Surfactants and Detergents From Sulfated N-Alkyl-D-Gluconamides

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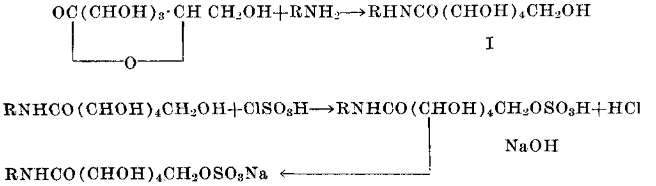
NUMEROUS patents describe the preparation of ethers, esters, amines, and amides of carbohydrates and their sulfated and sulfonated derivatives for detergent use (1), but apparently the sulfuric acid esters of long-chain aliphatic amides of D-gluconic acid have not been investigated. Recent large-scale production of fatty amines and rosin amine and the ready availability of D-gluconolactone from D-gluconic acid (2) has stimulated a study of the reaction products of these materials as intermediates for the preparation of interfacial modifiers.

This paper presents the synthesis of N-rosin-D-gluconamide and a series of N-alkyl amides of D-gluconic acid and their sulfated derivatives. Some physical and chemical properties of the sulfated products were determined and used to evaluate them as surface active agents. Comparative soil removal studies were also made with a number of the products, alone and in combination with builders, in hard and distilled water under conditions similar to those used in home laundry practices.

The octyl, decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl amines investigated were mixtures of at least 90% of the appropriate amine and about 10% of amines of slightly higher and lower molecular weight. The 2-ethylhexylamine and nonylamine (3,5,5-trimethylhexylamine) used were pure substances. The major components of the rosin amine were dihydroabietyl, tetrahydroabietyl, dehydroabietyl, and dextropimarylamines (3).

D-gluconic acid cannot readily be reacted with primary amines to form amides because the high temperature required for condensation decomposes the sugar acid. However D-glucono-delta-lactone which is easily crystallized by evaporating aqueous D-gluconic acid solution to 85% concentration can be reacted at relatively low temperatures to form substituted D-gluconamides (I) in excellent yield. Reaction of the substituted D-gluconamides with chlorosulfonic acid in dry methylene chloride and neutralization of the product with aqueous sodium hydroxide has readily produced N-alkyl-D-gluconamide sodium sulfates (II). This sequence of reactions may be illustrated as follows:



I

II

$$\underbrace{\mathrm{OC(CHOH)_3 \cdot CH}}_{\mathrm{O}}\ \mathrm{CH_2OH + RNH_2 \longrightarrow RHNCO(CHOH)_4CH_2OH}$$

$$\mathrm{RNHCO(CHOH)_4CH_2OH + ClSO_3H \longrightarrow RNHCO(CHOH)_4CH_2OSO_3H + HCl}$$

$$\mathrm{RNHCO(CHOH)_4CH_2OSO_3H \xrightarrow{NaOH} RNHCO(CHOH)_4CH_2OSO_3Na}$$

The monosulfates are assumed to have the sulfate group attached to carbon six since primary alcohol groups of sugars (4) generally esterify more rapidly than secondary hydroxyl groups. It has been found that the N-alkyl-D-gluconamide sodium monosulfates containing alkyl radicals of more than nine carbon atoms are incompletely soluble in 1% aqueous solution. Introduction of a second or third sulfate group conferred the solubility desired.

While the sulfated N-alkyl-D-gluconamides are not as stable in aqueous solution as sulfonated detergents, the sulfate radical is sufficiently firmly attached to the molecule to allow their satisfactory use in neutral, mildly acid, or alkaline solutions.

Preparation of N-alkyl-D-gluconamides

N-2-Ethylhexyl-D-gluconamide. The N-alkyl- and N-rosin-D-gluconamides were prepared by interaction of D-glucono-delta-lactone and the primary amines in hot methanol. The desired products readily crystallized from their reaction mixtures. A typical procedure for the synthesis of N-2-ethylhexyl-D-gluconamide is the following. To a solution of 23.2 g. (0.18 mole) 2-ethyl-hexylamine in 250 ml. hot methanol was added 32 g. (0.18 mole) D-glucono-delta-lactone. The reaction mixture was refluxed for 30 minutes and then cooled to room temperature. The white crystalline product which formed was removed by filtration, washed with ethanol, and dried at 60°C. A first crop of 27.9 g. was obtained which melted at 116°-118°. Two more crops totalling 24.6 g. were isolated from the mother liquor, giving a total yield of crude product of 95% of theory. After recrystallization from ethanol, the N-2-ethylhexyl-D-gluconamide melted at 117°-118°.

TABLE I

Analysis and Yields of N-alkyl-D-gluconamides

N-R-D-Gluconamide, R	M.P., °C.	Nitrogen Found, %	Nitrogen Theory,[a] %	Crude Yield,[b] %
2-Ethylhexyl	117-118	4.5	4.5	95
Octyl	156-157	4.6	4.6	96
Nonyl	131-133	4.4	4.4	96
Decyl	153-154	4.2	4.2	90
Dodecyl	152-154	3.8	3.9	95
Tetradecyl	153-154	3.6	3.6	83
Hexadecyl	145-147	3.4	3.3	90
Octadecyl	144-146	3.2	3.1	93
Rosin	141-142	3.0	2.7	89

[a] The mean molecular weight of primary amine content of each amine mixture used approached the theoretical value of the pure amine.

[b] The crude products were practically pure and could be used directly in the sulfation reaction.

Table I lists the N-alkyl-D-gluconamides that have been prepared by this procedure together with their melting points, nitrogen analyses, and yields.

Sulfation of N-alkyl-D-gluconamides

N-2-Ethylhexyl-D-gluconamide Sodium Sulfate. A solution of 7.0 g. (0.6 mole) of chlorosulfonic acid in 20 ml. dry methylene chloride was added portionwise to a suspension of 18.4 g. (0.6 mole) N-2-ethylhexyl-D-gluconamide in 200 ml. dry methylene chloride. The reaction mixture was stirred and gently refluxed during the 15-minute period of addition of the chlorosulfonic acid and an additional 4 hours. Methylene chloride and hydrogen chloride were removed in a

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stream of dry air. The white residue of N-2-ethylhexyl-D-gluconamide sulfuric ester was dissolved in 50% ethanol and neutralized to pH 7.1 with sodium hydroxide solution. The solution was then concentrated in vacuo to dryness and gave 23.1 g. of product.

Essentially the same procedure was used for preparing all of the sulfated N-alkyl-D-gluconamides.

Since free sodium sulfate could be detected in each product, some hydrolysis of chlorosulfonic acid or of the sulfated N-alkyl-D-gluconamides had occurred. In Table II the amount of free sodium sulfate found is tabulated for each substance prepared. These values were determined by two methods. Those marked with an asterisk were obtained by the method of Ogg, Willets, and Cooper (5), in which an aqueous solution of sulfated product was titrated with standard barium chloride solution, using the sodium salt of tetrahydroxyquinone as an indicator. The remaining values were determined by extracting the less soluble sulfated gluconamides with cold water and precipitating the sulfate ions in the extract as barium sulfate. The more soluble products were dissolved in a large volume of water for barium sulfate precipitation at 50°C. The percentage of sodium sulfate and the degree of sulfation that had taken place were calculated from the weight of barium sulfate obtained.

TABLE II

Composition and Degree of Sulfation of N-Alkyl-D-Gluconamide Sodium Sulfates

Product	N-R-D-Gluconamide Sodium Sulfate, R	Active Compound, %	Sodium Sulfate, %	Sulfation (% of Theory)
A	2-Ethylhexyl	97	3	92
B	n-Octyl	94	6*	83
C	Nonyl	98	2*	94
D	Decyl	93	7*	78
E	Dodecyl	94	6	80
F	Dodecyl (sesquisulfate)	99	1	97
G	Tetradecyl	94	6	80
H	Tetradecyl (sesquisulfate)	95	5	89
I	Tetradecyl (sesquisulfate)	34	66	....
J[a]	Tetradecyl (sesquisulfate)	34	57	....
K	Tetradecyl (disulfate)	93	7*	86
L	Hexadecyl (sesquisulfate)	94	6*	84
M[b]	Hexadecyl (sesquisulfate)	34	2	....
N	Hexadecyl (disulfate)	92	8*	83
O	Octadecyl (sesquisulfate)	95	5	89
P	Octadecyl (disulfate)	97	3*	93
Q	Rosin (sesquisulfate)	99	1	95
R	Rosin (disulfate)	94	6	84
S	Rosin (trisulfate)	95	5	91

[a] Contains 9% medium viscosity carboxymethyl cellulose.
[b] Contains 64% sodium tripolyphosphate.
* Determined by method of Ogg, Willets, and Cooper (5).

Evaluation of N-alkyl-D-gluconamide Sodium Sulfates as Surfactants and Detergents

Harris (6) has compiled a series of tests for evaluating the fundamental properties of surface active agents. Those utilized in this investigation are the following: 1. determination of surface and interfacial tension values, 2. Draves-Clarkson wetting test, 3. canvas disc wetting test, 4. acid stability, 5, alkali solubility and stability, 6. metallic ion stability, 7. limesoap dispersion, 8. lather test, and 9. organic solvent solubility. In addition to the tests described by Harris the soil-removing efficiency of the products was determined by the detergent test.

1. Surface and interfacial tension data were obtained at room temperature (25°-28°C.) by the ring method using a du Noüy tensiometer. The values shown in Table III have not been corrected for ring-liquid relationships; however they are adequate for comparative purposes. All of the compounds reduced the surface tension of water and the interfacial tension of water against mineral oil to a marked degree in 1% concentration. Upon dilution however the compounds of lower molecular weight (2-ethyl-hexyl and n-octyl substituted) were not so effective. In compounds in which the alkyl substituents contained 12 to 18 carbon atoms, or were rosin groups (20 carbon atoms), dilution did not significantly change the surface activity. Comparison of the surface tension values of the monosulfated with those of the more highly sulfated compounds containing the same alkyl substituents shows that the degree of sulfation above one equivalent does not alter the surface tension to any great extent at the various concentrations used. A mixture of N-tetradecyl-D-gluconamide sodium sesquisulfate with 66% by weight of sodium sulfate did not appreciably change the surface tension effect of the sulfated gluconamide. However the addition of 64% of sodium tripolyphosphate to hexadecyl gluconamide sodium sesquisulfate markedly reduced the surface tension of water below that obtained with the sesquisulfate alone. Effective surface active agents generally reduce the surface tension of water to 25-35 dynes per cm. and the interfacial tension below 5 dynes per cm. in about 0.1% solutions.

TABLE III

Surface and Interfacial Tension Values of N-Alkyl-D-Gluconamide Sodium Sulfates and Their Mixtures With Builders (25°-28°C.)

Products	Surface Tension, Dynes per cm.			Interfacial Tension, Dynes per cm.		
	Concentration			Concentration		
	1.0%	0.25%	0.0625%	1.0%	0.25%	0.0625%
A	28.2	45.2	43.2	2.6	3.5	6.6
B	24.7	34.9	47.3	3.6	3.5	5.5
C	26.3	37.5	49.2	2.1	7.2	7.4
D	23.1	23.0	25.5	2.0	2.7	8.0
E	25.9	25.9	26.2	1.5	2.6	4.4
F	25.9	24.1	24.5	2.0	2.0	2.1
G	25.7	25.5	25.6	1.9	2.9	3.3
H	25.1	24.5	25.7	2.1	2.1	2.1
I	25.4	24.2	26.5	2.8	2.3	5.1
J	25.6	23.9	26.6	3.7	2.1	4.7
K	28.0	25.1	28.3	5.5	2.5	5.0
L	38.9	40.1	43.6	5.3	6.5	8.7
M	29.5	32.9	37.6	4.5	5.8	5.2
N	39.9	39.9	39.9	2.3	4.3	7.3
O	45.2	45.0	48.3	4.9	7.9	9.6
P	45.1	45.0	45.8	3.4	3.3	5.8
Q	29.0	29.5	30.4	4.5	1.6	2.3
R	29.6	30.9	32.0	1.6	2.4	3.0
S	30.3	30.3	32.4	1.6	2.8	3.1

2. Draves-Clarkson wetting test (6, 7): The wetting time of the various compounds alone and with builders

TABLE IV

Draves-Clarkson Wetting Test

Product	Wetting Time, sec.			
	Concentration			
	0.5%	0.25%	0.125%	0.0625%
A	>180			
B	3.2	>180		
C	11.4	>180		
D	2.4	5.0	25.0	>180
E	23.8	68.1	112.6	>180
F	7.7	12.3	42.3	>180
G	>180			
H	40.9	70.0	94.0	>180
I	31.2	62.6	98.3	>180
J	28.8	47.8	136.5	>180
K	32.5	49.0	141.3	>180
L	>180			
M	>180			
N	>180			
O	>180			
P	>180			
Q	10.4	18.5	76.9	>180
R	31.8	62.4	160.9	>180
S	20.4	33.3	>180	

is given in Table IV. While N-2-ethylhexyl-D-gluconamide sodium sulfate reduced the surface tension of water considerably, a 0.5% solution did not wet the surface of cotton fibers very rapidly. The three most effective agents of the series are the decyl substituted monosulfate and the dodecyl and rosin substituted sesquisulfates. They are satisfactory at both the lower and higher dilutions.

3. Canvas disc wetting test (6, 8): As with the Draves-Clarkson test, the two best wetting agents by this procedure are the decyl-D-gluconamide sulfate and dodecyl-D-gluconamide sesquisulfate (Table V).

TABLE V

Canvas Disc Wetting Test

Product	Wetting Time, sec.				
	0.5%	0.25%	0.125%	0.0625%	0.031%
A	>180				
B	28.0	>180			
D	2.8	5.9	13.3	87.9	>180
E	14.7	37.8	71.1	130.0	>180
F	6.9	12.5	23.6	135.9	>180
G	>180				
H	11.3	18.4	27.4	160.6	>180
I	37.0	69.5	125.0	>180	
J	38.1	66.9	124.5	>180	
K	22.3	34.3	56.3	122.9	>180
L	>180				
M	>180				
N	>180				
O	>180				
P	>180				
Q	13.9	31.2	67.4	127.8	>180
R	22.2	40.2	75.7	141.6	>180
S	26.6	69.6	>180		

The tetradecyl substituted sesquisulfate wets the canvas disc considerably faster than the cotton skein. On the other hand, the rosin-D-gluconamide sesquisulfate was less efficient with the canvas disc.

4. Acid stability (6): In this test 1.0 g. of surface active agent was refluxed for 15 minutes in 100 ml. of solutions of 0.1, 1.0, 3.0, and 10% sulfuric acid. Decomposition was indicated by loss of foaming power and by precipitation in some cases. In general, it was difficult to determine the acid stability of these compounds as the amides hydrolyze to amines which with hydrochloric or acetic acids form soluble salts which foam. However the sulfuric acid salts of the higher aliphatic amines are not appreciably soluble, and hydrolysis with sulfuric acid can be recognized by the formation of a precipitate and a decrease in foaming. Several of the longer-chained alkyl substituted monosulfates were not evaluated for acid stability because of their low water solubility. From Table VI it is apparent that all of the samples were unaffected by slightly acid solutions. However increasing the acidity to 1% caused partial or complete decomposition at boiling temperatures.

TABLE VI

Acid Stability

Product	1% Aqueous Solution Heated to Boiling	Refluxed with Sulfuric Acid 15 min.			
		0.1%	1.0%	3.0%	10%
A	Stable	Stable	D no ppt.		
B	Stable	Stable	PD no ppt.	PD no ppt.	PD no ppt.
C	Stable	D no ppt.			
D	Stable	Stable	PD no ppt.	PD no ppt.	PD no ppt.
F	Stable	Stable	PD ppt.	PD ppt.	PD ppt.
H	Stable	Stable	PD ppt.	PD ppt.	PD ppt.
K	Stable	Stable	PD ppt.	PD ppt.	PD ppt.
L	Stable	Stable	Stable	PD ppt.	PD ppt.
N	Stable	Stable	Stable	PD ppt.	PD ppt.
O	Stable	Stable	PD ppt.	PD ppt.	PD ppt.
P	Stable	Stable	PD ppt.	PD ppt.	PD ppt.
Q	Stable	Stable	PD ppt.	D ppt.	
R	Stable	Stable	PD ppt.	D ppt.	
S	Stable	Stable	PD ppt.	PD ppt.	D ppt.

Stable=clear or slightly cloudy; + foaming.
PD=partial decomposition; decrease in foaming.
D=decomposition; no foaming.
ppt.=formation of a precipitate.

5. Alkali solubility and stability (6): Table VII shows that the N-R-D-gluconamide sodium monosulfates containing the shorter alkyl groups exhibited greater surface tension lowering of strong alkali solutions than the longer alkyl substituted compounds. This is probably due to their greater solubility. The higher sulfated compounds were also quite efficient wetting agents in alkaline solutions, apparently for the same reason. All of the products were unstable in 25% alkali solution at reflux temperature for 15 minutes.

TABLE VII

Alkali Solubility—Temperature 25° ±2°

This Table Represents the Maximum Concentrations of Caustic Soda and Wetting Agents That Give Clear Solutions

Product	Wetting Agent, %	Sodium Hydroxide, %	Surface Tension, Dynes per cm.
A	0.93	32.9	28.0
B	0.93	32.9	31.7
C	0.93	32.9	25.5
D	0.1	2.7	29.3
E	0.1	2.7	28.6
F	0.93	32.9	41.7
G	0.1	2.7	30.8
H	0.93	32.9	47.8
K	0.93	32.9	50.1
L	0.1	2.7	37.2
N	0.1	2.7	38.7
O	0.1	2.7	42.3
P	0.1	2.7	42.6
Q	0.1	2.7	32.0
R	0.1	2.7	34.4
S	0.93	32.9	41.5

6. Metallic ion stability (6): Stability values for the metallic ions used are recorded in Table VIII. The monosulfates of the longer chained alkyl substituted compounds and the sesquisulfate and disulfate of the rosin D-gluconamides were not completely soluble in 1% solution and could not be tested. All of the soluble products however had good stability toward the more common metallic ions. In general, least stability was obtained with the barium and lead salts. The latter results however can be attributed to the pres-

TABLE VIII

Metallic Ion Stability

Product	Ca	Mg	Cu	Al	Ba	Fe	Pb	Zn	Ni
A	100	100	100	100	7	100	100	100	100
B	100	100	100	100	7	100	35	100	100
D	100	100	100	100	7	60	12	100	100
F	100	100	100	100	11	100	25	100	100
H	100	100	100	100	17	100	37	100	100
K	100	100	100	100	17	100	57	100	100
L	100	100	100	100	37	100	71	100	100
N	100	100	100	100	33	100	44	100	100
S	100	100	100	100	7	100	21	100	100

ence of sodium sulfate in the N-substituted D-gluconamide sulfates. Products that were dialyzed to remove sodium sulfate were completely stable to lead ions and showed improved stability to barium ions. Further confirmation of this is the observation that aqueous solutions containing amounts of sodium sulfate equal to those present in the sulfated products were found to have approximately the same barium and lead ion stability as the crude products.

7. Lime soap dispersion: A measure of lime soap dispersion was obtained by the method of Harris (6), which is a modification of the procedure described by Ramachandran and his associates (9). Detergents having dispersion numbers of 10 to 40 were considered to be effective lime soap removers. Moderately satisfactory agents have dispersion numbers not greater than 80. The monosulfates of the higher alkyl substituted D-gluconamides, and the sesquisulfate and disulfate of the rosin-D-gluconamides were not soluble enough to produce the 10% aqueous solutions required for the test.

TABLE IX

Lime Soap Dispersion

Product	Dispersion Number
A	>80 (curd)
B	60
D	50
F	10
H	10
I	20
J	20
N	10
L	10
M	30
O	10
P	10
S	10

In Table IX it is shown that the higher alkyl sesqui, di, and trisulfated D-gluconamides have excellent potential value as lime soap dispersants. The monosulfated-D-gluconamides containing alkyl substituents of less than 12 carbon atoms do not appear to be as effective.

8. Lather value (6): The foaming action of the surface active agents was determined in distilled water and in water of 300 ppm. of hardness (calcium ions) by the method of Ross and Miles (10). The lather value of all of the surface active agents tested was not changed appreciably by hard water (Table X). In the monosulfate series an optimum lather value appears to have been reached with the decyl substituted D-gluconamide monosulfate; the contiguous monosulfated compounds were considerably lower in lathering power. The sesquisulfates of the higher substituted alkyl D-gluconamides foamed better than their monosulfate analogs. In the case of the rosin products the sesquisulfate and trisulfate were more active than the disulfate. Lather values of the built products J and M were not significantly different than the corresponding unbuilt ones, but the concentrations of active compound in the former were 60% less. Commercial detergents generally produce foams 8 to 14 cm. in height in hard water.

9. Organic solvent solubility: All of the surface active agents prepared were relatively insoluble in acetone, carbon tetrachloride, ethanol, and benzene and consequently have no potential value for use in dry cleaning preparations.

TABLE X

Lather Values (25° ±0.2°)

Product	Height of Foam with 0.05% Solution			
	Distilled Water		300 ppm. Hard Water	
	At once	After 5 minutes	At once	After 5 minutes
	cm.	*cm.*	*cm.*	*cm.*
A	1.3	0	1.0	0
B	2.1	0	2.5	0
C	0.6	0.5	0	0
D	8.1	7.2	8.0	6.8
E	3.0	2.8	3.1	2.7
F	9.5	8.5	9.5	8.5
G	3.4	2.6	2.6	1.9
H	6.9	6.7	7.9	7.4
I	7.0	6.6	13.0	12.9
J	8.6	8.3	12.0	11.9
K	4.5	4.0	4.5	4.0
L	11.4	10.8	9.7	9.5
M	12.3	11.8	8.7	8.3
N	10.6	10.5	9.2	8.9
O	12.8	12.5	8.0	7.8
P	13.0	12.4	10.2	10.0
Q	9.5	9.1	9.4	9.7
R	6.8	6.4	6.3	5.9
S	10.5	9.7	9.3	8.2

Detergent test[3] (11): Certain of the products were evaluated for their soil-removing efficiency by measuring the change in light reflectance which they produced on laundering soiled cotton test fabric. The fabric was cut into samples 4 inches by 6½ inches and at least three replicates were used for each set of laundering conditions. Launderings were done in the launderometer at 60°C. in distilled water and in water of 150 and 300 ppm. hardness in concentrations

TABLE XI

Soil-Removing Efficiency of Detergents at Different Concentrations in Water of Varying Hardness at 60°C.

Product	Hardness of Water	Soap Index at Different Concentrations of Detergent Solution				
		0.05%	0.15%	0.25%	0.35%	0.50%
1[a]	Distilled	.44	.72	1.00	....	....
	150 ppm.	....	.34	.62	.91	....
	300 ppm.	....	.35	.32	.44	.86
2[b]	Distilled	.41	.67	.94	....	....
	150 ppm.	....	.47	.66	.59	....
	300 ppm.	....	.47	.59	.51	....
D	Distilled	.29	.32	.44	....	....
	150 ppm.	....	.35	.59	.55	....
	300 ppm.	....	.40	.52	.56	....
F	Distilled	.33	.52	.69	....	....
	150 ppm.	....	.64	.68	.61	....
	300 ppm.	....	.63	.61	.60	....
H	Distilled	.33	.62	.79	....	....
	150 ppm.	....	.64	.77	.68	....
	300 ppm.	....	.52	.68	.65	....
I	Distilled	.30	.37	.58	....	....
	150 ppm.	....	.31	.48	.52	....
	300 ppm.	....	.41	.50	.60	.61
J	Distilled	.27	.41	.64	....	....
	150 ppm.	....	.40	.59	.67	....
	300 ppm.	....	.47	.59	.62	.69
L	Distilled	44	.81	.87	....	....
	150 ppm.	....	.73	.76	.85	....
	300 ppm.	....	.63	.60	.63	.70
M	Distilled	.60	.96	1.01	....	....
	150 ppm.	....	.81	.87	.82	....
	300 ppm.	....	.59	.80	.73	.52
P	Distilled	.41	.84	.98	....	....
	150 ppm.	....	.84	.88	1.02	....
	300 ppm.	....	.55	.63	.67	.78
S	Distilled	.37	.26	.29	....	....
	150 ppm.	....	.29	.30	.30	....
	300 ppm.	....	.26	.36	.48	....

[a] Soap 93%.
[b] Sodium lauryl sulfate 47%. Sodium sulfate 48%.

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[3] The detergent test was conducted by the Bureau of Human Nutrition and Home Economics.

of 0.05, 0.15, 0.25, 0.35, and 0.50% of the detergent as received (Table XI).

In Table XII is reported the soil-removing efficiency of the experimentally developed detergents expressed as the soap index, that is, the efficiency of the detergent compared with that of the soap used as the standard. The soap index is calculated by dividing the spread of the detergent (the difference between the light reflectance readings before and after laundering in the detergent solution) at 60°C. and a specified concentration in either distilled or hard water by the spread obtained with the soap at the same temperature and at 0.25% concentration in distilled water. For the most part differences in index value of 0.20 and above are significant.

TABLE XII

Soil-Removing Efficiency of Various Detergents at 0.25% Concentration in Distilled and Hard Water at 60°C.

Detergent	Active Ingredient	Soap Index	
		Distilled Water	300 ppm. Hard Water
Soaps[a]	%		
Soap 1	92.5	1.00	.32
Soap 2r	96.4	1.08	.29
Built soap 1r	77.8	1.03	.25
Salts of alkyl sulfates[a]			
Sodium lauryl sulfate 3r	38.2	.78	.40
Sodium lauryl sulfate 5r	18.7[b]	.90	.59
Sodium salts of alkyl aryl sulfonates[a]			
Alkyl aryl sulfonate 5r	31.6	.55	.35
Sodium salts of sulfated esters[a]			
Sulfated glyceryl ester 1r	29.6	.64	.39
Sulfated glyceryl ester 2r	......[b]	.84	.48
Sodium salts of sulfonated amides[a]			
Fatty acid amide sulfonate 2r	30.4	.63	.41
Fatty acid amide sulfonate 3r	......[b]	.86	.45
Sodium salts of sulfated alkyl gluconamides			
Detergent D; decyl derivative	93	.44	.52
Detergent F; dodecyl derivative	99	.69	.61
Detergent H; tetradecyl derivative	95	.79	.68
Detergent I; tetradecyl derivative	34	.58	.50
Detergent J; tetradecyl derivative	34[c]	.64	.59
Detergent L; hexadecyl derivative	94	.87	.60
Detergent M; hexadecyl derivative	34[b]	1.01	.80
Detergent P; octadecyl derivative	97	.98	.63
Detergent S; rosin derivative	95	.29	.36
Water	......	.27	.24

[a] Reported previously. See reference (11).
[b] Built with 15% or more alkaline salts.
[c] Contains carboxymethyl cellulose.

The data show that as the length of the alkyl chain in the active ingredient of the detergent increases, the detergent improves in soil-removing ability. Of the detergents that contain approximately the same amount of the decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl substituted gluconamide sodium sulfates, respectively, the N-decyl-D-gluconamide sodium monosulfate was the least effective of the series in removing soil from the test fabric; the dodecyl and the tetradecyl substituted sesquisulfates were increasingly effective. These three products in distilled water at 0.25% concentration were, respectively, 44, 69, and 79% as efficient as the soap. They were about as effective in hard water as in distilled and the amount of hardness (150 or 300 ppm.) made little difference.

Somewhat higher in soil-removing ability than the tetradecyl substituted sesquisulfate were the hexadecyl substituted sesquisulfate and the octadecyl substituted disulfate. In distilled water, throughout the concentrations studied, they removed as much soil as soap. They were somewhat less effective in hard water although at 0.25% concentration in 300 ppm. water they were almost twice as efficient as the soap used as the standard.

The detergent made from the hexadecyl substituted sesquisulfate and built with a large amount of sodium tripolyphosphate was the most efficient of the experimentally developed detergents that were evaluated for soil removal. In distilled water it was slightly more effective than the soap, and in water of 150 and 300 ppm. hardness reached its maximum soil-removing efficiency at 0.25% concentration with index values of 0.87 and 0.80, respectively. At higher concentrations in hard water it was less efficient.

Under the conditions used in these experiments the detergent containing 95% N-rosin-D-gluconamide sodium trisulfate and 5% sodium sulfate was the least efficient of those tested. In both distilled and hard water it was no more effective in removing soil than water without detergent.

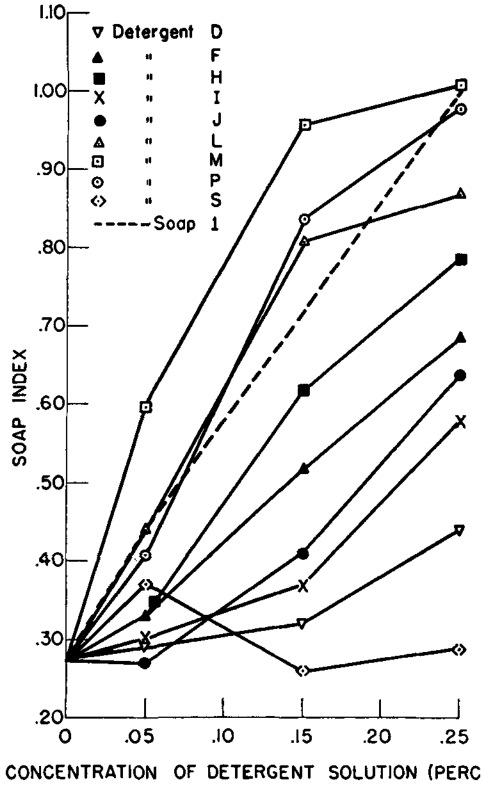

FIG. 1. Soil-removing efficiency of detergents D through S and soap 1 in distilled water at 60°C.

Figures 1 and 2 show the soil-removing ability in distilled water and in water of 300 ppm. hardness of the experimentally developed detergents compared with the soap used as the standard. Under the conditions of this study, in distilled water at concentrations of 0.05 and 0.15%, the N-hexadecyl-D-gluconamide sodium sesquisulfate built with sodium tripolyphosphate was more effective than soap. The detergents, N-hexadecyl-D-gluconamide sodium sesquisulfate without alkaline builder and N-octadecyl-D-gluconamide sodium disulfate, removed about as much soil as soap. All other detergents that were evaluated for soil removal in distilled water were less effective than the soap. On the other hand, in water of 300 ppm. hardness at concentrations of 0.35% and below, all the detergents evaluated, except the rosin substituted tri-

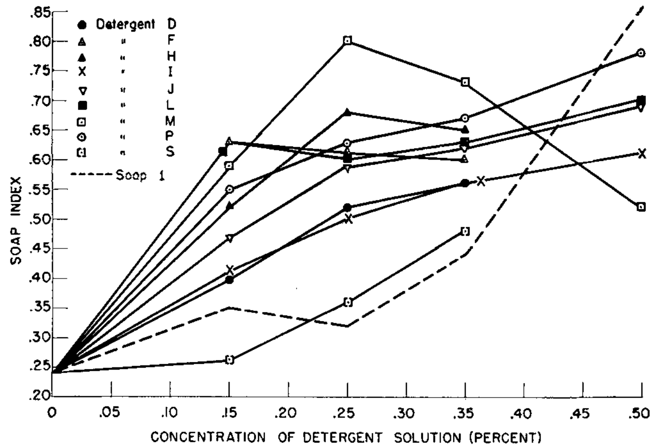

FIG. 2. Soil-removing efficiency of detergents D through S and soap 1 in water of 300 ppm. hardness at 60°C.

sulfate, were considerably more effective in removing soil than the soap used as the standard.

Summary

A number of N-alkyl-D-gluconamides and a rosin substituted D-gluconamide were prepared in good yield by reacting long chain fatty amines and rosin amine with D-glucono-delta-lactone. Reaction of these compounds with chlorosulfonic acid yielded sulfates of various degrees of substitution whose sodium salts exhibited marked surface active properties. Soil-removal tests with cotton fabric showed several of these products to be effective detergents in hard water.

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ABSTRACTS . . . . Don Whyte, Editor

• Oils and Fats

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Use of trichloroacetic acid in the purification of lipids. R. M. Johnson and P. R. Dutch (Detroit Inst. Cancer Res., Detroit, Mich.). *Proc. Soc. Expt. Biol. Med.* **78**, 662(1951). Purified lipids may be extracted from tissue with ethanol-ether solution if the tissue is first extracted with 10% trichloroacetic acid solution made 0.4M with $MgCl_2$.

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