stearate +E.O.	9.6	9.9	7.6	9.9	5.6	6.1
Lactose oleate	12.5	11.1	5.9	9.9	6.6	5.7
Lactose oleate +E.O.	11.4	10.9	9.5	11.0	6.4	6.4
Lactose tallowate	9.4	8.1	8.5	10.4	5.3	5.3
Lactose tallowate +E.O.	11.3	8.8	5.8	8.5	4.4	4.3
Sucrose palmitate	15.1	14.9	7.3	11.4	5.8	6.5
Sucrose palmitate +E.O.	3.3	3.0	6.0	7.3	2.6	3.7
Control	16.1	14.7	7.7	12.1	6.7	7.4

[a] ΔR, increase in reflectance after washing.

[b] E.O. is ethylene oxide.

with 1 liter solutions of the esters at concentrations of 0.10 and 0.02%. Mechanical stirring was necessary to attain good solution or dispersion of the esters prior to washing. Detergency was measured by the increase in reflectance, ΔR, after washing. The detergencies of the esters and their oxyethylated products were compared at two water hardnesses (50 and 300 ppm). A commercially available nonionic surfactant, Triton X-100 (Rohm and Haas Co., Philadelphia, Pa.), was used as a control. Results appear in Tables I and II.

Emulsion stability was measured in an Atlab Emulsion Test Apparatus. A 0.20% aqueous solution of the ester (25 ml) was shaken with 25 ml petrolatum in a 2 oz wide mouth bottle for 3 min. The emulsion was poured into the viewer, and the time required for a 10% separation of either phase was recorded. Again Triton X-100 was used as a control. Results are given in Table III.

Lime soap dispersant requirements (lsdr) were determined according to the method of Borghetty and Bergman (8). This test gives the amount of lime soap dispersing agent that must be added to 100 g sodium oleate to keep the calcium and magnesium soaps dispersed in water of 330 ppm hardness expressed as calcium carbonate. Results are included in Table III.

DISCUSSION

As previously cited (1), formation of fatty esters of sucrose can be affected by interesterification of an excess of the latter with the appropriate methyl ester. The reaction often is carried out at 60-90 C using DMF or dimethyl sulsoxide (DMSO) as solvent with potassium carbonate as catalyst and application of a mild vacuum to remove methyl alcohol as it is formed. Studies of variation in reaction conditions have been carried out (9), as well as an investigation of the influence of solvents on the degree of acylation of sucrose (10). It was, therefore, rather surprising that extension of this general method to interesterification of lactose with methyl stearate led to complete recovery of the latter. Accordingly, variations in reaction conditions were investigated all with negative results. These parameters included the use of solvents, such as DMF, DMSO, and N-methyl-2-pyrrolidinone; higher temperatures (up to 150 C); decreases in pressure; and use of catalysts other than potassium carbonate, e.g. potassium t-butoxide, potassium hydroxide and sodium methoxide.

An explanation of the apparent lack of reactivity of lactose toward interesterification with methyl esters in

TABLE III

Surface Active Properties

Compounds	Emulsification time (sec)	Lime soap dispersant requirement (percent)
Lactose laurate	17	9
Lactose laurate +E.O.[a]	95	8
Lactose myristate	23	9
Lactose myristate+E.O.	14	9
Lactose palmitate	198	15
Lactose palmitate +E.O.	62	10
Lactose stearate	63	30
Lactose stearate +E.O.	52	13
Lactose oleate	214	11
Lactose oleate +E.O.	97	9
Lactose tallowate	190	17
Lactose tallowate +E.O.	178	11
Sucrose palmitate	180	11
Sucrose palmitate +E.O.	103	21
Control	52	4

[a] E.O. is ethylene oxide.

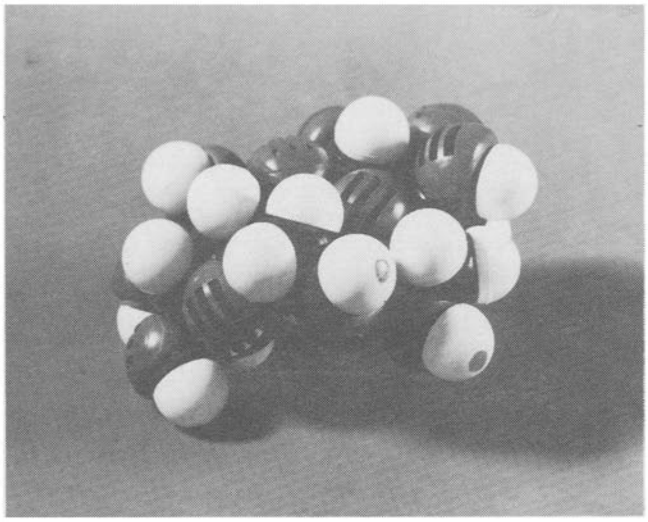

FIG. 2. Lactose model; primary hydroxyl groups indicated with dots.

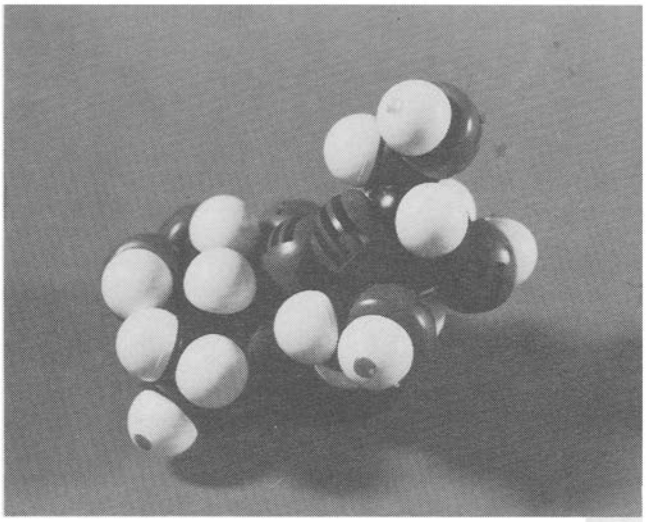

FIG. 3. Sucrose model; primary hydroxyl groups indicated with dots.

contrast to the results obtained with sucrose was afforded by a study of Ealing CPK atomic models (Fig. 2 and 3). Examination of the lactose and sucrose molecules constructed from these models (the primary hydroxyls are marked for clarity) indicates that the two primary hydroxyl groups in lactose are close spatially to each other and are blocked markedly in contrast to the three primary hydroxyls in sucrose. The same conclusion can be reached by use of Dreiding models. To overcome this steric factor, the use of a powerful acylating agent, such as an acyl halide, was required.

Successful acylation of lactose was achieved by use of fatty acyl halides in conjunction with an HCl acceptor, such as pyridine. Initial experiments were carried out at 90 C in N-methyl-2-pyrrolidinone, but it was later observed that this approach was effective even at room temperature.

Tables I and II summarize the detergency data obtained by use of our lactose esters at concentrations of 0.1% and 0.02%, respectively. As expected, the ΔR values are greater in Table I, obtained by use of the more concentrated solutions (0.10%), than are those in Table II (0.02%). Comparison of the ΔR values from 50 and 300 ppm hard water show no great difference with Testfabrics (cotton-polyester) or U.S. Testing (cotton) cloths, but differences were appreciably greater with EMPA (cotton) swatches. In general, for the series of lactose esters, ΔR values were best for the lower members of the series, the laurate, myristate, and palmitate, probably because of increased solubility. Furthermore, although the addition of ethylene oxide to the esters increased their solubility in water, the addition appeared to have no salutary effect upon detergency. Similar results have been reported for oxyethylated sucrose esters (11). The washing performances of the lactose and sucrose esters with Testfabrics cloth were somewhat inferior to those of the control detergent.

Greater emulsifying power, as shown by longer emulsion times in Table III, was displayed by the higher mol wt members of the ester series because of their greater lipophilic bulk. Once again, the addition of ethylene oxide appeared to offer only a solubility advantage but none in performance. Best lsdr were displayed by lower molecular members of the series, probably because of greater water solubility. This is borne out by the fact that the ethylene oxide adducts of the lactose esters all show improved lsdr over those which are not oxyethylated.

It can be stated that the fatty esters of lactose appear to possess performance characteristics which equal or sometimes surpass those of the analogous sucrose esters. However, an economical synthetic approach to the lactose esters still needs to be developed.

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