Efficient Synthesis of Fatty Monoglyceride Sulfates from Fatty Acids and Fatty Acid Methyl Esters

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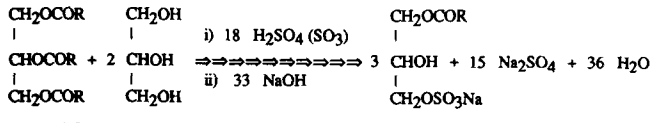
An efficient high yield synthesis of fatty monoglyceride sulfates from fatty acids or fatty acid methyl esters, glycerine and chlorosulfuric acid in chloroform using stoichiometric amounts of reagents was developed. Sodium coco monoglyceride sulfate was prepared in 79% yield with 93% purity from coco fatty acids. Similarly, sodium palm kernel monoglyceride sulfate in 57% yield and sodium palm monoglyceride sulfate in 71% yield were obtained from palm kernel fatty acid methyl esters and palm fatty acids, respectively. This new synthetic method produced better quality products with higher active ingredients and improved yields without having to use such cost prohibitive, high purity, fatty acid monoglycerides, and it reduced the undesirable aqueous sodium sulfate by-product by 60% over a current commercial process. The product's composition and purity were confirmed by cationic titration, infrared and C-13 NMR spectroscopy.

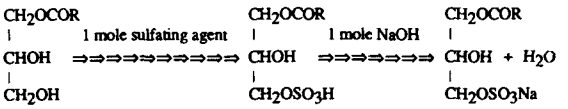
Fatty monoglyceride sulfate salts are well known as mild and effective anionic detergents, and have been incorporated in various cleaning products in the United States and other countries. A major household consumer products' company markets VEL beauty bar, which is based on sodium coco monoglyceride sulfate salts.

The first broad patent covering monoglyceride sulfate salts was issued to Harris (1) in 1935 and reissued to Colgate-Palmolive-Peet Company in 1938 (2). The manufacturing process for sodium coco monoglyceride sulfate currently used by Colgate-Palmolive Company for its VEL detergent bar is based on patented processes (1-10) developed between 1938-1959. It consists of the reaction of two moles of glycerine with one mole of coconut oil and 18 moles of fuming sulfuric acid (20-30% oleum) to produce three moles of coco monoglyceride sulfate and 15 moles of sodium sulfate after neutralization with 33 moles of sodium hydroxide solution. The 3-fold excess of oleum is necessary to solubilize the very viscous product formed before neutralization, and thus generates 9.5 kg of undesirable 30% aqueous solution of sodium sulfate per kg of coconut oil used. The disposal of such a large volume of diluted sodium sulfate is a major drawback. The monoglyceride sulfate of about 75% purity is finally isolated by extraction with aqueous isopropyl alcohol, followed by removal of solvents by evaporation, and is always contaminated with sodium sulfate and a mixture of unreacted glycerides.



Alternative synthetic routes using stoichiometric amounts of effective sulfating agents were sought to produce purer products and to eliminate undesirable sodium sulfate produced in the current process. A literature survey on the syntheses of monoglyceride sulfate revealed that there were only few alternative routes available (10-19), and most were inefficient. Ammonium salts of monoglyceride sulfate were prepared from glycerine and fatty acids, but no yields of the products were reported (11).

Many syntheses of sodium monoglyceride sulfates were reported based on sulfating fatty monoglycerides with chlorosulfuric acid-sodium chloride (12,13), concentrated sulfuric acid (14,15), sulfur trioxide-pyridine complex (13,16), chlorosulfuric acid-triethylphosphate (17), or oleum (14,18,19). Neutralization using stoichiometric amounts of base totally eliminated undesirable sodium sulfate and produced purer products.



In order for a direct sulfation of monoglycerides to produce an acceptable product, the purity of the monoglycerides must be very high (20). Commercial grades of monoglycerides are about 60% pure and need difficult distillation processes to increase monoglyceride levels to 90-96%. The cost of such high purity monoglycerides needed for sulfation has priced them completely out of consideration for a commercial monoglyceride sulfate process.

This report describes some preliminary results obtained on the alternative general synthesis of sodium monoglyceride sulfates from fatty acids or fatty acids methyl esters and glycerine using chlorosulfuric as a sulfating agent (21).

EXPERIMENTAL SECTION

Infra-red spectra were recorded on an Perkin-Elmer 983 Spectrometer. C-13 NMR spectra were obtained on an Varian FT-80A Spectrometer. The following compounds were obtained and used without further purification: hydrogenated palm kernel fatty acid methyl esters (Henkel, Inc., Fort Lee, NJ; Edenor ME AS-12), hydrogenated palm fatty acids (Henkel; Edenor HPA), hydrogenated coconut oil (Colgate-Palmolive Company, Jeffersonville Plant, IN), hydrogenated coco fatty acids (Emery 626, Emery Chemicals, Cincinnati, OH), Oleum (Baker, Phillipsburg, NJ), chlorosulfuric acid (Aldrich Chemical Co., Milwaukee, WI). Common chemicals and solvents were obtained from Baker.

Preparation of sodium coco monoglyceride sulfate from hydrogenated coconut oil. Sodium coco monoglyceride sulfate is prepared by a modified procedure of the current commercial process as follows: 20% oleum (343.24 g, 3.71 combined mole of H_2SO_4 and SO_3) was added to a 1-liter, three-necked, round bottom flask equipped with a heavy-duty mechanical stirrer, pressure-equalizer addition funnel, and an outlet from the top

of the addition funnel to an oil bubbler to vent the residual SO_3. Glycerine (36.83 g, 0.40 mole) was added dropwise to the vigorously stirring oleum in the flask and reaction temperature was maintained below 30°C. The reverse addition leads to similar results. As glycerine was added, it formed a very viscous, colorless material which was stirred at ambient temperature for 1 hr. Molten hydrogenated coconut oil (134.64 g, 0.20 mole) was added in small proportions to the reaction mixture with vigorous stirring. The original colorless mixture became light brown, then dark orange as the reaction progressed. The temperature of the reaction was maintained at 40–45°C by external cooling during the addition of coconut oil to the acids mixture. After the addition of coconut oil was complete, the thick mass was heated with vigorous stirring at 50°C for 1.5 hrs in a water bath. The orange viscous material was then cooled with an external ice bath to ambient temperature and slowly poured onto a stirring suspension of 500 g of ice and 600 ml of n-butanol in a 3-liter beaker. An additional 200 ml of n-butanol was added and the mixture was stirred for 0.5 hr. A clear phase separation took place. The organic upper layer was separated and the aqueous layer was extracted with an additional 200 ml of n-butanol. The combined alcohol extracts were washed with 200 ml of water and slowly brought to pH 6.5 at 30°C by dropwise addition of 30% NaOH to the stirred solution. After neutralization was complete, the precipitated Na_2SO_4 was removed by filtration, and the slightly brownish solution was concentrated on a rotary evaporator. The tan concentrate was stirred with 500 ml of acetone and filtered. The brown filtrate contained an oily mixture of unreacted glycerides. The white solid was pumped under vacuum overnight to remove traces of solvent to yield 182 g of product. Sodium coco monoglyceride sulfate was obtained in 66% yield based on 84% active ingredient, which was determined by cationic titration with benzethonium chloride in methylene blue indicator. The product composition was confirmed by IR and C-13 NMR spectroscopy (Table 1). The product was recrystallized from ethanol and the pure product had a decomposition point at 132–133°C.

Preparation of sodium monoglyceride sulfate from hydrogenated coco fatty acids. Glycerine (23.02 g, 0.25 mole) was added in a 1-liter, three-necked flask equipped with an efficient mechanical stirrer, dropping funnel, thermometer, and reflux condenser connected to a pressure outlet to vent gaseous HCl produced in the reaction. The reflux condenser was mounted on top of the dropping funnel so that distilled $CHCl_3$ could be recovered. Chlorosulfuric acid (93.22 g, 0.80 mole, 7% excess) in 100 ml of $CHCl_3$ was added dropwise to the vigorously stirring suspension of glycerine and $CHCl_3$ at a temperature maintained below 30°C. The hydrogen chloride gas generated is vented and diluted in cold water. After all $ClSO_3H$ had been added, the very viscous, colorless material was stirred at ambient temperature for 0.5 hr to expel all gaseous HCl generated during the reaction. Hydrogenated coco fatty acids (51.37 g, 0.25 mole) dissolved in 100 ml of $CHCl_3$ was slowly added to the glycerine trisulfuric acid mixture at ambient temperature. The colorless material became slightly brown and the temperature of the viscous material gradually rose to 40°C. The mixture was then heated to 65°C for 1.5 hr, at which time ca 170 ml of $CHCl_3$ was recovered by distillation. The dark brown viscous material was cooled to 10°C and slowly poured into a 1:1 mixture of ice (700 g) and n-butanol (700 ml) with stirring. The brownish solution was stirred for 0.5 hr and the top alcohol layer was separated. The aqueous layer was further extracted with n-butanol (2 × 100 ml). The combined alcohol layer was slowly neutralized with 30% aqueous NaOH to pH 6.5 maintaining temperature below 20°C. The neutralized material was allowed to settle and some of the inorganic salt was filtered out. The brown solid obtained after solvent removal by rotary evaporation was washed with 500 ml of acetone and pumped under vacuum to yield 32.4 g of sodium coco monoglyceride sulfate (79% yield based on 93% active ingredient as determined by cationic titration). The composition of the product was

TABLE 1

IR and C-13 NMR Spectral Data of Sodium Monoglyceride Sulfates (MGS)

Compound	IR Frequency KBr (cm^{-1})	C-13 NMR Chemical Shift D_2O (ppm)
Sodium Coco-MGS	3360(s,sh), 2920(s), 2855(s), 1730(s,sh), 1470(m), 1270(s), 1230(s), 1175(m), 1070(m), 1030(m), 825(s)	16, 25, 32, 32.2, 32.5, 34.5, 36.5, 67.5, 70, 71.6, 177.6
Sodium Palm Kernel-MGS	3420(br), 2820(s), 2850(s), 1730(s), 1470(m), 1250(s), 1229(s), 1180(m), 1070(m), 1030(m), 820(br)	16.2, 25, 27.2 32.2, 32.5, 34.5, 36.5, 67.5, 70, 71.5, 177.5
Sodium Palm-MGS	3360(s,sh), 2920(s), 2850(s), 1730(s,sh), 1470(m), 1270(s), 1230(s), 1175(m), 1070(m), 1025(br), 825(s)	

(s) = strong, (m) = medium, (br) = broad, (sh) = shoulder.

confirmed by IR and C-13 spectroscopy (Table 1). The acetone extracts on concentration gave 18.5 g of an oil containing mostly free acids and mixtures of glycerides.

Preparation of sodium palm monoglyceride sulfate from hydrogenated palm fatty acid. Chlorosulfuric acid (384.52 g, 3.32 mole) was diluted with 100 ml of $CHCl_3$ in a 2-liter, three-necked flask equipped with a mechanical stirrer, dropping funnel, thermometer, reflux condenser, and pressure outlet vent fed into ice-water. Glycerine (92.08 g, 1 mole) was added dropwise over 0.5 hr from the dropping funnel to the stirred solution maintaining the temperature below 30°C. The HCl gas produced was vented and scavenged with ice-water mixture. The viscous, colorless material was stirred at ambient temperature for 0.5 hr to remove all gaseous HCl produced during the reaction. Hydrogenated palm fatty acids (273.64 g, 1 mole) partially dissolved in 300 ml of $CHCl_3$ was slowly added to the glycerine trisulfuric acid, and the initial colorless viscous material became brown and then dark brown. An additional 50 ml of $CHCl_3$ was added and the mixture was heated at reflux for 2 hrs and distilled $CHCl_3$ was not recovered. The acids mixture was then transferred to a 2-liter separatory funnel and cooled to ambient temperature. A slurry of $NaHCO_3$ (460 g, 5.5 mole) in 1500 ml of isopropanol, 500 ml of n-butanol and 600 ml of water was made and kept cold on an ice-water bath. The pH electrode was inserted constantly. The acids mixture was slowly added to the bicarbonate slurry with vigorous stirring with an efficient mechanical stirrer. Even though copious amounts of CO_2 gas was evolved during the neutralization, careful addition of the acids mixture and stirring helped to reduce the foam and maintain pH of the mixture near neutrality (6.5–7.5). After complete addition, the final pH of the slurry was adjusted to 6.5 with aqueous NaOH. Additional 500 ml each of isopropanol and n-butanol were added to facilitate efficient stirring of the thick and viscous product. The mixture was heated to dissolve all organic sulfate product and filtered hot through Celite. The slightly brown solution was allowed to solidify at ambient temperature. The solid product was filtered and the filtrate was concentrated on a rotary evaporator. The combined solids were pumped under vacuum to remove remaining solvent. This method gave 385.5 g of sodium palm monoglyceride sulfate (70.6% yield based on 85.3% active ingredient). Spectral data were shown in Table 1. Carbon-13 NMR spectrum of this surfactant could not be obtained due to poor solubility in D_2O solvent.

Preparation of sodium palm kernel monoglyceride sulfate from hydrogenated plam kernal fatty acid methyl esters. Glycerine (23.02 g, 0.25 mole) diluted in 50 ml of $CHCl_3$ was added to a 1-liter, three-necked flask equipped with an efficient mechanical stirrer, thermometer, reflux condenser mounted on the top of an additional funnel and a pressure outlet tube to vent HCl gas. Chlorosulfuric acid (93.22 g, 0.80 mole, 6.7% excess) in 50 ml of $CHCl_3$ was added slowly to the stirring suspension of glycerine-chloroform, maintaining a reaction temperature below 30°C. The colorless, semisolid viscous material thus produced was stirred for 0.5 hr at an ambient temperature to expel all gaseous HCl produced. Slow addition of liquid hydrogenated palm kernel fatty acid methyl esters (57.74 g, 0.25 mole) in 100 ml of $CHCl_3$ produced a clear brown solution which was then heated at 64°C for 2 hrs, recovering ca 160 ml of $CHCl_3$ in the dropping funnel. The dark brown viscous material was then cooled and slowly added to a cold mixture of 600 ml of n-butanol and 700 g of ice. The mixture was stirred for 0.5 hr and the top organic layer was separated. The aqueous layer was extracted with fresh n-butanol (2 × 150 ml). The combined alcohol extract was neutralized with 30% NaOH to pH 6.5. After solvent removal by rotary evaporation, 123.3 g of sticky brown material was obtained. The crude product was stirred with 600 ml of acetone, then filtered and vacuum pumped to yield 83 g of sodium palm kernel monoglyceride sulfate (57% yield based on 68% active ingredient). The acetone extracts on concentration produced 33.67 g of an oil-containing fatty material. The product was further purified by recrystallization from ethyl alcohol, and the purified product had a decomposition point at 159–160°C. The product composition was confirmed by IR and C-13 NMR spectroscopy (Table 1).

RESULTS AND DISCUSSION

A novel and efficient general synthesis of sodium fatty monoglyceride sulfates from hydrogenated fatty acids or their methyl esters, glycerine and chlorosulfuric acid developed is shown in Scheme 1.

In stage I, glycerine is sulfated with chlorosulfuric acid in chloroform at ambient temperature. By rate of addition of $ClSO_3H$, the reaction is maintained at a reasonable rate—below 30°C. The reverse addition of glycerine to $ClSO_3H$ produces similar results, however, it is more efficient as it reduces the addition time.

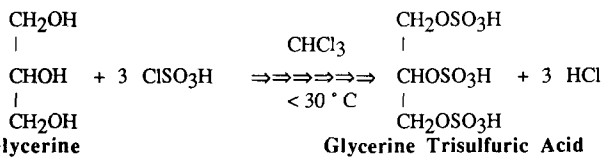
The stage II reaction involves condensation of fatty acids or fatty acid methyl esters with glycerine trisulfuric acid generated in stage I at 60°C. Use of chloroform as a solvent in stages I and II reduces the viscosity of the reaction medium and helps smooth mixing and stirring of all reactants. If desired, chloroform may be left in the reaction mixture.

Neutralization and extraction of stage II reaction mixture is carried out by two different methods. The stage II acid mixture is extracted with n-butyl alcohol-water, and then neutralized with 30% aqueous $NaHCO_3$ or NaOH. Alternatively, neutralization and extraction is carried out simultaneously with $NaHCO_3$ slurry of n-butanol/isopropanol-water. Better quality products are produced by the latter method. Hydrolysis of the ester linkages of the monoglyceride sulfate are sensitive to acidic and basic pH. Maintaining neutral pH is critical in order to minimize undesirable by-products. After solvent removal, sodium coco monoglyceride sulfate is obtained from hydrogenated coco fatty acids in 79% yield (93% active ingredient) using this procedure. Sodium palm kernel monoglyceride sulfate is prepared similarly, from hydrogenated palm kernel fatty acid methyl esters in 57% yield (68% active ingredient). The active ingredient level is determined by cationic titration with benzethonium chloride in methylene blue indicator.

The composition of products is confirmed by their characteristic IR and C-13 NMR spectroscopic data (see Experimental Section). Sodium coco monoglyc-

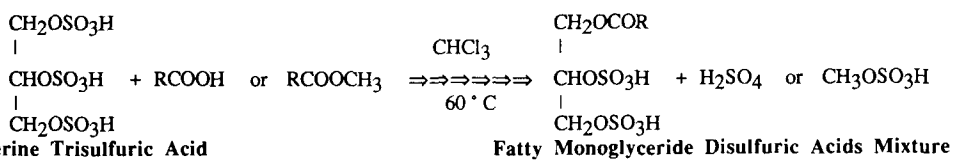
Reaction Scheme

Stage I. Sulfation of Glycerine



Glycerine — **Glycerine Trisulfuric Acid**

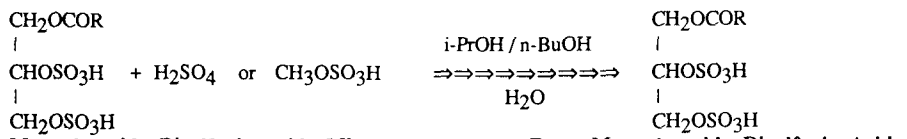
Stage II. Condensation of Glycerine Trisulfuric Acid with Fatty Acid or Methyl Ester



Glycerine Trisulfuric Acid — **Fatty Monoglyceride Disulfuric Acids Mixture**

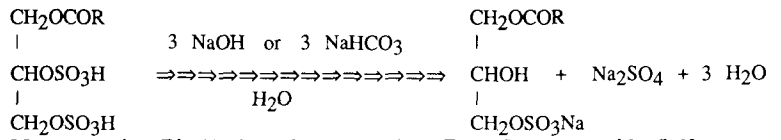
Stage III. Extraction and Neutralization of Monoglyceride Disulfuric Acids Mixture

Extraction :



Fatty Monoglyceride Disulfuric Acids Mixture — **Fatty Monoglyceride Disulfuric Acid**

Neutralization :



Fatty Monoglyceride Disulfuric Acid — **Sodium Fatty Monoglyceride Sulfate**

SCHEME 1

eride sulfate prepared by this new synthesis has identical physical and spectral properties to that produced by the current commercial process.

Sodium palm monoglyceride sulfate is efficiently prepared in 71% yield from hydrogenated palm fatty acids. The procedure used in making this surfactant is similar to general synthetic methods, except that chloroform solvent is not recovered in the stage II reaction, and the stage II acid is extracted and neutralized in aqueous alcohol slurry of $NaHCO_3$ (see Experimental Section). After the usual work up, sodium palm monoglyceride sulfate is obtained in 71% yield (85% active ingredient). The product is identified by its characteristic IR spectral data. Typical batch compositions of all products prepared are given in Table 2.

The synthesis of monoglyceride sulfate from fatty acid methyl esters by this method is not as efficient as that from fatty acids. Because an additional ester hydrolysis reaction step to produce fatty acids is involved with the ester before it can react with glycerine trisulfuric acid to form the stage II product, fatty acids can directly condence with glycerine trisulfuric acid.

stage I and II reaction intermediates. However, R.A. Bauman (personal communication) studied the Muncie Processes (3-6) of making monoglyceride sulfates in detail and proposed the following reaction mechanism based on isolated and observed products in the stages I to III. The stage II reactions of triglycerides and fatty acids with glycerine trisulfuric acid (stage I product) and sulfuric acid were rapid as they formed stabilized carbenium ions by neighboring group assistance. The stage II acids mixture composed mainly of α-monoglyceride disulfuric acid and β-monoglyceride disulfuric acid, the latter being less favorable both sterically and statistically. However, both diacids isomers generate the same stabilized carbenium ion which produced the desired product in the stage III reaction. A small amount of α-monoglyceride and β-monoglyceride "free oil" by-products were also produced as elaborated in the reaction mechanism. Since this new synthesis involves the same chemistry and reactions, a similar reaction mechanism is expected. However, formation of isomeric α-monoglyceride β-sulfate by-product in the stage III is unlikely, as it is not stable in aqueous solution and will produce more stable monoglyceride upon hydrolysis.

Spectroscopic studies of sodium monoglyceride sulfates. Spectroscopic analysis of sodium monoglyceride sulfates confirmed the composition and structure. The

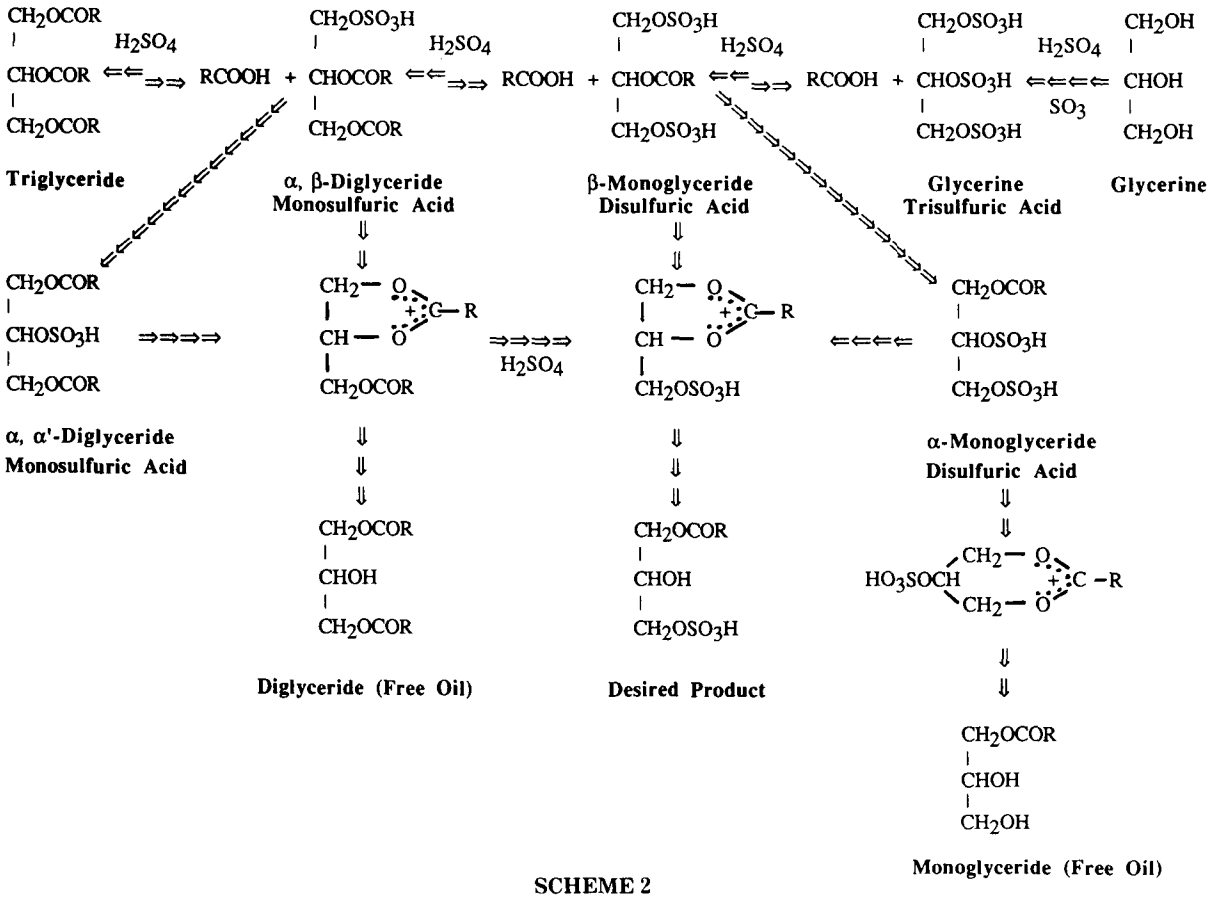
TABLE 2

Typical Composition of Sodium Monoglyceride Sulfates (MGS) Prepared

Composition	Na Coco-MGS #	Na Palm-MGS	Na Palm Kernel-MGS
Sodium MGS (Act. Ing.)	93.0 (75%)	85.0%	68.0%
Free Fatty Acids	0.9 (4)	—	11.2
Fatty Acid Sodium Salts	— —	3.0	—
Sodium Sulfate (Alc. Insol.)	2.6 (8)	5.5	8.0
Free Oil (Ethyl Ether Sol.)	2.6 (12)	5.0	10.4
Water	0.9 (1)	1.5	2.4

Values in the parentheses show the analysis of current commercial product.

Reaction Mechanism



SCHEME 2

infra-red spectra (KBr pellet) of sodium monoglyceride sulfate salts prepared from coco fatty acids, coconut oil, palm kernel oil, palm kernel fatty acid methyl esters and palm fatty acids are very similar and show characteristic absorption for hydroxyl, carbonyl and sulfate groups. The strong and broad absorption at 3360 cm^{-1} (shoulder at 3450-3475 cm^{-1}) is due to the hydrogen bonded secondary alcohol; strong absorption at 1730 cm^{-1} (shoulder at 1740 cm^{-1}) is characteristic of ester carbonyl groups. The infra-red spectral data of all samples are consistent with the proposed structure of sodium monoglyceride sulfates and are given in Table 1.

Proton magnetic resonance spectra of purified sodium monoglyceride sulfates in D_2O show poor resolution due to broad absorptions and no structural information is obtained. However, C-13 NMR spectra in D_2O solvent gives confirmatory and diagnostic structural information. The C-13 NMR spectrum of Sodium coco monoglyceride sulfate shows upfield alkyl carbon absorptions at 16, 25, 27, 32, 32.2, 32.5, 34.5 and 36.5 ppm. These absorptions are assigned to alkyl carbons of long fatty alkyl chains and no finer structural information can be obtained, as expected. However, three distinct and well separated peaks at 67.5, 70 and 71.5 ppm are undoubtedly due to the three glycerine car-

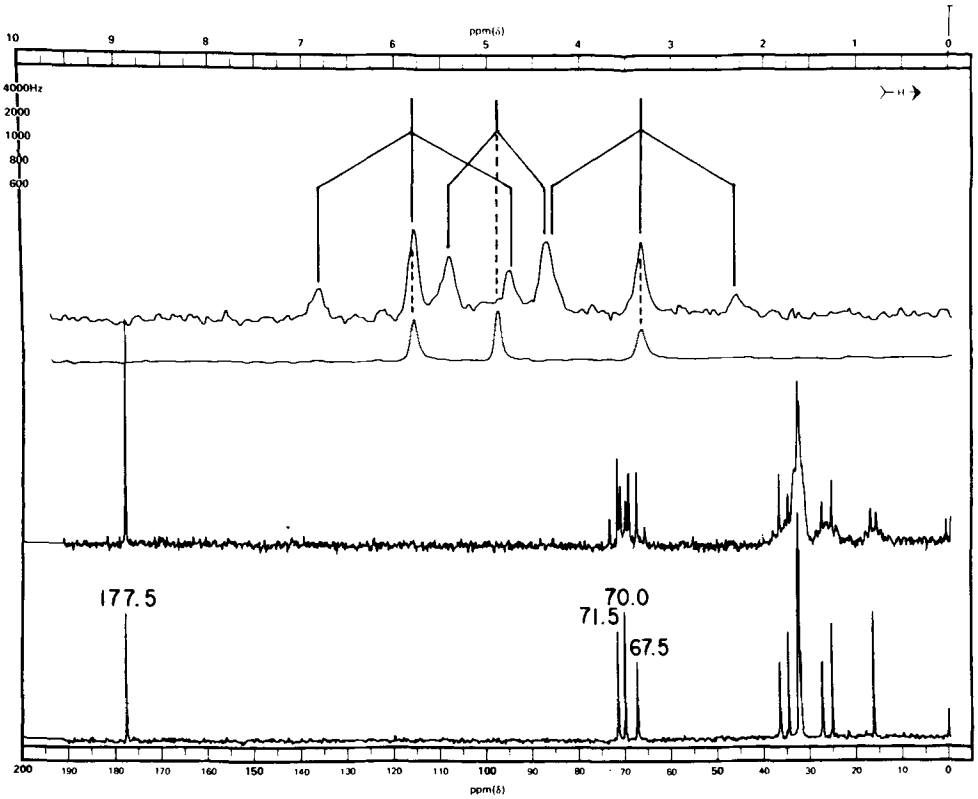


FIG. 1. Carbon-13 NMR Spectrum of Sodium Coco Monoglyceride Sulfate in D_2O.

bons as shown in Figure 1. The central peak at 70 ppm gives a 1:1 doublet on a proton-coupled spectrum (middle trace) and can be safely assigned to the central secondary carbon containing one proton. The terminal primary carbons each containing two protons gave expected 1:2:1 triplet splitting pattern on a proton-coupled spectrum as shown in expanded portion of the spectrum (top trace). The downfield absorption at 71.5 ppm is assigned to the primary carbon atom directly bonded to the carbonyl ester group, as it is more deshielded than the other primary carbon attached to the sulfonyl ester group which is assigned to the absorption at 67.5 ppm. As expected, both the terminal primary carbons gave 1:2:1 triplet splitting pattern due to the two attached protons. These assignments are consistent with known examples that have been cited in the literature (22). The downfield absorption at 177.5 ppm is assigned to carbonyl ester carbon. From the above C-13 NMR and IR spectral interpretation, the structure of sodium coco monoglyceride is unequivocally established and confirmed as was originally proposed. The C-13 NMR spectra of other analogues are very similar, as expected. The C-13 NMR spectrum of sodium palm monoglyceride sulfate could not be obtained due to poor solubility in D_2O solvent. The chemical shifts of different analogues are given in Table 1.

This new syntheses of sodium monoglyceride sulfate is a practical and general one. Chlorosulfuric acid used in sulfating glycerine in the stage I reaction generates HCl gas which could be commercially recovered and recycled to produce $ClSO_3H$ with fresh SO_3 gas. This study describes the preliminary results of a viable new synthesis of monoglyceride sulfates from fatty acids of hydrogenated coconut oil, palm oil and methyl esters of hydrogenated palm kernel oil fatty acids. The important feature of this general synthesis is that it does not generate large amounts of aqueous sodium sulfate; in fact, it reduces the sodium sulfate by-product by 60% (on dry basis) over the current commercial process.

This process uses only stoichiometric amounts of reagents and can be adapted to make monoglyceride sulfates from any fatty acids and or fatty acid methyl esters. This synthetic method produced high quality products in excellent yields from readily available, inexpensive, raw materials without having to use high purity and costly fatty acid monoglycerides. Since only a stoichiometric amount of sulfating agent is used in this process, an inert solvent is necessary to reduce the viscosity of glycerine trisulfuric acid in the stage I in order to stir the mixture efficiently and also to dissolve fatty acids/methyl esters in the stage II reaction.

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