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Silicon-Modified Carbohydrate Surfactants III: Cationic and Anionic Compounds

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Ionic siloxanyl-modified carbohydrate surfactants have been synthesized by alkylation/esterification of precursors containing tertiary amino functions. Depending on the reaction strategy, the siloxanyl moiety is part of the alkylating agent or the substrate. Polyhydroxylated tertiary amines can be quaternized by siloxanyl-modified chloroacetic acid esters or epoxysiloxanes in the presence of glacial acetic acid. The esterification of tertiary amines bearing carbohydrate and siloxanyl subunits by cyclic acid anhydrides yields, after neutralization, carboxylate salts. The reaction of hydroxyl groups and sulfamic acid leads to sulfates. The new substances were characterized by means of ^{13}C NMR spectroscopy, gas chromatography, elemental analysis and their solubility profile. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Anionic siloxane surfactants of the carboxylate,[1–3] sulfonate[4–7] and sulfate[8] type are well known. The same is true for cationic[9–13] and zwitterionic surfactants of the sulfobetaine[14,15] and carbobetaine[16–18] types. The interest in these substances stems from their superior properties as fabric-conditioning agents, wetting agents on low-energy surfaces, paint additives and adjuvants in cosmetic and agrochemical formulations.[7,12]

In certain cases the ionic substructures have been modified by nonionic ones. It is possible to incorporate oligoalkylene oxide units into the spacer between the siloxanyl moiety and the ionic head group[9] (Fig. 1a). Alternatively, polysiloxanes can be modified by separated quaternary ammonium and oligoalkylene oxide units in a comb-like structure.[13] The same concept has been applied to carbobetaine and oligoalkylene oxide substructures[16,17] (Fig. 1b). In all these cases, the additional nonionic moiety improves the compatibility with anionic surfactants.

Although hydroxyl groups attached to the spacer[19] and even close to the hydrophobic siloxanyl moiety[6] have been known for a long time in ionic siloxane surfactants, their importance as part of the hydrophilic head has been stressed only recently.[12] It was found that a single hydroxyl group already considerably influences the aggregation behavior in solution and the adsorption on hydroxylated surfaces. So far no attempt has been made to incorporate powerful polyhydroxylated carbohydrate moieties into ionic siloxane surfactants.

On the other hand, carbohydrate-modified ionic hydrocarbon-based surfactants have already been synthesized. The reaction of D-gluconic acid δ-lactone and *N*,*N*-dimethyltrimethylenediamine yields a gluconamide which can be quaternized by alkyl halogenides.[20] In an attempt to counteract the decreasing reactivity of alkyl halogenides with chains that are too long, the chloroacetic acid and 3-chloropropionic acid esters of fatty alcohols[21] and the fatty alkyl esters of *p*-toluenesulfonic acid[22] have been used as effective alkylating agents. Quaternary fatty alkyl glucammonium salts are also known.[23,24] Thus long-chained epoxides are used for the alkylation of polyhydroxylated primary or secon-

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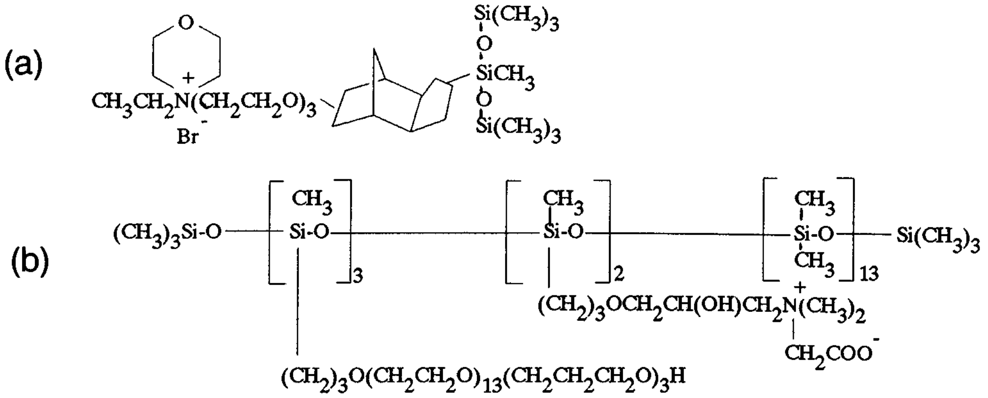


Figure 1

dary amines. The products can be quaternized by dimethyl sulfate. The esterification of long-chained alkenyl succinic anhydrides with sorbitol or mannitol yields monoesters. The remaining carboxylic acid function can be neutralized.[25–27] Surfactants of this type considerably improve the wetting behavior of gelatine solutions. In nature, sulfated steroid glycosides and glycerine-based lipids[28] are well known. Glucammonium salts of paraffin sulfonic acids have been used in cosmetic formulations.[23,29]

This paper shows that certain of the concepts outlined above can be applied successfully to the synthesis of carbohydrate-modified ionic siloxane surfactants.

2 METHODS AND MATERIALS

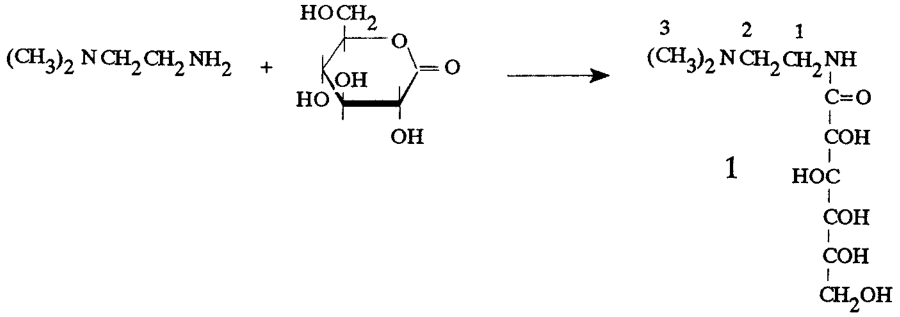
2.1 Methods

The ^{13}C NMR spectra were recorded on a Varian XL 300 spectrometer. In certain cases APT experiments (Attached Proton Test, 75 MHz frequency, delay time 7 ms) were carried out to determine the multiplicity. Deuterated DMSO served as solvent and internal standard. Column GC experiments were carried out on a Varian 1400 chromatograph (temperature program 50→280 °C, heating rate 10 °C min^{-1}, FID). A 0.5 m steel column (1/8 inch) packed with Chromosorb W-AW-DMCS (80–100-mesh, modified with 10% SE 30 as separation phase) was used. The elemental analysis data were determined on a Carlo Erba analyzer, model 1106.

2.2 Materials

2.2.1 Carbohydrates

D-Gluconic acid δ-lactone (GA; Riedel de-Haen) and *N*-methyl-D-glucamine (NMGA) (Fluka) are commercialy available. O^5-α-D-Glucopyranosyl-D-arabinonic acid lactone (GPAL) can be synthesized by lactonization of the potassium arabinonate in the presence of ion exchangers (sulfonic acid form).[30] The potassium salt was a gift from Südzucker AG Mannheim.



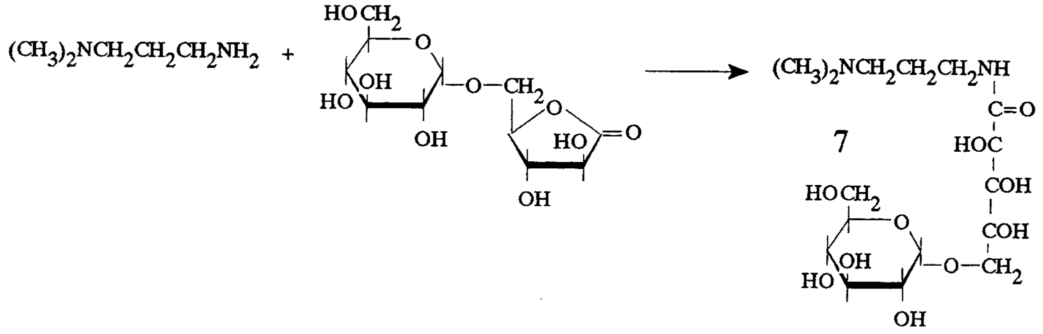
Scheme 1

2.2.2 Polyhydroxylated dialkylaminoalkylamides

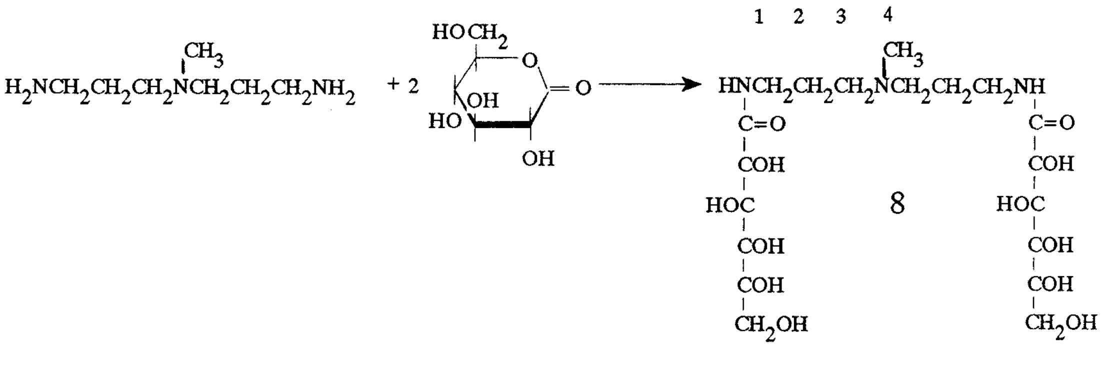
Tertiary amino functions containing gluconic acid amides and gluycopyranosyl arabinonic acid amides were synthesized according to literature procedures.[20,32,33]

N,*N*-Dimethylethylenediamine (MED), *N*,*N*-dimethyltrimethylenediamine (MTD), *N*,*N*-diethylethylenediamine (EED), *N*,*N*-diethyltrimethylenediamine (ETD), *N*,*N*-dibutylethylenediamine (BED), *N*,*N*-dibutyltrimethylenediamine (BTD) and *N*,*N*-bis(3-aminopropyl)-methylamine (PMA) are commercially available (Aldrich) and were used without further purification.

The reactions between primary and tertiary amino functions containing polyamines and polyhydroxylated lactones (molar ratio RNH_2: lactone = 1:1) were carried out in refluxing methanol (5 h reaction time) and yielded regioselectively the corresponding amides (Schemes 1–3). The complete conversion of the amine was followed by means of gas chromatography. After removing the solvent, the remaining solids or wax-like materials were dispersed in diethyl ether. White solids were precipitated; the diethyl ether could be sucked off and replaced by n-pentane. The amides were washed several times in n-pentane and finally dried as white powders under reduced pressure (10 mmHg, room temperature). The amides synthesized and their ^{13}C NMR data are summarized in Tables 1 and 2. The ^{13}C NMR signal assignments for the carbohydrate subunits are identical to those already



Scheme 2



Scheme 3

Table 1 Synthesis of polyhydroxylated amides **1–8**

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Amine	MED	EED	BED	MTD	ETD	BTD	MTD	PMA
Lactone	GA	GA	GA	GA	GA	GA	GPAL	GA

Table 2 ^{13}C NMR data of the dialkylaminoalkylamides **1–8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
C-1	36.08	36.26	36.40	36.86	37.11	37.05	36.83	36.84
C-2	57.93	51.34	52.70	26.96	26.45	26.78	26.95	26.52
C-3	45.04	46.41	53.37	56.96	50.29	51.51	56.85	54.97
C-4	—	11.61	28.90	45.20	46.25	53.25	45.07	41.47
C-5	—	—	19.95	—	11.50	28.85	—	—
C-6	—	—	13.85	—	—	20.09	—	—
C-7	—	—	—	—	—	13.89	—	–

published for hydrocarbon-based amino-amides.[33]

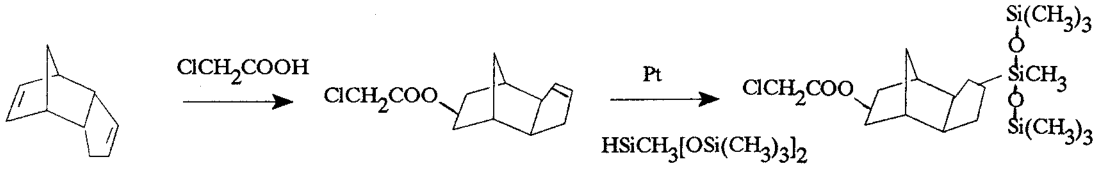
2.2.3 Siloxanyl-modified amines, epoxides, esters and polyhydroxylated nonionic compounds

1,1,1,3,5,5,5-Heptamethyltrisiloxane (M_2D^H) was prepared according to a literature procedure described elsewhere.[34]

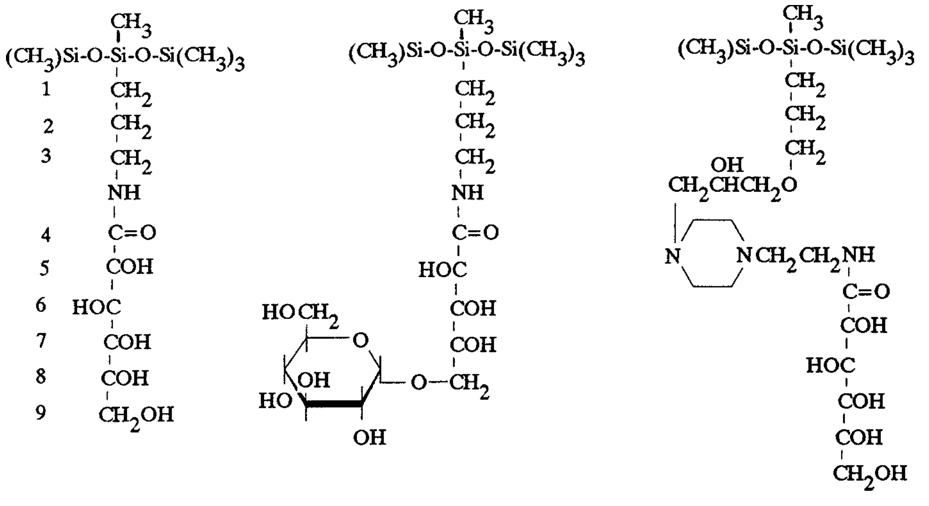
3-(3-Aminopropyl)-1, 1, 1, 3, 5, 5, 5-heptamethyltrisiloxane (**9**) (b.p. 139–142 °C/ 50 mmHg) was prepared from M_2D^H and allylamine in the presence of the alkanol-treated Lamoreaux platinum catalyst[35] (SiH:C=C: Pt=1:1:10^{-4}; 8 h reflux) according to a literature procedure.[36]

3-[3-(Oxiranylmethoxy)propyl]-1, 1, 1, 3, 5, 5, 5-heptamethyltrisiloxane (**10**) (M_2D^{Ep}, b.p. 129–132 °C/3 mmHg) was prepared from M_2D^H and allyl glycidyl ether in analogy to the aminosiloxane **9**.

2(3) - (1,1,1,3,5,5,5-Heptamethyltrisiloxanyl)-5(6)-chloroacetyl-2, 3, 3a, 4, 5, 6, 7, 7a-octahydro-4, 7-methano-1*H*-indene (**11**) (M_2D^{Es}, b.p.



Scheme 4



(12) (13) (14)

Figure 2

132–140 °C/0.15 mmHg) can be synthesized from *endo*-dicyclopentadiene. After acid-catalyzed esterification at the norbornene ring with chloroacetic acid under *endo*→*exo* skeleton rearrangement the remaining cyclopentene ring double bond can be hydrosilylated[37] (Scheme 4).

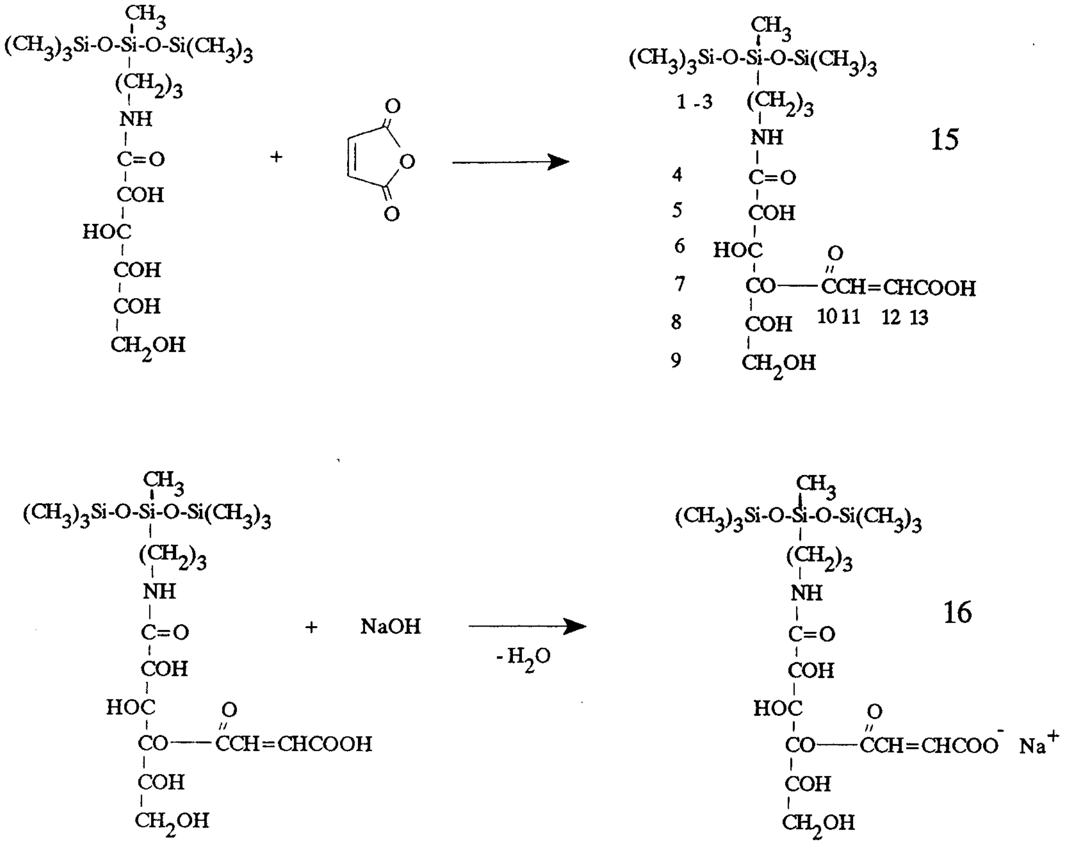
The synthetic procedures yielding siloxanyl-modified polyhydroxylated amides and amines have been described in earlier papers. The straight-chained amides **12** and **13** are accessible from the aminopropyl-substituted siloxane **9** and lactones by nucleophilic ring opening.[38] The polyhydroxylated aminoamide **14** can be synthesized from the siloxanyl-modified epoxide **10** and a piperazinyl gluconamide[33] (Fig. 2).

2.2.4 Siloxanyl-modified carboxylates and sulfates

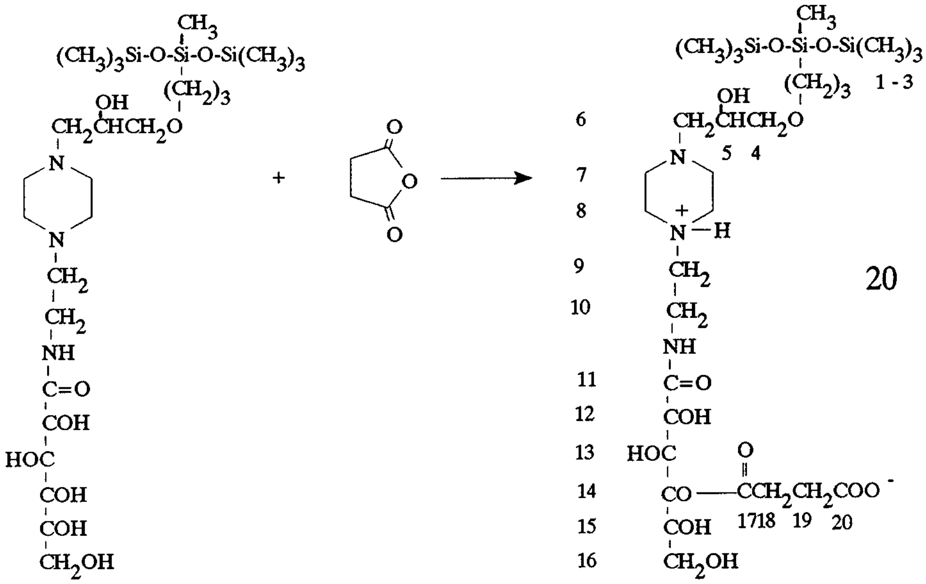
The polyhydroxylated straight-chained amides **12** and **13** were esterified in dry dioxane with maleic anhydride (MA) (molar ratio amide:anhydride = 1:1) in the presence of about 1% by wt of an anhydride ring-opening catalyst (I_2, CS_2, triethylamine). After the solvent had been removed, the solids were dispersed in n-pentane, precipitated and dried. In a stoichiometric reaction the remaining carboxylic acid functions were neutralized with various bases in methanol (Scheme 5).

Thus, 8 g (28.6 mmol) of the aminosiloxane **12** and 5.12 g (28.6 mmol) D-gluconic acid δ-lactone were heated to reflux in 35 ml methanol. After 6 h the solvent was removed and the viscous oil obtained was dispersed in 40 ml n-pentane. A white product was precipitated. The solid material was separated from the hydrocarbon and dried in vacuum (10 mmHg, room temperature). (12.5 g of **12**) A white powder was obtained. The material was poorly soluble in water.

The gluconamide **12** (6.9 g; 15 mmol) and 10 mg I_2 were dispersed in 30 ml dry dioxane. To dissolve the gluconamide, the mixture was heated to 90 °C. After cooling to room temperature, a solution of 1.47 g (15 mmol) maleic anhydride in 5 ml dry dioxane was added.



Scheme 5



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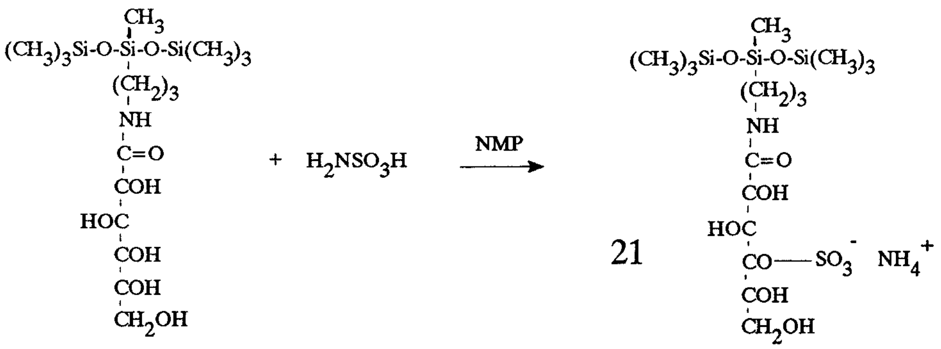
Scheme 6

During 1.5 h the mixture was heated to 90 °C and maintained there for 6 h. After the end of the reaction, the solvent was removed in vacuum and the wax-like material dispersed in 30 ml n-pentane. By vigorous agitation a white material could be precipitated. The white wax separated from the solution was subjected to two additional precipitation cycles in n-pentane and finally 7.8 g of a white, slightly yellow wax (**15**) were obtained after drying in vacuum (10 mmHg, room temperature).

A 2 g (3.6 mmol) portion of the ester **15** and 0.7 g (3.6 mmol) *N*-methyl-D-glucamine were dissolved in 10 ml methanol and heated to reflux for 1 h. The solvent was removed and the slightly yellow powder was dispersed in 30 ml n-pentane. The solid material formed a bottom layer, n-pentane was sucked off and after drying 2.5 g of an almost white powder (**18**) were obtained. The substance could be dissolved in water.

For the esterification of the polyhydroxylated piperazinyl-substituted aminoamide (**14**) with succinic anhydride (SA), a separate ring-opening catalyst was not used. Due to the presence of tertiary amino functions in the molecule a neutralization step was not necessary (Scheme 6).

Hydroxyl groups of the gluconamide **12** have been sulfated by sulfamic acid in *N*-methylpyrrolidone[7,8] (Scheme 7). Thus, 3 g (6.56 mmol) of the gluconamide **12** were dissolved in 20 ml *N*-methylpyrrolidone (NMP) under an argon atmosphere. Sulfamic acid (0.64 g, 6.56 mmol) was added at room temperature and afterwards the mixture was heated to 90 °C for 7 h. After the



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Scheme 7

Table 3 Elemental analysis data of the maleic acid derivatives and the sulfate (%)

Compd	Amide	anhyd.	Base/Acid	Product consistency	C Calc.	Found	H Calc.	Found	N Calc.	Found
15	**12**	MSA	—	White wax	43.24	41.70	7.39	7.10	2.52	3.10
16	**12**	MSA	NaOH	White powder	41.52	39.90	6.93	6.78	2.43	2.33
17	**12**	MSA	$(C_2H_5)_3N$	Yellow syrup	47.56	46.20	8.84	8.31	4.26	4.06
18	**12**	MSA	MGA	Yellow powder	43.20	42.65	7.73	7.95	3.73	3.70
19	**13**	MSA	KOH	Yellow powder	41.37	41.10	6.62	6.52	1.93	1.89
20	**14**	SA	—	Yellow powder	46.83	45.56	8.21	8.19	5.65	5.37
21	**12**	MSA	H_2NSO_3H	Yellow powder	34.65	31.77	7.58	7.04	5.05	6.29

end of the reaction a mixture of 30 ml diethyl ether and 50 ml n-hexane was added. A viscous bottom layer separated and could be isolated. This material was mixed with 30 ml diethyl ether and 20 ml n-hexane. Again, a bottom layer could be isolated, which was dispersed in 20 ml diethyl ether. A tough wax precipitated which was washed four times with 20 ml diethyl ether to remove, stepwise, remaining traces of *N*-methylpyrrolidone. After drying in oil vacuum (0.7 mmHg, 40 °C) 2.6 g of a yellow powder (**21**) were obtained. Despite the above-described purification procedure, traces of NMP were detected by means of gas chromatography and in the ^{13}C NMR spectrum. The substance was instantaneously soluble in water and tended to form strongly foaming aqueous solutions under agitation.

Table 4 ^{13}C NMR data (δ ppm) of compounds 12, 13 and 14

	12	**13**	**14**
C-1	14.39	14.45	13.16
C-2	22.87	22.97	22.88
C-3	41.21	41.26	72.90
C-4	172.42	173.04	73.50
C-5	73.68	73.60	66.99
C-6	70.16	70.75	61.41
C-7	71.57	68.87	52.75
C-8	72.49	69.50	53.36
C-9	63.43	98.91	56.74
C-10	—	71.63	35.48
C-11	—	72.43	172.44
C-12	—	70.19	73.50
C-13	—	72.28	70.08
C-14	—	60.84	71.44
C-15	—	—	72.04
C-16	—	—	63.40

In Tables 3–6 the products, elemental analysis and ^{13}C NMR data of the carboxylates and the sulfate are summarized.

2.2.5 Cationic polyhydroxylated siloxane surfactants

Quaternization of tertiary amino functions containing aminoalkylamides (see Section 2.2.2) yields polyhydroxylated ammonium salts. The chloroacetic acid ester of the siloxanyl-modified dicyclopentadiene[9] **11** and the epoxysiloxane[19] **10** have been used as alkylating agents (Scheme 8). *N*-[3-(*N*′,*N*′-Dimethyl)aminopropyl)]gluconic acid amide 1 g (3.6 mmol) and 1.6 g (3.6 mmol) 2(3)-(1, 1, 1, 3, 5, 5, 5-heptamethyltrisiloxanyl)-5(6)-chloroacetyl-2,3,3a,4,5,6, 7, 7a-octahydro - 4, 7 - methano - 1*H* - indene (**11**) and 10 mg KI were dissolved in 20 ml dry ethanol. The mixture was heated to reflux for 25 h. The solvent was removed and the wax-like material dispersed in 25 ml n-pentane. A solid was precipitated and was washed in n-pentane five times. After drying in vacuum (10 mmHg, room temperature) 2.3 g of a yellow, hygroscopic powder (**25**) are obtained.

N-[3-(*N*′, *N*′-Dimethyl)aminopropyl)]gluconic acid amide (0.83 g; 2.97 mmol), 1 g (2.97 mmol) of the epoxysiloxane **10** and 0.178 g (2.97 mmol) glacial acetic acid were dissolved in 25 ml dry methanol at room temperature. The mixture was heated in a steel autoclave to 95 °C for 8 h. Afterwards the solvent was removed and the wax obtained was dispersed in a mixture of 20 ml

Table 5 ^{13}C NMR data (δ ppm) of the maleic acid derivatives 15, 16, 19 and 20

	15a	**15b**	**16a**	**16b**	**20**	**19a**	**19b**
C-1	14.44	14.44	14.62	14.43	13.26	14.44/14.60	
C-2	22.24	22.96	22.89	22.89	22.98	22.94/22.77	
C-3	42.21	41.35	41.57	41.27	72.87	41.24/41.58	
C-4	175.92	172.59	175.91	172.57	73.50	173.03/173.14	
C-5	73.44	81.57	73.40	81.40	65.07	73.69	73.52
C-6	69.51	68.09	69.22	67.95	60.23/61.08	70.09	70.73
C-7	80.22	71.68	80.31	71.57	53.06/53.17	79.24	68.82
C-8	72.91	72.66	72.73	72.56	52.16/52.88	69.49	
C-9	62.94	63.54	62.87	63.43	56.67/54.49	98.82/98.73	
C-10	165.45	165.45	165.35	165.35	35.38	71.72	71.80
C-11	132.06	132.17	130.35	130.35	177.60	72.41	72.74
C-12	133.84	133.84	135.78	136.29	73.43/81.50	70.18	
C-13	165.82	165.28	168.42	168.42	69.45/70.08	72.20	73.09
C-14	—	—	45.40	45.40	80.21/71.64	60.80	65.58
C-15	—	—	8.77	8.77	73.14/73.03	165.29	
C-16	—	—	—	—	62.96/63.52	128.71	
C-17	—	—	—	—	174.47	136.07	
C-18	—	—	—	—	28.06	167.40	
C-19	—	—	—	—	29.86	—	
C-20	—	—	—	—	175.72	—	

diethyl ether and 20 ml n-hexane. The precipitate was isolated and dried in vacuum (0.7 mmHg, room temperature); 1.8 g of a yellow, amorphous solid (**29**) were obtained.

The experiments, product yields, elemental analysis and ^{13}C NMR data are summarized in Tables 7–10.

3. RESULTS AND DISCUSSION

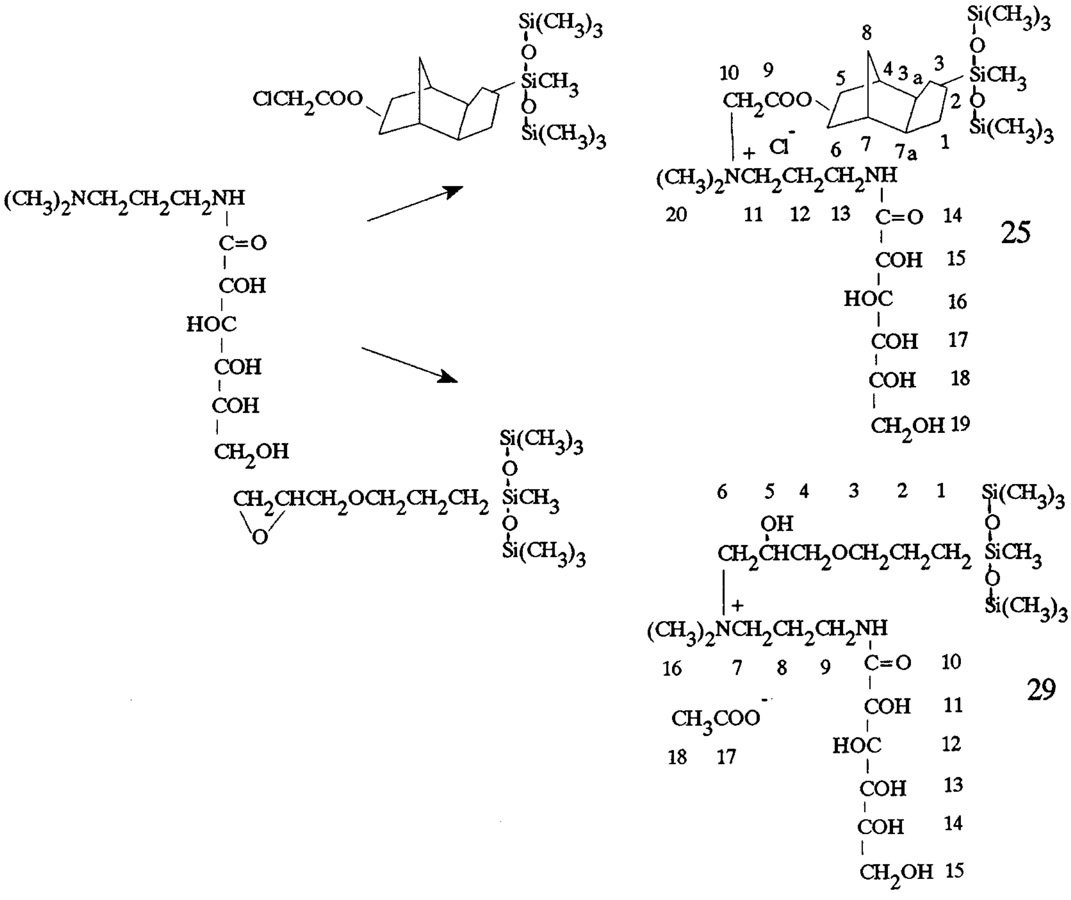
3.1 Siloxanyl-modified carboxylates and sulfates

In earlier papers of this series,[33,38] we have discussed in detail three basic strategies to support the limited hydrophilic power of monosaccharides in siloxane surfactants: (1) the use of disaccharide derivatives (this means the substitution of one OH group of a carbohydrate moiety by a complete monosaccharide structure), (2) the incorporation of a hydrophilic spacer into the surfactant molecule and (3) the addition of a hydrophilic modifying element. The synthesis of ionic species represents a fourth attempt to improve the water solubility of siloxanyl-modified carbohydrate surfactants.

The esterification of unprotected carbohydrates usually leads to mixtures of mono- and more highly-acylated species. The product distribution depends strongly on the carbohydrate structure as well as on the reaction conditions.[40] In a few cases, selective reactions have been observed. Thus in benzoyl chloride/pyridine mannitol yields the esters of the primary hydroxyl groups exclusively. Unfortunately the esterification of saccharose gives mixtures of mono- and more highly substituted esters; this inhibits a broader industrial application. The

Table 6 ^{13}C NMR data (δ ppm) of the sulfate 21

C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	$-COSO_3^-$
14.43/ 13.91	22.90/ 22.70	41.28/ 41.61	172.25/ 171.96/ 175.61/ 175.70	73.62/ 73.28/ 73.12/ 73.94	70.17/ 69.33/ 69.81/ 69.91/ 69.71	71.54/ 71.11	72.45/ 72.72/ 72.22	63.39/ 62.81/ 62.96/	77.13/ 78.78/ 79.78/ 80.09/ 81.40



Scheme 8

Table 7 Quaternizations: reactants, conversions and product consistency of compounds 22–33

Compound	Silicon Compd	Amide	Solvent[a]	Reaction time (h) Temp. (°C)	Conversion (%)	Yield (%)	Product consistency
22	**11**	**1**	EtOH	25/reflux	90–95	79	Yellow powder
23	**11**	**2**	ni + i-PrOH (83:17)	30/reflux	95	75	Yellow wax
24	**11**	**3**	ni	32/reflux	90–95	70	Brown syrup
25	**11**	**4**	EtOH	25/reflux	100	88	Yellow powder
26	**11**	**5**	ni + i-PrOH (80:20)	35/reflux	100	84	Yellow wax
27	**11**	**6**	ni	39/reflux	100	81	Yellow wax
28	**11**	**7**	EtOH	20/reflux	100	92	Bright yellow powder
29	**10**	**4**	MeOH	8/95	85–90	90	Yellow wax
30	**10**	**5**	MeOH	8/95	10	—	Brown syrup
31	**10**	**6**	MeOH	12/95	10	—	Brown syrup
32	**10**	**8**	MeOH	10/95	40	—	Brown powder
33	**10**	**7**	MeOH	15/95	70–80	54	Brown powder

[a] Abbreviations: MeOH, methanol; EtOH, ethanol; i-PrOH, isopropanol; ni, nitromethane.

Table 8 Elemental analysis data (%) for compounds 22–29 and 33

	C		H		N	
Compd	Calc.	Found	Calc.	Found	Calc.	Found
22	48.70	48.21	8.26	8.21	3.92	3.61
23	50.10	51.40	8.48	8.81	3.77	3.63
24	52.59	51.10	8.89	8.70	3.51	3.72
25	49.42	48.60	8.37	8.34	3.84	3.33
26	50.76	50.82	8.59	8.93	3.70	3.23
27	53.16	52.00	8.98	9.00	3.44	3.28
28	48.81	47.70	8.02	7.65	3.25	3.24
29	46.12	45.11	8.87	8.82	4.14	3.96
33	46.01	45.48	8.41	8.46	3.46	3.57

benzoylation of gluconic acid amide and glucopyranosyl arabinonic acid amide also yields mixtures of mono and higher esters.

In line with these earlier results, we found that the esterification of the hydroxyl groups of siloxanyl-modified gluconamides[41] does not proceed regioselectively.

In the ^{13}C NMR spectrum of **15** (Table 5) two signal sets of different intensity emerge. Due to an APT spectrum, the strong signal at 80.22 ppm indicates the formation of an ester of a secondary hydroxyl group. Because the signal at 71.68 ppm describing the C-7 alcohol in an unsubstituted state (see also signal assignment for the unsubstituted gluconamide **12**), is of considerably weakened intensity, the corresponding ester was identified as the main product. A weak signal for a second esterified secondary hydroxyl group

Table 9 ^{13}C NMR data (δ ppm) of selected ammonium salts[a]

	22	**25**	**26**	**27**	**28**		**29**	**33**
C-9	164.62/164.95	165.03/164.74	164.61/164.40	164.34	164.37/164.65	C-4	74.35	73.57
C-10	61.98/61.76	61.99	62.90	62.81	61.95	C-5	66.14	66.05
C-11	61.17/61.35	60.71	54.90	59.62/59.80	60.77	C-6	63.79	63.86
C-12	35.28	22.51	23.38	23.32/23.20	22.53	C-7	62.24/62.39	62.20
C-13		34.97	35.49/35.01	35.45/35.10	35.04	C-8	22.51	22.65
C-19	51.52/51.48					C-9	35.06	35.20
C-20		50.88/50.70	46.14	51.61	50.99/50.81	C-16	51.39/51.46	
C-21			8.40/7.45	24.80		C-21		51.56/51.34
C-22				19.40/19.07				
C-23				13.40/13.27				

[a] Siloxanyl-modified esters and ethers of dicyclopentadiene consist of up to seven isomers. The structure elucidation and NMR signal assignment for these structures have been discussed in detail elsewhere.[37,39] The signal sets for the carbohydrate moieties are almost identical to those already published in an earlier paper.[33] The complete signal sets are given for two selected structures in Table 10.

emerges at 81.57 ppm. Due to its low-field shift it belongs to C-5 or C-8. As the weak signals for C-7, C-8 and C-9 correspond to unsubstituted structures it was assigned to C-5. As a consequence of the existence of two main isomers (ratio 80:20) the signals for other carbon atoms are often split (Fig. 3).

The same is true for the esterified disaccharide derivative **19**. The signal at 65.58 ppm belongs to an esterified primary alcohol group (C-14). The signal at 79.24 ppm describes an esterified secondary hydroxyl group. As the signals for C-1, C-2, C-3, C-4 and C-9 are split, this secondary ester belongs to C-5, C-6 or C-7 (C-1 to C-4 are too distant to respond with split signals on two esterifications of the glucosyl ring). C-5 shows a split signal (73.69 and 73.52 ppm) and therefore has not been esterified. In contrast, the most high-field shifted secondary alcohol peak (68.82 ppm) has no corresponding signal in an acceptable distance. Probably C-7 is the second esterification position.

So far, we have not been able to identify the sulfation pattern (Table 6, compound **21**). As can be seen from the data, a multiplet of signals for sulfated carbon atoms emerges between 77 and 82 ppm (Fig. 4). This complicated situation is confirmed by signal multiplets or strong line-broadening effects for the other carbon atoms. Probably every hydroxyl group of the starting material is sulfated. To a minor extent double sulfations are also probable, as is the existence of a few unsulfated molecules.

In an attempt to synthesize highly soluble sulfobetaines, we tried to react the maleic acid half-ester (**15**) with 1,1-dimethyl-3-methylsulfinic acid-4-sulfomethylpyrrolidinium betaine[15] in dioxane/water (Scheme 9). Unexpectedly, the reaction led to the elimination of the siloxanyl moiety.

The solubility profiles (Table 11) prove that the incorporation of a carboxylate substructure strengthens the water solubility (compounds **12, 17** and **18**). The same effect can be achieved by a sulfate group (compound **21**). In both cases, however, this trend is accompanied by a significantly reduced oil solubility. To counter this undesired effect, in exploratory experiments we incorporated carboxylic acid anhydrides (5-norbornene-2,3-dicarboxylic anhydride, phthalic anhydride and dodec-2-enyl succinic anhydride) which have better oil solubility. According to

Table 10 ^{13}C NMR data of compounds 25 and 29

Compound **25**[a]		Compound **29**	
C-atom	δ (ppm)	C-atom	δ (ppm)
1 + 2/3 (unsubst.)	32.96/32.82/32.61/32.47	1	13.09
2/3(Si-subst.)	29.02/28.91	2	22.80
3a	48.96/48.69/48.13	3	73.95
4/7	45.80/45.42/44.75/44.10	4	74.35
5/6 (unsubst.)		5	66.14
5/6 (0-subst.)	78.54	6	63.79
7a		7	62.24/62.39
8	28.83	8	22.51
9	165.28/164.74	9	35.06
10	61.99	10	173.25
11	60.71	11	73.31
12	22.51	12	70.02
13	34.97	13	71.29
14	173.28	14	72.84
15	73.80	15	63.36
16	70.14	16	51.39/51.46
17	71.44	17	174.59
18	72.26	18	23.82
19	63.27		
20	50.88		

[a] The peaks for C-5/6 (unsubst.) and C-7a are covered by the DMSO signals (38.6–40.3 ppm). Spectra in other solvents (i.e. $CDCl_3$) showed significant peak shifts.

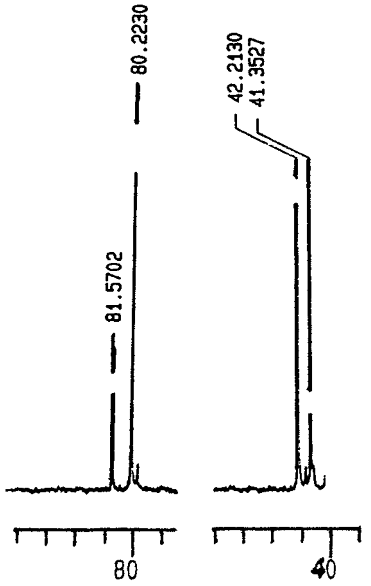


Figure 3 ^{13}C NMR spectrum of compound **15**: region at 80 ppm (esterified secondary alcohols) and at 41 ppm (C-3).

NMR data, the esterification pattern is similar to that of compound **15**. These products are quite oil-soluble, but almost insoluble in water. Because of the poor water solubility of these products we did not carry out detailed investigations.

The synthetic routes described above depend on allylamine as a starting compound. To bypass this troublesome material, we used the amino-amide **14** as a precursor for an esterification reaction. In this particular case the more accessible epoxysiloxane **10** can be used as starting material. The reaction with succinic anhydride yields immediately an ampholyte[42] which is readily soluble in water. According to the ^{13}C NMR spectrum the esterification pattern is identical to that discussed in detail for substance **15**. The signal splitting for the carbon atoms attached to the piperazine ring should be due to the combined effects of a flexible esterification position and a variable state of N-atom protonation.[43] Attempts to use maleic anhydride yielded a significantly less water-soluble, brownish solid. Although the corresponding ^{13}C NMR spectrum shows no major changes, alkylation reactions at the activated double bond[44] may have taken place.

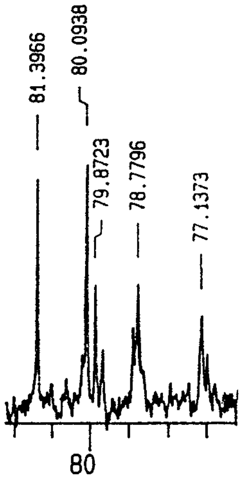


Figure 4 ^{13}C NMR spectrum of compound **21**: region at 80 ppm (sulfated secondary alcohols).

Scheme 9

Table 11 Solubility[a] of selected compounds in solvents of different polarity

Compd	H_2O	NMP	NOP	Hall comid M8-10	Xylene	1,2,3-Trimethyl benzene	Isophorone	Octyl acetate	Rape-oil methyl ester	Paraffin oil
12	–	+	+	+	+	–	–	–	–	–
17	+	+	–	–	–	–	–	–	–	–
18	+	+	–	–	–	–	–	–	–	–
13	+	+	+	–	–	–	–	–	–	–
19	+	+	–	–	–	–	–	–	–	–
14	+	+	+	+	+	+	+	+	+	–
20	+	+	+	+	+	+	–	–	–	–
21	+	+	–	–	–	–	–	–	–	–
24	+/–[b]	+	+	+	+	+	+	+	–	–
25	+	+	+	–	–	–	–	–	–	–
27	+/–[b]	+	+	+	+	+	+	+	–	–
28	+	+	–	–	–	–	–	–	–	–
29	+	+	–	–	–	–	–	–	–	–
33	+	+	–	–	–	–	–	–	–	–

[a] Solubility of 7.15% surfactant in the solvent at room temperature. Abbreviations: NMP, *N*-methylpyrrolidone; NOP, *N*-octylpyrrolidone; Hallcomid M8–10, C_8–C_{10} carboxylic acid amides.

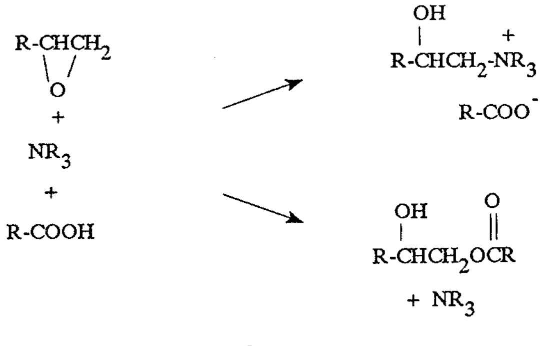
[b] +/–, turbid solution.

3.2 Quaternary ammonium salts

Both the siloxanyl-modified chloroacetic acid ester **11** and the allyl glycidyl ether derivative **10** were found to be suitable alkylating agents for carbohydrate-modified tertiary amines.

The three substructures of the tertiary amines have been varied systematically to determine the scope of these alkylations, by adjusting (1) the size of the carbohydrate, (2) the length of the alkylene bridge and (3) the size of the alkyl groups attached to the tertiary nitrogen atom. The data given in Table 7 show that for the chloroacetic acid ester derivative the quaternization does not depend on the size of the carbohydrate (compounds **25** and **28**). Quantitative quaternizations of mono- and di-saccharide derivatives are possible. An essential precondition for a quantitative alkylation is a sufficiently long alkylene bridge to insulate the tertiary amino function from electronic (amide structure) influences. In contrast to the experiments with trimethylene-bridged derivatives (compound **25**), the reactions in the presence of the shorter -CH_2CH_2- bridge (compound **22**) did not yield the quaternary ammonium salts quantitatively. Unreacted chloroacetic acid derivative was detected by means of gas chromatography and finally extracted from the reaction mixture. On the other hand, the size of the alkyl groups was found to have no significant influence on the conversion. In both reaction series [-$(CH_2)_3$-spacer 100%, compounds **25–27**; -$(CH_2)_2$- spacer 90%, compounds **22–24**] the conversion remained constant.

Attempts to use alkyl ethers instead of esters (i.e. $ClCH_2CH_2OR$, $ClCH_2CH_2OCH_2CH_2OR$) as



Scheme 10

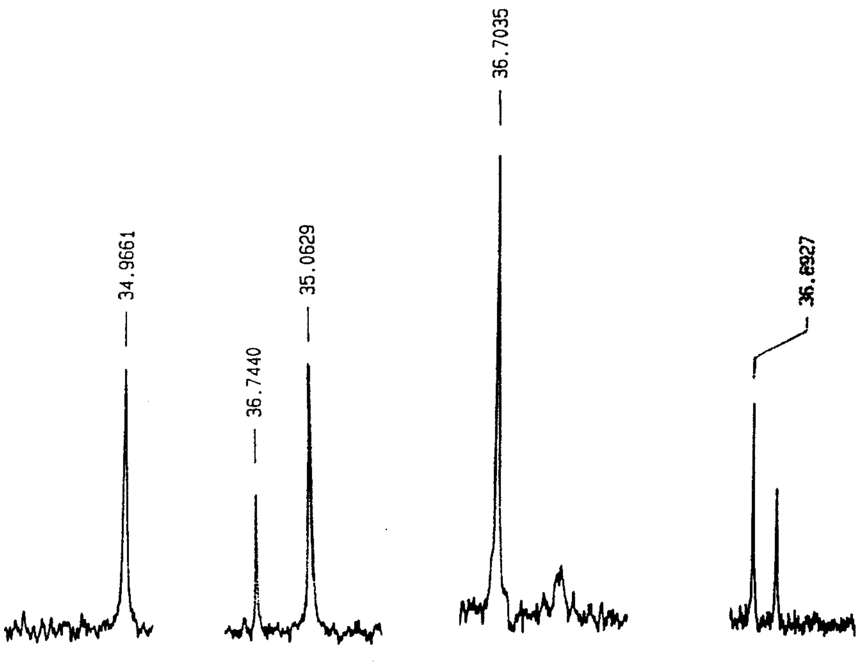
alkylating agents failed. Due to higher reaction temperatures and extended reaction times, dark brown mixtures of quaternized products, starting materials and unidentified rearrangement products were obtained in all these cases.

For the siloxanyl-modified epoxide as alkylating agent in combination with acetic acid, the situation changed considerably. Even in the presence of a trimethylene spacer, two methyl groups and the small gluconic acid moiety (compound **29**), complete quaternization was not observed (Fig. 5). This is due to the ability of tertiary amines and aminoamides[45] to catalyze the esterification of epoxides as latent alcohol sources with acids (Scheme 10). By means of gas chromatography we found, instead of unreacted epoxide, the siloxanyl-modified ester (Fig. 6). As expected, the product yield decreases if the more hindered glucopyranosyl arabinonic acid derivative is used (compound **33**).

The choice of the alkyl groups has a striking influence on the reaction path. The substitution of one methyl group by a longer alkyl chain (compound **32**) shifts the equilibrium considerably towards the esterification side. The diethyl- and dibutyl-substituted tertiary amines were found to be excellent esterification catalysts (compounds **30** and **31**). Only minor proportions of quaternized products are formed. Obviously the possibilities of applying the easily accessible epoxysiloxanes in a final alkylating step are restricted by the steric demands of the tertiary amine substrates.

The ^{13}C NMR signal assignments were established by considering well-known data sets for siloxanyl-modified quaternary dicyclopentadienyl derivatives[37,39] and epoxide-based secondary and tertiary amines bearing carbohydrate moieties[33,38] (Tables 9 and 10).

The solubility in organic solvents depends on the size of the carbohydrate, the spacer type and the chain length of the alkyl groups. Due to the hydrophilic power of a disaccharide moiety, derivatives of this type are less soluble in weak polar organic liquids than gluconic acid ones (Table 11, compounds **25** and **28**). The same



(25) (29) (30) (32)

Figure 5 –CONH–$\underline{C}H_2$– region of the ^{13}C NMR spectra of compounds **25** (100% quaternization), **29** (80%), **30** (10%) and **32** (35%).

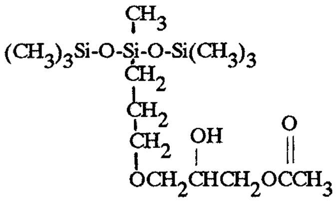


Figure 6

effect can be caused by a hydrophilic spacer. Additional hydroxyl groups improve the water solubility. Hydrocarbon structures (compare compounds **25** and **29**) shift the balance to the organic side. The incorporation of butyl instead of methyl groups improves the organic solubility considerably. In conjunction with a dicyclopentadienyl moiety, excellent organic soluble, charged carbohydrate surfactants are accessible (e.g. compound **27**).

The results show that siloxanyl-modified chloroacetic acid esters and epoxides are versatile starting materials for the synthesis of quarternary ammonium salts. Products of different property profiles can be synthesized. The robust chloroacetic acid route paves the way for the synthesis of flexibly shaped quarternary ammonium salts. Allyl alcohol, propargyl alcohol and but-2-yne-1,4-diol could be favored candidates for further investigations. The possibilities of applying epoxysiloxanes seem to be more restricted on *N,N*-dimethylalkylamino structures. Since the already existing industrial process for the quaternization of trimethylamine[19] can be adopted with minor modifications, this strategy should also be considered.

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