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Silicon-Modified Carbohydrate Surfactants I: Synthesis of Siloxanyl Moieties Containing Straight-Chained Glycosides and Amides

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New siloxanyl-modified carbohydrate surfactants of the amide and glycoside type have been synthesized by coupling between defined as well as higher-molecular-weight siloxanes and carbohydrate structures via spacers of different lengths and hydrophilic power. Linear and branched monohydrogen di-, tri-, tetra- and penta-siloxanes and polyhydrogen siloxanes as well as mono- and di-saccharide lactone structures have been found to be good starting materials for the synthesis of amides, often in quantitative yield, whereas glycosides had to be prepared in low-yield multistep sequences including protection/deprotection steps. Selected strategies were applied to polysiloxanes yielding quantitatively a broad variety of carbohydrate-modified comb-like structures. The new substances were characterized by means of ^{13}C NMR spectroscopy, GC, capillary GC, GC–MS coupling and elemental analysis.

Keywords: siloxanes; carbohydrate modified; surfactants; saccharide

INTRODUCTION

Carbohydrate-modified hydrocarbons have been known for a long time. Due to the introduction of strict toxicological and ecological regulations for surfactants in the past decade, interest in this long-known surfactant group has revived and has led to production on an industrial scale.[1]

The following selection illustrates the variety of the existing structures:

(1) esters of long-chained fatty acids;[2–4]
(2) α/β-alkylpolyglycosides by chemical[5] or enzymic synthesis;[6,7]
(3) alkyl ethers of carbohydrates,[8,9]
(4) alkylglucamines by reductive amination of carbohydrates with fatty amines[10,11] or by alkylation of primary and secondary aminosaccharides;[12,13]
(5) *N*-acyl derivatives of aminosaccharides[10,14–16] or alkylamides of aldonic and uronic acids;[17,18]
(6) alkylurethanes[12,19,20] and ureas.[19,21]

Although silicon-containing structures (Si–O–C bonds) have been extensively used as protecting groups in carbohydrate chemistry,[22] only a few attempts have been made to synthesize hydrolytically stable Si–C linked species.

Glycosides bearing siloxanyl moieties have been claimed by Greber[23] and Sejpka.[24] In both cases acid-catalysed Fischer glycosidations are described, despite the known tendencies of unprotected reducing carbohydrates to oligomerize and of siloxanes to equilibrate under such conditions.

In an attempt to avoid the above problems, Stadler[25] followed a multistep procedure on the route to carbohydrate–polysiloxane graft copolymers. Peracetylation, glycosidation with an alkenol, hydrosilylation and finally deacetylation yield mainly β-glycosides of polysiloxanes. Recently, results on the successful enzymic grafting of amylose to aldonamide structures containing polysiloxanes were published.[26] A step in this synthetic sequence is the known[27] reaction of aldonolactones with primary amino functions of polysiloxanes. Because primary amino functions in polysiloxanes are usually derived from the hydrosilylation of allyl amine, a reaction which results in poor yields, a constant cross-linking tendency and high toxicity of the unsaturated amine, the availability of such functionalized polymers is limited.

In an approach to modify starch, the OH groups

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were functionalized randomly with an epoxysilane in the presence of an excess of alkali.[28,29] After neutralization the Si–O–C bonds of the alkoxysilane structure were replaced by Si–O–Si links, yielding a rather undefined cross-linked copolymer.

So far, no attempt has been made to synthesize systematically carbohydrate surfactants containing low-molecular-weight as well as polymeric silicon moieties, in order to determine the structure dependence of their physicochemical properties. The urgency of this task derives from the contradiction between the claimed superior interfacial properties of silicon surfactants and the lack of detailed information about the reasons for these findings. Additionally, future demands for improved biodegradability will probably have to be met by the incorporation of renewable raw materials. The properties of these types of surfactants will have to be known at that point.

METHODS AND MATERIALS

Methods

^{13}C NMR spectra were recorded on a Varian XL 300 spectrometer. Epoxides and amines were dissolved in $CDCl_3$; amides and glycosides were dissolved in deuterated DMSO. The solvent signals served as internal standard. Column GC experiments were carried out on a Varian 1400 chromatograph (temperature programme: 50 °C → 280 °C; heating rate 10 °C min^{-1}; FID). A 0.5 m steel column ($\frac{1}{8}$ inch) packed with Chromosorb W-AW-DMCS (80–100 mesh, modified with 10% SE 30 as separation phase) was used. The capillary GC–MS coupling experiment (temperature programme: 200 °C → 260 °C; heating rate 3 °C min^{-1}; electron impact mass spectra, 70 eV) was carried out on an HP 5985 B spectrometer. The 50 m glass capillary was poly(ethylene glycol) (PEG)-modified. The elemental analysis data were determined on a Carlo Erba analyser, model 1106.

Siloxanes

Pentamethyldisiloxane (MM^H) and 1,1,1,3,3,5,5-heptamethyltrisiloxane (MDM^H) are commercially available from ABCR Karlsruhe, Germany.

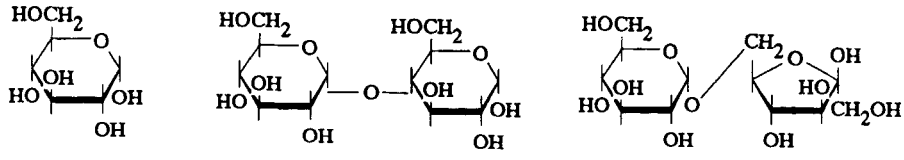
1,1,1,3,5,5,5-Heptamethyltrisiloxane (M_2D^H) and tris(trimethylsiloxy)silane (M_3T^H) were prepared according to equilibration procedures described elsewhere.[30]

In analogy, 1,1,1,5,5,5-hexaethyl-3-methyltrisiloxane was synthesized by equilibration of poly(methylhydrogensiloxane) (1.8 g, prepared from dichloromethylsilane by hydrolysis) in an excess of hexaethyldisiloxane (28 g, prepared from triethylchlorosilane by hydrolysis in an aqueous alkaline solution) at 115 °C. A polystyrene-based ion exchanger (1 g, Wofatit OK 80, active form $-SO_3^-$) served as catalyst. After the equilibrium was reached (12 h reaction time, product composition controlled by GC) the catalyst was filtered off and the trisiloxane was distilled at 230–240 °C under atmospheric pressure.

Tetramethyldisiloxane (M^HM^H) is accessible from the hydrolysis of dimethylchlorosilane. 1,1,3,3,5,5-Hexamethyltrisiloxane (M^HDM^H, b.p. 120–125 °C) and 1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane ($M^HD_3M^H$, b.p. 88–92 °C/17 mmHg) were synthesized by equilibration of polydimethylsiloxane (3 g, prepared from dichlorodimethylsilane by hydrolysis) in an excess of tetramethyldisiloxane (30 g) in the presence of the above-mentioned ion exchanger, i.e. Wofatit OK 80 (1 g, 140 °C, 12 h reaction time).

The following polyhydrogensiloxanes, allyl glycidyl ether derivatives of siloxanes (Ep) and aminosiloxanes were gifts from Bayer AG Leverkusen and Goldschmidt AG Essen (abbreviations used in this paper are given in parentheses after each formula)

$(CH_3)_3Si[OSi(CH_3)_2]_{20}[OSi(H)CH_3]_{20}OSi(CH_3)_3$
$(MD_{20}D^H_{20}M)$
$(CH_3)_3Si[OSi(CH_3)_2]_{20}[OSi(H)CH_3]_{10}OSi(CH_3)_3$
$(MD_{20}D^H_{10}M)$
$(CH_3)_3Si[OSi(CH_3)_2]_{20}[OSi(H)CH_3]_5OSi(CH_3)_3$
$(MD_{20}D^H_5M)$
$(CH_3)_2(Ep)Si[OSi(CH_3)_2]_{15}Si(CH_3)_2(Ep)$
$(M^{Ep}D_{15}M^{Ep})$
$(CH_3)_2(Ep)Si[OSi(CH_3)_2]_{22}Si(CH_3)_2(Ep)$
$(M^{Ep}D_{22}M^{Ep})$
$(CH_3)_3Si[OSi(CH_3)_2]_2[OSiCH_3(Ep)]_2OSi(CH_3)_3$
$(MD_2D^{Ep}_2M)$
$(CH_3)_3Si[OSiCH_3(Ep)]_{10}Si(CH_3)_3$
$(MD^{Ep}_{10}M)$
$(CH_3)_3Si[OSi(CH_3)_2]_{11}[OSiCH_3(Ep)]_7Si(CH_3)_3$
$(MD_{11}D^{Ep}_7M)$
$(CH_3)_3Si[OSi(CH_3)_2]_{56.6}[OSiCH_3(Ep)]_{5.4}Si(CH_3)_3$
$(MD_{56.6}D^{Ep}_{5.4}M)$
$(CH_3)_3Si[OSi(CH_3)_2]_{100}[OSiCH_3(Ep)]_5Si(CH_3)_3$
$(MD_{100}D^{Ep}_5M)$
$H_2N(CH_2)_2NH(CH_2)_3SiCH_3[OSi(CH_3)_3]_2$
(1)



glucose maltose palatinose

Figure 1

Glycosides

Siloxanyl-modified glycosides were synthesized in a four-step sequence which includes peracetylation, glycosidation, deacetylation and hydrosilylation.

Glucose (D-glucopyranose; gluc), maltose (O^4-α-D-glucopyranosyl-D-glucopyranose; malt) and palatinose (isomaltulose, O^6-α-D-glucopyranosyl-D-fructofuranose; palat) were used as starting materials (Fig. 1).

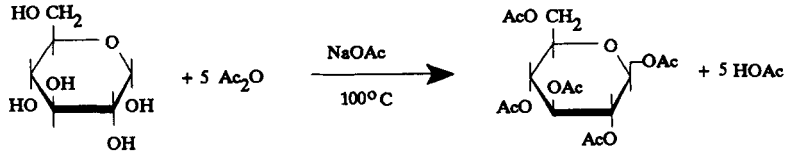
The carbohydrates were peracetylated according to a standard procedure[31] (Table 1; Eqn [1]: 2.5 g (3×10^{-2} mol) of sodium acetate and 35 cm^3 of acetic anhydride were heated to 100 °C, then 5 g (2.77×10^{-2} mol) of glucose was added and the reaction temperature was maintained for 1.5 h. The mixture was poured onto ice (200 cm^3). After 2 h the precipitate was filtered off, dissolved in 25 cm^3 CH_2Cl_2 and washed several times with saturated HCO_3^- solution and water. Finally the solvent was removed under reduced pressure.

In a Lewis acid-catalysed substitution reaction the C-1 acetyl group was replaced by prop-2-yn-1-ol (prop) or but-3-yn-1-ol (but) yielding acetylated β-akynylglycosides[32] Table 2, Eqn [2]: 5 g (1.28×10^{-2} mol) of 1,2,3,4,6-penta-O-acetyl-β-D-glucopyranose was dissolved in 60 cm^3 of dry CH_2Cl_2. At 0 °C 3.59 g (6.4×10^{-2} mol) of prop-2-yn-1-ol and 18.3 g (1.29×10^{-1} mol) of $BF_3 \cdot Et_2O$ were added. The reaction temperature was maintained for 5 h. The solution was poured into ethyl acetate, washed several times with saturated HCO_3^- solution and dried over Na_2SO_4. The solvent mixture was removed under reduced pressure.

Diethylamine dissolved in methanol was found to

Table 1 Peracetylated carbohydrates

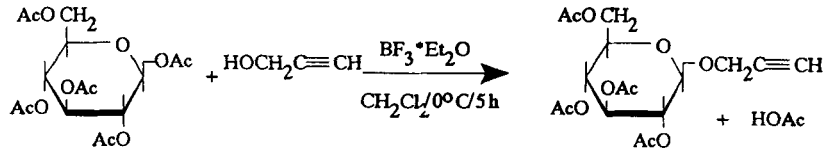
Compound		Reaction time (h)	Yield (%)	C (%) (calc.)	C (%) (found)	H (%) (calc.)	H (%) (found)	^{13}C NMR (ppm) C-1	^{13}C NMR (ppm) C-2
2	gluc(ac)5	1.5	53	49.26	49.24	5.64	5.63	92.45	
3	malt(ac)8	6	50	49.59	49.56	5.60	5.59	97.14	
4	palat(ac)8	6	35	49.59	49.86	5.60	5.78		109.25



[1]

Table 2 Acetylated alkynylglycosides

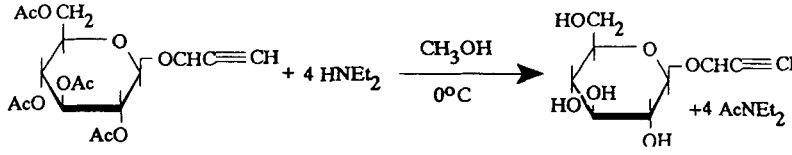
Compound		Yield (%)	^{13}C-NMR (ppm) C-1	C-2	C-7	C-8	C-9	C-10
5	gluc(ac)4-prop	68	99.39		56.60	79.65	76.83	
6	gluc(ac)4-but	65	101.36		68.62	20.66	81.78	70.98
7	malt(ac)7-prop	70	96.98		56.55	79.69	76.80	
8	malt(ac)7-but	74	96.81		69.19	20.67	81.80	70.81
9	palat(ac)7-prop	42		108.20	50.27	78.14	75.26	



[2]

Table 3 Alknyl glycosides

Compound		Yield (%)	^{13}C-NMR (ppm) C-1	C-2	C-7	C-8	C-9	C-10
10	gluc-prop	80	103.34		59.21	81.40	78.46	
11	gluc-but	82	105.08		70.81	21.84	85.17	73.24
12	malt-prop	87	103.14		59.22	81.10	79.49	
13	malt-but	86	104.75		70.78	21.75	85.5	71.99
14	palat-prop	78		111.80	78.84	75.92		



[3]

be an efficient deacetylation mixture (Table 3, Eqn [3]. Prop-2-ynyl-(O^2,O^3,O^4,O^6-tetra-*O*-acetyl)-β-D-glucopyranoside (0.4 g, 10^{-3} mol) was dissolved in 2.5 cm^3 of dry methanol. At 0 °C 1 cm^3 of diethylamine was added and the mixture was stored at this temperature for 24 h. Volatile substances were removed under reduced pressure and the syrup obtained was dissolved in 1 cm^3 of methanol. After the addition of diethyl ether (2 cm^3) bright crystals were precipitated which could be filtered off and dried.

In a platinum-catalysed hydrosilylation step, 1,1,1,3,5,5,5-heptamethyltrisiloxane (M_2D^H; m_2d; 20 h) or tris(trimethylsiloxy)silane (M_3T^H; m_3t; 38 h) can be added to the triple bond (Table 4, Eqn [4]). Under an argon atmosphere, prop-2-inyl-β-D-glucopyranoside (2 g, 9×10^{-3} mol) was dissolved in 10 cm^3 dioxane and 2.1 g (9×10^{-3} mol) M_2D^H. The platinum catalyst (0.45 cm^3 of a 0.01 M solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropanol) was added and the mixture was stirred at 100 °C for 20 h. The solvent was removed under reduced pressure.

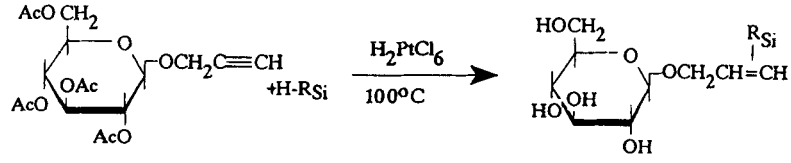
Amides

Preparation of amino-functionalized siloxanes

3-(γ-Aminopropyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (**23**) (b.p. 139–142 °C/50 mmHg) was prepared[33] from M_2D^H and allylamine in the presence of the alkanol-treated Lamoreaux platinum catalyst[34] (argon atmosphere; SiH/C=C/Pt= 1 : 1 : 10^{-4}; 8 h reflux).

Siloxane derivatives bearing a primary and a secondary amino function were prepared via epoxides, which are easily accessible from hydrogensiloxanes and allyl glycidyl ether[35] (argon atmosphere; SiH/C=C/Pt= 1 : 1.2 : 2 × 10^{-4}; reaction time 4–10 h at 130–145 °C). It was found that the above-mentioned Lamoreaux platinum catalyst yields the epoxides almost quantitatively (Table 5, Eqn [5]).

Under argon, 19.98 g (6.75×10^{-2} mol) of tris(trimethylsiloxy)silane (M_3T^H) and 9.24 g of (8.1×10^{-2} mol) allyl glycidyl ether were mixed. The Lamoreaux catalyst (0.088 g, 3% wt platinum content, 1.35×10^{-5} mol Pt) was added. The tem-



[4]

Table 4 Siloxanyl-modified alkenyl glycosides

Compound		Yield (%)	^{13}C NMR (ppm) C-1	C-2	C-7	C-8	C-9	C-10	$SiCH_3$	$Si(CH_3)_3$
15	gluc-prop-m_2d	80	103.38		71.09	147.57 145.50	125.58 129.00		0.09	1.88
16	gluc-prop-m_3t	92	103.46		71.78	144.30	129.15			1.73
17	gluc-but-m_2d	82	104.14		69.63	17.97	146.10 147.90	128.10 130.90	0.09	1.94
18	gluc-but-m_3t	76	104.11		69.68	20.78	147.50 146.30	129.10 126.70		1.73
19	malt-prop-m_2d	79	103.37		71.27	147.53 145.58	125.76 129.20		0.17	1.95
20	malt-but-m_2d	90	104.04		71.83	18.23	146.02 147.90	130.81 128.50	0.01	2.00
21	malt-but-m_3t	84	104.16		71.46	20.83	147.20	129.30 126.80		1.94
22	palat-prop-m_2d	66		109.40	72.35	146.40 148.30	125.20 127.80		0.11	2.01

[a] gluc, glucosyl; prop, propenyl; but, butenyl; malt, maltosyl, palat, palatinosyl.

perature was raised to 145 °C and maintained for 10 h. The hydrosilylation product was isolated by vacuum distillation.

By similar hydrosilylations of allyl glycidyl ether, monofunctional α,ω-difunctional siloxanes and polyhydrogensiloxanes were converted into the epoxide derivatives (Table 6, Eqns [6] and [7]).

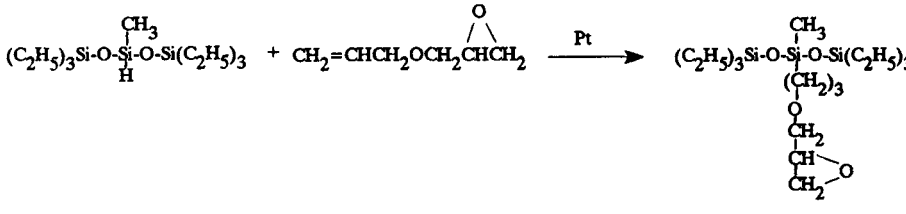
Nucleophilic opening of the epoxide ring with an excess of a diamine in refluxing methanol yielded the desired low-molecular-weight aminoalkylsiloxanes. The reaction time and product distribution strongly depends on the amine structure (Tables 7 and 8, Eqns [8]–[10]).

Ethylenediamine (30 g, 0.5 mol) was dissolved in 30 cm^3 of methanol. The mixture was heated to reflux temperature. 3-[3-(Oxiranylmethoxy)propyl]-1,1,1,3,5,5,5-heptamethyltrisiloxane (M_2D^{Ep}, 30 g, 8.93×10^{-2} mol, 10 min) was added dropwise. The reaction was continued for 20 min. Methanol and excess ethylenediamine were removed under reduced pressure (90 °C/1 mmHg). The siloxanyl-modified diamine (**34**) was obtained as a pale yellow oil. Optionally the substance could be distilled in a vacuum (b.p. 215–222 °C/7.5 mmHg).

Ethylenediamine was used to open epoxide rings attached to structures other than M_2D^{Ep} (Table 9,

Table 5 Synthesis of monofunctional epoxysiloxanes

Product	H-siloxane	Conversion (% GC)	Yield (%)	B.p. (°C/mmHg)	^{13}C-NMR (shift ppm) C-1	$SiCH_3$	$Si(CH_3)_2$	$Si(CH_3)_3$
24	MM^H	100	82	130–135/7.5	13.62		−0.15	1.55
25	MDM^H	100	74	120–125/2.5	13.80		0.11/1.34	1.86
26	MD^HM	97	85	129–132/3	13.32	−0.71		1.43
27	M_3T^H	91	57	162–167/7.5	10.43			1.51
28	$[(C_2H_5)_3SiO]_2CH_3SiH$	86	35	137–147/0.7	13.61	−0.46	6.14 ($SiCH_2$)	6.66 (CH_3)

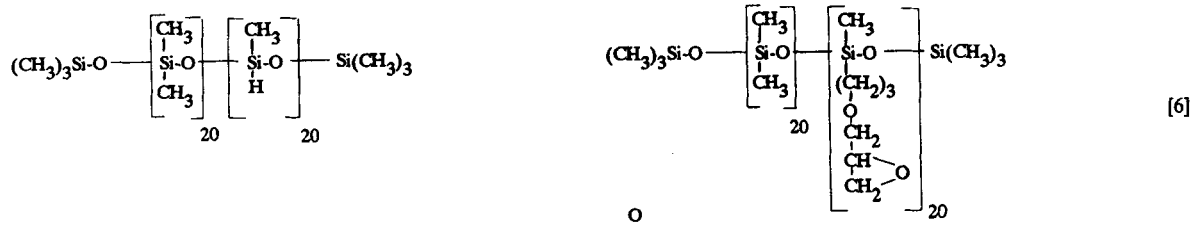


[5]

Table 6 Synthesis of polyfunctional epoxysiloxanes

Product	H-siloxane	Conversion (% GC)	Yield (%)	B.p. (°C/mmHg)	^{13}C-NMR (shift ppm) C-1	$SiCH_3$	$Si(CH_3)_2$	$Si(CH_3)_3$[b]
29	M^HDM^H	100	55	174–187/1	13.15		0.22^I 0.42^{II}	
30	$M^HD_3M^HD_3$	100	100[a]		13.71		0.19^{III} 1.22^{IV} 1.09^V	
31	$MD_{20}D^H_{20}M$	100	100[a]		13.35	−0.64	0.92	1.69
32	$MD_{20}D^H_{10}M$	100	100[a]		13.27	−0.66	0.95	1.68
33	$MD_{20}D^H_5M$	100	100[a]		13.30	−0.66	0.95	1.68

[a] Volatile material till 90 °C/1 mmHg was distilled off.
[b] *Key* : $\equiv Si^I-O-Si^{II}-O-Si^I\equiv$ $\equiv Si^{III}-O-Si^{IV}-O-Si^V-O-Si^{IV}-O-Si^{III}\equiv$



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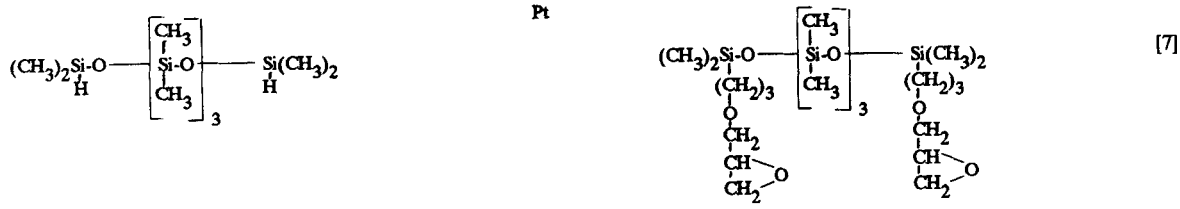


[7]

Eqns [11] and [12]). The reactions were carried out with a 5 : 1 molar amine excess. After the quantitative conversion, excess ethylenediamine and the solvent were removed under reduced pressure (max. 90 °C/1 mmHg).

Preparation of amides

In a final reaction step, different lactone rings (Fig. 2) were opened by nucleophilic attack of the aminoalkylsiloxanes described above (Tables 10–12, Eqns [13]–[15]).

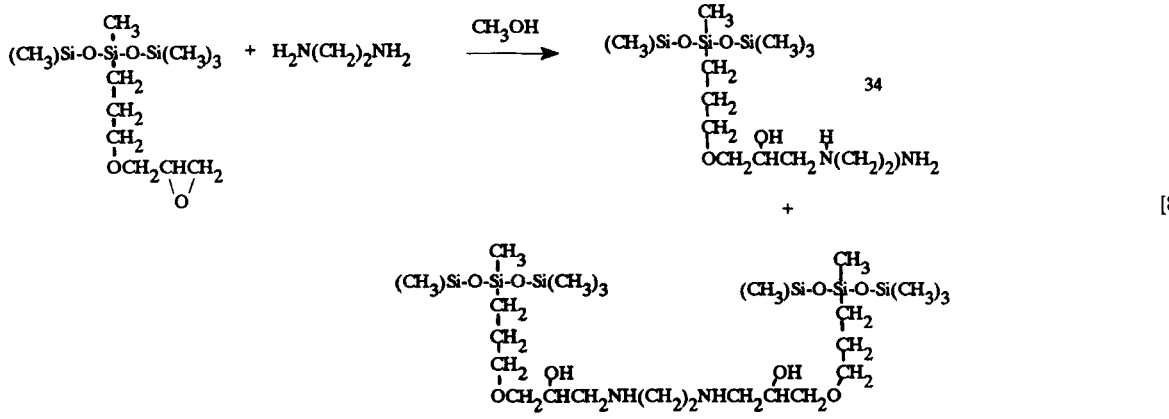
γ-Hydroxybutyric acid amides were synthesized in a steel autoclave (80 °C, 10 h reaction time). Reactions with the other lactones were carried out either in refluxing methanol or, in the cases of ethanol and isopropanol, at 70 °C for about 6 h. For volatile aminosiloxanes the complete conversion was controlled by means of GC. After evaporation of the

Table 7 Alkylation of different diamines with $MD^{Ep}M$ (**25**) in methanol

Product	Amine	Molar ratio, amine/epoxide	Reaction time (min)	Product ratio, mono-/bis- (% GC)	B.p. (°C/mmHg)
34	$H_2N(CH_2)_2NH_2$	1 : 1	120	72 : 28	
		5 : 1	20	100 : 0	215–222/7.5
35a	$H_2NCH_2CH(CH_3)NH_2$	1 : 1	120	50 : 50	
35b		5 : 1	90	92 : 8	217–227/7.5
36	$H_2N(CH_2)_3NH_2$	1 : 1	300	80 : 20	225–227/6.5

Table 8 ^{13}C NMR data of the monoalkylation products (shifts in ppm)

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
34	13.08	22.77	73.45	73.68	68.29	52.08	51.85	41.10	
35a	13.25	22.94	73.47	73.86	68.56	52.29	57.81/57.94	46.20/46.29	21.62/21.80
35b	13.25	22.94	73.47	73.86	68.40	52.42	54.65/55.10	49.45/49.80	21.62/21.80
36	13.17	22.86	73.53	73.76	68.24	52.31	47.30	33.15	39.92



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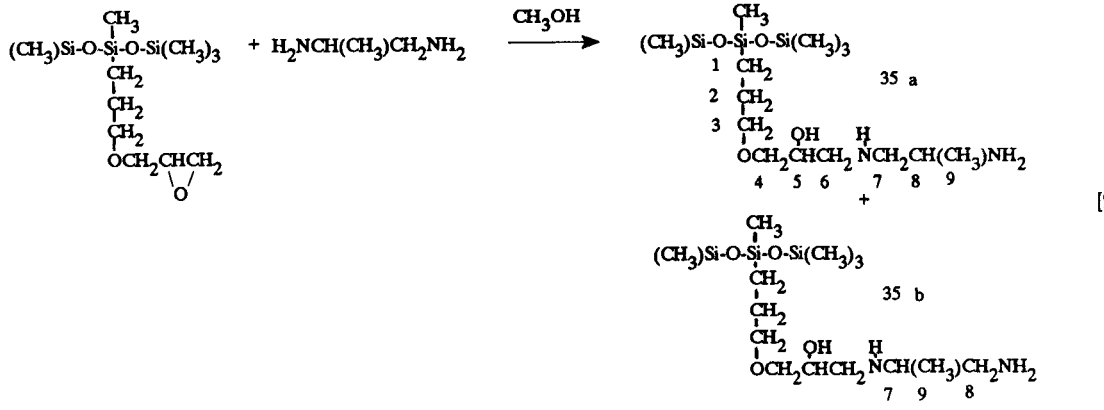
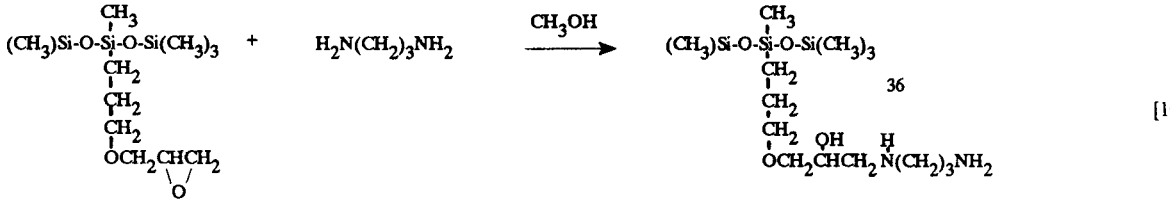


[9]



[10]

solvent, the products were washed several times in diethyl ether or n-pentane, depending on their solubility.

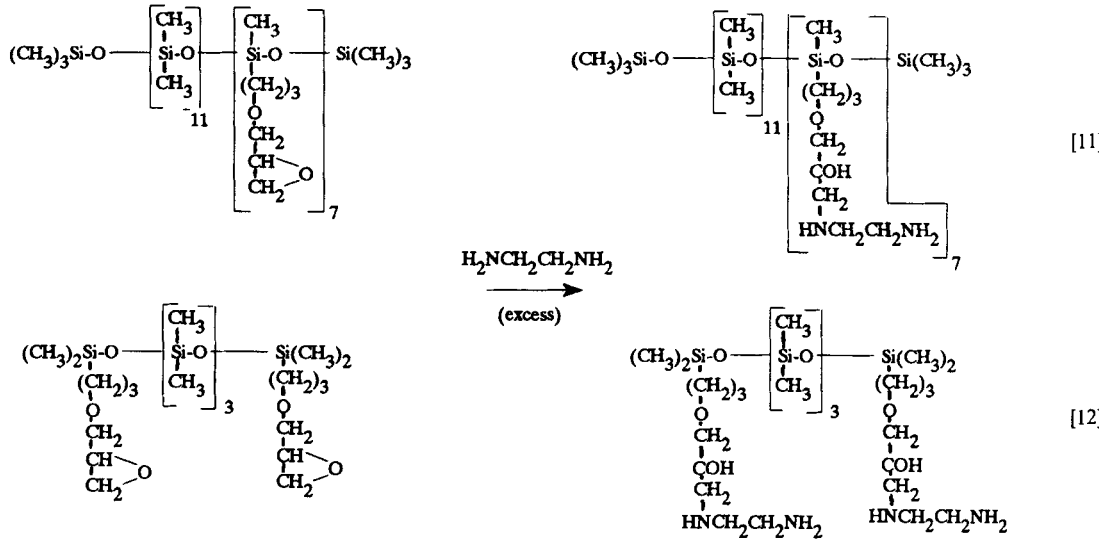
Thus 23 g (5.81×10^{-2} mol) of the aminosiloxane (**34**) and 22.5 g (5.8×10^{-2} mol) glucopyranosyl arabinonic acid lactone were dissolved in 150 cm^3 of methanol. The mixture was heated to reflux temperature for 5 h. The solvent was removed

Table 9 Synthesis of diamines by monoalkylation of epoxysiloxanes with ethylenediamine

Product	Siloxane	Solvent	Cross-linking[a]
37	MM^{Ep}	Methanol	–
38	MDM^{Ep}	Methanol	–
39	M_3T^{Ep}	Methanol	–
40	$[(C_2H_5)_3SiO]_2CH_3Si^{Ep}$	Methanol	–
41	$M^{Ep}DM^{Ep}$	Methanol	–
42	$M^{Ep}D_3M^{Ep}$	Methanol	–
43	$M^{Ep}D_{15}M^{Ep}$	Methanol	+
		Ethanol	–
44	$M^{Ep}D_{22}M^{Ep}$	Methanol	+
		Ethanol	+
		Isopropanol	–
45	$MD^{Ep}_{10}M$	Methanol	–
46	$MD_2D^{Ep}_2M$	Methanol	–
47	$MD_{20}D^{Ep}_{20}M$	Methanol	–
48	$MD_{11}D^{Ep}_7M$	Methanol	–
49	$MD_{20}D^{Ep}_{10}M$	Methanol	–
50	$MD_{20}D^{Ep}_5M$	Methanol	–
51	$MD_{56.6}D^{Ep}_{5.4}M$	Methanol	+
		Ethanol	–
52	$MD_{100}D^{Ep}_5M$	Methanol	+
		Ethanol	+
		Isopropanol	–

[a] +, Observed; –, not observed.

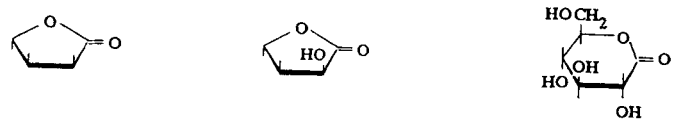
under reduced pressure and a powdery, partly wax-like material was obtained. Due to the presence of traces of methanol, the substance had considerable solubility in diethyl ether (40 cm^3). The solvent was removed in vacuum and the powder obtained was dispersed in a second portion of diethyl ether. The solvent could be sucked off and the precipitate was dried under reduced pressure. The amide (**67**) was obtained as a yellow powder readily soluble in water.



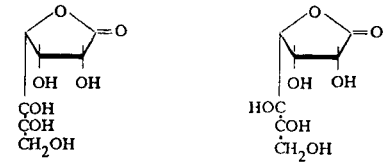
[11]

[12]

γ-butyrolactone (bl) (+/-)α-hydroxy-γ-butyrolactone (hb) D-gluconic acid δ-lactone (gl)



D-heptagluconic acid γ-lactone (hl) D-glycero-l-manno-heptanoic acid γ-lactone (gm)



glucopyranosyl arabinonic acid lactone (gp)

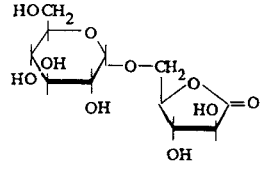


Figure 2

RESULTS AND DISCUSSION

Glycosides

The four-step reaction sequence (peracetylation, alkynolysis, deacetylation and hydrosilylation) was used because previous Fischer glycosidation experiments confirmed the undesired influences of carbohydrate oligomerization and siloxane equilibration on the product uniformity.

Peracetylations of palatinose repeatedly gave lower yields than those for glucose and maltose.

Table 10 Reactions of aminosiloxanes with lactones

Product	Amine	Lactone[a]	Solvent[b]	Product	Amine	Lactone[a]	Solvent[b]	Product	Amine	Lactone[a]	Solvent[b]
53	**23**	hb	MeOH	**69**	**35**	gl	MeOH	**85**	41	gp	MeOH
54	**23**	gl	MeOH	**70**	**35**	gp	MeOH	**86**	**42**	gp	MeOH
55	**23**	hl	MeOH	**71**	**36**	bl	MeOH	**87**	**43**	gl	EtOH
56	**23**	gp	MeOH	**72**	**36**	gl	MeOH	**88**	**44**	bl	iPrOH
57	**1**	bl	MeOH	**73**	**36**	gp	MeOH	**89**	**44**	gl	iPrOH
58	**1**	hb	MeOH	**74**	**37**	bl	MeOH	**90**	**45**	gl	MeOH
59	**1**	gl	MeOH	**75**	**37**	gl	MeOH	**91**	**46**	gl	MeOH
60	**1**	hl	MeOH	**76**	**37**	gp	MeOH	**92**	**46**	gp	MeOH
61	**1**	gp	MeOH	**77**	**38**	bl	MeOH	**93**	**47**	gl	MeOH
62	**34**	bl	MeOH	**78**	**38**	gl	MeOH	**94**	**48**	gl	MeOH
63	**34**	hb	MeOH	**79**	**38**	gp	MeOH	**95**	**49**	gl	MeOH
64	**34**	gl	MeOH	**80**	**39**	bl	MeOH	**96**	**50**	gl	MeOH
65	**34**	hl	MeOH	**81**	**39**	gl	MeOH	**97**	**51**	bl	EtOH
66	**34**	gm	MeOH	**82**	**39**	gp	MeOH	**98**	**51**	gl	EtOH
67	**34**	gp	MeOH	**83**	**40**	gp	MeOH	**99**	**52**	bl	iPrOH
68	**35**	bl	MeOH	**84**	**41**	gl	MeOH	**100**	**52**	gl	iPrOH

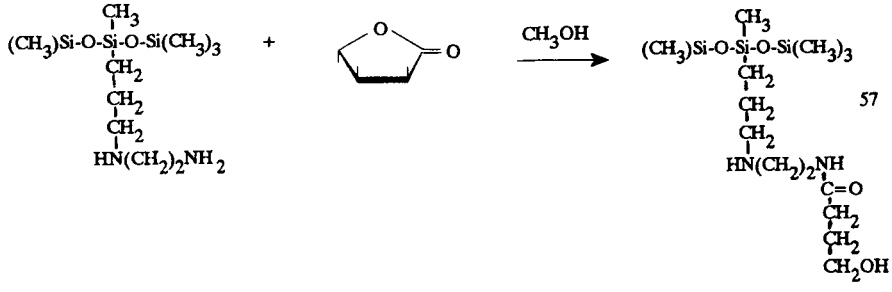
[a] See Fig. 2 for corresponding structures
[b] iPrOH, isopropanol.

Table 11 ^{13}C NMR data of selected compounds (shifts in ppm)

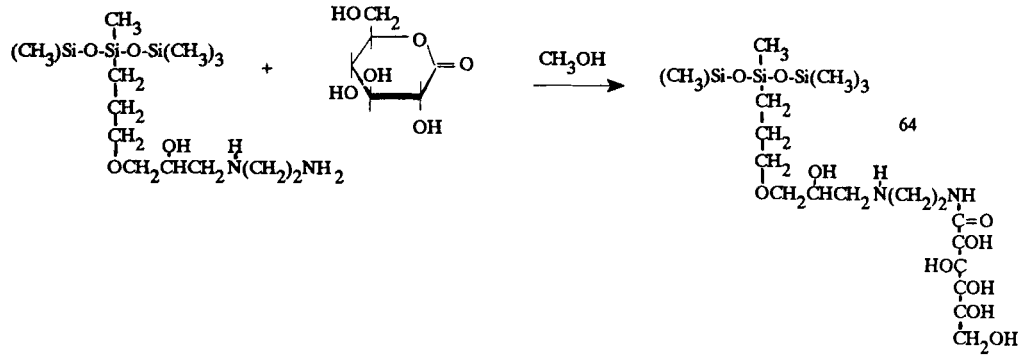
C atom	**54**	**56**	**62**	**64**	**65**	**67**	**69a**	**69b**	**72**
1	14.39	14.45	13.14	13.19	13.25	13.20	13.22	13.22	13.20
2	22.87	22.97	22.88	22.93	23.00	22.94	22.96	22.96	22.93
3	41.21	41.26	72.97	73.04	73.17	73.06	73.08	73.08	73.04
4	172.42	173.04	73.47	73.49	73.60	73.51	73.54	73.54	73.57
5	73.68	73.60	68.56	68.47	68.48	68.51	68.43/68.59	68.75/68.97	68.46
6	70.16	70.75	52.70	52.50	52.52	52.57	52.76/52.84	52.10/ 52.50	52.91
7	71.57	69.50	48.88	48.60	48.61	48.74	54.31/54.45	50.02/50.18	47.09
8	72.49	68.87	38.83	38.19	38.34	38.30	43.52/43.88	44.16/44.24	29.35
9	63.43	98.91	172.16	172.65	173.53	173.53	172.12/172.17	172.63/172.68	36.72
10		71.63	32.19	73.60	73.60	73.67	73.60/73.67	73.73/73.81	172.41
11		72.43	28.69	70.17	74.77	70.90	70.23	70.14	73.71
12		70.19	60.36	71.50	68.12	69.14	71.49	71.49	70.13
13		72.28		72.20	71.57	68.82	72.11/72.33	72.27/72.46	71.51
14		60.84		63.41	72.07	98.95	63.43	63.43	72.46
15					64.42	71.69	21.62/21.80	21.62/21.80	68.46
16						72.48			
17						70.18			
18						72.37			
19						60.84			

Table 12 Elemental analysis data of selected compounds (%)

	C		H		N	
Compound	(calc.)	(found)	(calc.)	(found)	(calc.)	(found)
54	42.01	41.79	8.53	8.75	3.06	2.80
56	42.78	42.05	7.80	8.05	2.37	2.47
61	43.67	43.59	8.22	8.35	4.43	4.27
62	47.30	47.08	9.54	9.77	5.81	5.89
64	43.90	43.51	8.71	8.78	4.88	4.54
65	43.70	43.77	8.61	8.82	4.63	3.95
67	44.19	44.10	8.22	8.35	3.96	3.75
70	45.00	44.83	8.33	8.62	3.88	3.64
73	45.00	44.78	8.33	8.63	3.88	3.76
76	45.57	44.90	8.22	8.26	4.43	4.00
79	44.19	43.60	8.22	8.62	3.96	3.83



[13]



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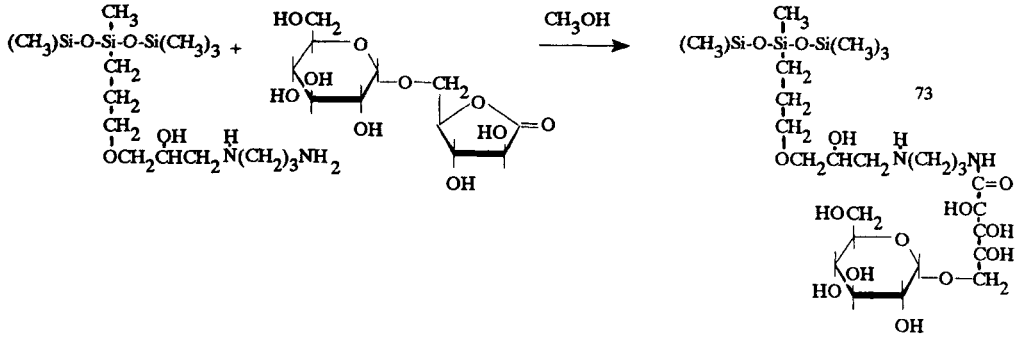
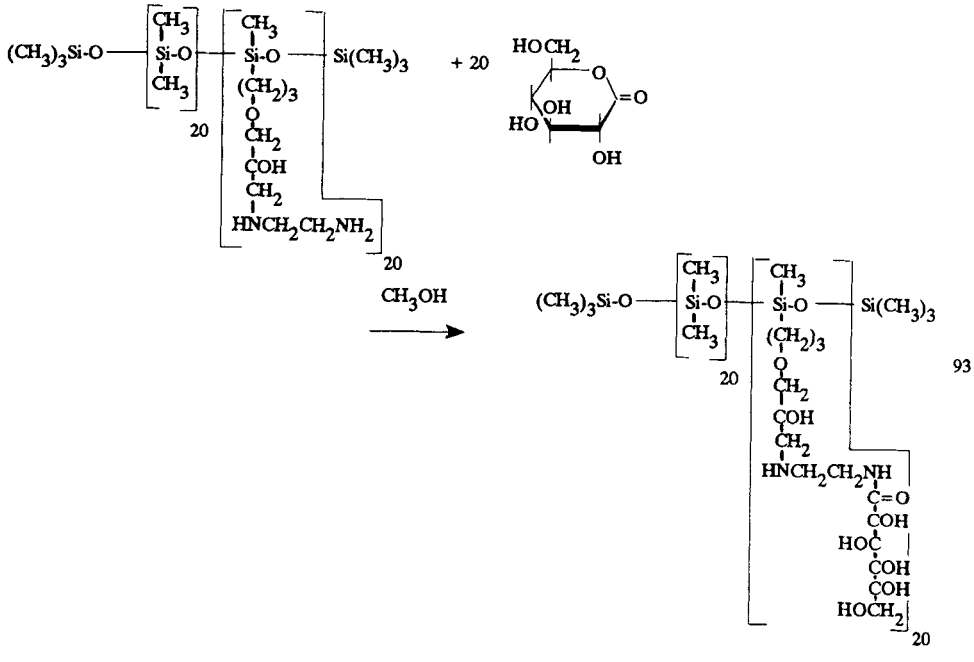


[15]



[16]

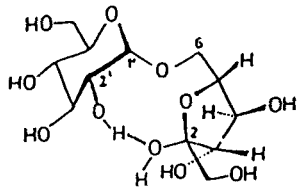


Figure 3

The reason for this effect is the formation of an intramolecular hydrogen bond between the oxygen atom of the 2-OH group and the hydrogen atom of the 2′-OH group[36] (Fig. 3).

The alkynolysis of the anomeric acetyl group preferentially yields β-glycosides. The $BF_3 \cdot Et_2O$ catalyst suppresses the rearrangement of the β-glycoside more than the other Lewis catalysts (e.g. $ZnCl_2$)[32]. Consequently the ^{13}C NMR signal for the anomeric C-1 atom in compound **5** (β-glucoside 100 ppm; Table 2) was accompanied by a very weak signal for the α-glycoside (96 ppm) just above the detection limit. Therefore the content of the α-glycoside was estimated to be in the region of about 5%.

There are two possibilities after incorporation of the multiple bond. Stadler[25] first added protected allyl glycosides to a polysiloxane backbone by hydrosilylation before the deprotection of the OH groups was carried out. Although the hydrosilylation of the triple bond of protected glycosides by the tri- and tetra-siloxanes can proceed rapidly, it had not been possible to deprotect to OH-groups in a final step without cleaving the Si–O–Si bonds. The tendency to form polysiloxanes and hexamethyldisiloxane is too strong for such low-molecular-weight siloxanyl structures.

Therefore the glycosides were first deprotected and, in a subsequent catalytic reaction, hydrosilylated. Hydrosilylations of multiple bonds in the presence of OH groups usually yield silyl ethers by dehydrocondensation.[37] Solvents like dioxane are able to mask the OH groups[38] and give access to the desired products.

Glycosides, especially those of the disaccharide type, are weakly soluble in dioxane. Therefore unusually long reaction times had to be applied. The amount of catalyst necessary for the reactions is 10 to 100 times greater than in conventional hydrosilylations of triple bonds.[38] This means that the presence of a bulky carbohydrate moiety has an inhibiting influence on the hydrosilylation.

Additionally, the size of the carbohydrate moiety strongly affects the regioselectivity of a the reaction. The analysis of the ^{13}C NMR data showed that in compound **16** the γ-isomer is formed exclusively, while compound **15** already contains about 15% of β-product. The smaller trisiloxane can be added to a position closer to the carbohydrate ring. Spacer extension for a single CH_2 unit has the same effect. In compound **18** the bigger tetrasiloxane is even attached to both possible positions.

Disaccharide structures further restrict the scope of the hydrosilylation. Attempted additions of M_3T^H to propynyl maltoside and propynyl palatinoside failed, whereas M_2D^H reacted in both cases. A spacer extension for one CH_2 unit makes the addition of the tetrasiloxane possible (compound **21**).

The siloxanyl-modified glycosides are yellow to brown waxes or syrups (glucosides) or powders (maltosides and the palatinoside).

The glucosides synthesized were found to be poorly soluble in water, indicating an imbalance between the weak hydrophilic monosaccharide moiety and a powerful hydrophobic siloxanyl unit. Disaccharide structures counterbalance the siloxane better and make the products sufficiently soluble in water.

Unfortunately, Fischer glycosidations of disaccharides also yield a broad product spectrum, from mono- to oligo-saccharide derivatives, because glycosidic links between the carbohydrate rings are formed and cleaved in an equilibrium process.[39] This fact further reduces the chances of obtaining defined and sufficiently water-soluble siloxanyl-modified glycosides via a route suitable for industrial purposes.

Amides

Siloxanyl-modified amines

The following two strategies were considered to solve the problem mentioned above: (1) the use of recently available disaccharide derivatives of lactone[18] and amine[14] types, and (2) the incorporation of a hydrophilic spacer which supports the carbohydrate moiety. To synthesize such spacers, the well-known allyl glycidyl ether derivatives were reacted with different amines in refluxing methanol (Eqns [8]–[10]). The results are listed in Table 7.

Ethylenediamine in a five-fold molar excess reacts fast enough to suppress the undesired formation of a bis-product. Due to the decreasing concentration of ethylenediamine in the final stages of the reaction, initially equimolar quantities of the reactants yield a minor amount of the bis-product. According to GC data this bis-product starts to appear after 70% of total epoxide conversion.

Table 13 Key signals in the MS fragmentation pattern of compounds **35a** and **35b**

35a					
m/z	395	366	221	73	44
Relative intensity (%)	9	44	85	64	100
Fragment	$M^{+} - CH_3$	$M^{+} - H_2NC(CH_3)H$	$C_7H_{21}O_2Si_3$	$H_2NC(CH_3)HCH_2NH$	$H_2NC(CH_3)H$
35b					
m/z	395	380	221	73	
Relative intensity (%)	10	58	72	65	
Fragment	$M^{+} - CH_3$	$M^{+} - H_2NCH_2$	$C_7H_{21}O_2Si_3$	$H_2NCH_2C(CH_3)HNH$	

The methyl-substituted ethylenediamine, 1,2-propylenediamine, cannot react fast enough with the epoxide to suppress the formation of the bis-product. The presence of the methyl group seems to reduce the nucleophilic power of this amine considerably.

According to a capillary GC–MS investigation of the distilled product, two different amines are formed. The signal assignment of the fragmentation pattern prove the assumption that the primary amino function adjacent to the methyl group reacts more slowly than the non-hindered one (Table 13, **35b**/**35a**=26.3%:73.7%, key signals at *m/z* 366 for isomer **35a** and *m/z* 380 for isomer **35b**).

Due to the different proportions of the isomers in the mixture, a division of the ^{13}C NMR signals into strong and weak signal sets was possible. The exact C-shift structures for both isomers in the mixture **35a**/**35b** were established on the basis of regular ^{13}C NMR and APT data (Table 8). Double signal sets at 46 ppm (strong) and 55 ppm (weak) represent the CH structures C-8 in **35a** and C-7 in **35b** whereas the CH_2 signal sets at 49 ppm (weak) and 57 ppm (strong) belong to C-8 in **35b** and C-7 in **35a**.

The extension of the alkylene spacer for one CH_2 unit between both amino functions in 1,3-propylenediamine further reduces its nucleophilic potential and the amount of bis-product increases.

Monofunctional siloxanyl amines bearing moieties other than M_2D were exclusively synthesized with ethylenediamine because of the quantitative conversion of the epoxide to the desired mono-product (Table 9). We never observed any significant influence of the size of the siloxane moiety on the reactivity of the epoxide. It was sufficient in all cases to distil off the methanol and the excess ethylenediamine.

All the monofunctional amines described in Tables 7 and 9 are colourless or slightly yellow oily liquids possessing a typical amine smell. Due to the presence of ether, hydroxy, and primary and secondary amino functions, they have considerable solubility in water.

α,ω-Difunctional di-, tri- and penta-siloxanes can be described in a similar manner.

Polymeric structures can also be converted quantitatively into amino derivatives. The diamine and the solvent for the reactions on polysiloxane structures have to be chosen carefully. Ethylenediamine in excess can react fast enough to avoid cross-linking. As predicted from results on monofunctionalized siloxanes, explorative experiments with 1,2- and 1,3-propylenediamine also yielded cross-linked polysiloxanes. Highly functionalized siloxanes can be converted in methanol. With a decreasing number of epoxy functions, the less polar ethanol (compounds **43** and **51**) and isopropanol (compounds **44** and **52**) have to be chosen. Experiments with such materials, in methanol and in certain cases even in ethanol, leads to the precipitation of a cross-linked silicone rubber.

Depending on the density of amino functions, many of these polymers can already be dissolved in water, while others remain insoluble.

The advantage of this technique is that it allows the synthesis of aminopolysiloxanes of almost any composition and avoids the problems of allylamine chemistry.

With a single exception, the ^{13}C NMR shift patterns of the N- and O-substituted hydrocarbon chains of the siloxanyl-modified amines in Table 9 are identical to that of compound **34**. In amine **39** the C-1 signal is high-field shifted to 10.20 ppm (compound **34**, C-1 13.08 ppm).

Amides

By nucleophilic ring opening, different lactones were converted into the corresponding amides. Although the formation of siloxanyl-modified amides from siloxanyl-modified esters and short-chained amines usually demands drastic reaction conditions[40]

(reaction temperature higher than 200°C) the lactones applied reacted under moderate ones (60–80 °C). Minor differences in reactivity are not due to varying ring sizes but to the number of OH groups attached to the ring.

γ-Butyrolactone (a five-membered ring) reacts more slowly and only at elevated temperatures compared with (+/−)α-hydroxy-γ-butyrolactone or D-gluconic acid δ-lactone (a six-membered ring).

The structure of the amine did not influence the course of the reaction significantly. In all cases the amide of the primary amino function was formed. Secondary amino or hydroxyl groups did not yield any considerable amount of by-products.

The ^{13}C NMR signal assignment for the amides (Table 11) took into consideration the data listed in Table 8.

Compound **62** makes it possible to determine the shifts of both CH_2 units attached to the ether bridge (C-3 and C-4, approx. 73.00 ppm and 73.50 ppm).

In compound **54** the hydroxylated C-5 is adjacent to the carbonyl function and shows a low-field shift (approx. 73.70 ppm). The signals for the atoms C-6 to C-9 were assigned according to the known data for sorbitol.[41] The signal sets for compounds **64** and **72** follow immediately.

The shift structure for the disaccharide derivatives **56** and **67** was established by consideration of the data for glucopyranosyl arabinonic acid lactone.[42]

This quantitative and regioselective reaction channel opens up the possibility of tailoring the properties of surfactants for a given low-molecular-weight siloxanyl moiety by two methods (Table 14). The water solubility of the surfactant can be due to the presence of a large polyhydroxylated carbohydrate unit. The spacer plays no role. In these cases (compound **56**) white or bright yellow powdery solids possessing a moderate solubility in weak polar organic solvents are obtained. Alternatively, a weakly hydrophilic carbohydrate or hydroxy-carboxylic acid moiety can be attached to a powerful hydrophilic spacer yielding viscous oils (**62**), thick syrups (**63**) or amorphous solids (**64**). Surfactants of this type remain soluble in water but possess remarkedly improved solubility in weak polar organic liquids (**62**). They lead to the conventional polyether surfactants with their polar groups delocalized along an extended hydrocarbon chain.

The combination of both hydrophilic spacer and strong hydrophilic carbohydrate (**67**) yields powdery substances with excellent water solubility. Surprisingly their solubility in organic solvents is usually not reduced (**56**→**67**). In certain cases minor changes in the spacer structure can improve the solubility in organic solvents remarkedly (**70**).

Therefore it can be concluded that an extended and heteroelement-modified hydrocarbon spacer causes improved solubility in heteroatom-substituted hydrocarbon solvents of varying polarity (Table 14).

Depending on the chain length, the consistency of α,ω-gluconamide-functionalized siloxanes ranges from hard powder (compound **84**) to wax (compounds **87** and **89**). The latter possess an unusually soft feel. The change from the gluconamide to the γ-hydroxybutyramide derivative yields a viscous syrup (compound **88**).

In general, surfactants of this type are less soluble in water than monofunctional derivatives of the same siloxane unit size.

Additionally, a series of gluconamide derivatives of different aminopolysiloxanes was synthesized (Table 10, compounds **90**, **91**, **93–96**, **98**, **100**).

The ^{13}C NMR shift patterns of the polyfunctional derivatives were found to be combinations of the siloxanyl shift data as shown in Table 5 and the spacer/carbohydrate data given for compounds **64** and **67** in Table 11.

These comb-like structures are powdery (high density on carbohydrate functions) or wax-like

Table 14 Solubility[a] of selected surfactants in solvents of different polarity

Compound	NMP	NOP	Hallcomid M8–10	Xylene	1,2,3-Trimethylbenzene	Isophorone	Octyl acetate	Rape-oil methyl ester	Paraffin oil
56	+	+	+	−	−	−	−	−	−
62	+	+	+	+	+	+	+	+	−
67	+	+	+	−	−	−	−	−	−
70	+	+	+	+	+	−	−	−	−
73	+	+	+	−	−	−	−	−	−

[a] Solubility of 7.15% surfactant in the solvent at room temperature. +, soluble; −, insoluble. NMP, *N*-methylpyrrolidone; NOP, *N*-octylpyrrolidone; Hallcomid M8–10, $C_8 - C_{10}$ carboxylic acid amide.

materials. Derivatives of γ-butyrolactone are viscous oils. They can be synthesized in a practically unlimited range of compositions and in quantitative yields if the appropriate solvent is applied.

Their solubility in water depends on the density of gluconamide moieties. Conversely, a decreasing number of carbohydrate units does not automatically improve the solubility in less polar organic solvents. It was found that in such cases an acceptable solubility was even more limited in isopropanol. This fact emphasizes the importance of a sufficiently longer spacer for good organic solubility. It further indicates that methyl groups attached to Si–O–Si backbones are different from those attached to hydrocarbon chains with respect to cohesion energy densities, and are therefore of limited value for this purpose. In separate papers the qualitative and quantitative differences will be explained.

REFERENCES

1. M. Eggersdorfer, S. Warwel and G. Wulff, *Nachwachsende Rohstoffe, Perspektiven für die Chjemie*, VCH, Weinheim, 1993, p. 33.
2. H. Bertsch, F. Püschel and E. Ulsperger, *Tenside* **2**, 397 (1965).
3. E. Ulsperger, L. Richter and F. Mainas, East German Patent DD 39625.
4. E. Ulsperger, L. Richter and F. Mainas, East German Patent DD 40624.
5. Ref. 1, p. 49.
6. V. P. Pelenc, F. M. B. Paul and P. F. Monsan, Patent WO 93/04185.
7. E. N. Vulfson, R. Patel, J. E. Beecher and A. T. Andrews, *Enzyme Microb. Technol.* **12**, 950 (1990).
8. E. Ulsperger and H.-D. Jacobi, *Monatsber. Deut. Akad. Wiss. Berlin* **6**, 475 (1964).
9. F. Micheel and P. Schiller, *Chem. Ber.* **101**, 3721 (1968).
10. H. Kelkenberg, *Tenside Surf: Det.* **25**, 8 (1988).
11. L. Guderjahn, M. Kunz and M. Schüttelhelm, *Tenside Surf. Det.* **31**, 146 (1994).
12. E. Ulsperger, *Tenside* **3**, 1 (1966).
13. E. Ulsperger, East German Patent DD 29053.
14. M. Kunz, *Zuckerindustrie* **113**, 273 (1988).
15. J. Klein, W. Behrens and M. Kunz, European Patent EP 255033.
16. G. Czichocki, G. Engler and E. Ulsperger, *J. Prakt. Chem.* **316**, 895 (1974).
17. C. L. Mehltretter and J. C. Rankin, US Patent US 2662073.
18. F. W. Lichtenthaler, *Carbohydrates as Organic Raw Materials*, VCH, Weinheim. 1991, p. 145.
19. E. Ulsperger and H.-D. Jacobi, *Fette Seifen Anstrichmittel* **64**, 1093 (1962).
20. E. Ulsperger, *Monatsber. Deut. Akad. Wiss. Berlin* **5**, 397 (1963).
21. E. Ulsperger, East German Patent DD 29379.
22. M. Lalonde and T. H. Chan, *Synthesis* 817 (1985).
23. G. Greber, H. Gruber and E. Mössl, Austrian Patent AT 393509.
24. J. Sejpka and F. Wimmer, European Patent EP 612759.
25. G. Jonas and R. Stadler, *Acta Polym.* **45**, 14 (1994).
26. V. v. Braunmühl, G. Jonas and R. Stadler, *Macromolecules* **28**, 17 (1995).
27. A. Kondo, K. Mita and R. Isushima, Japanese patent JP 62-68820; *Chem. Abstr.* **108**, 56828 (1988).
28. A. C. Sau, European Patent EP 401668.
29. R. L. Billmers, European Patent EP 385396.
30. R. Wersig, PhD Thesis, University of Rostock, 1994, p. 55.
31. Ref. 30, p. 59.
32. T. Takano, F. Nakatsubo and K. Murakami, *Carbohydr. Res.* **203**, 341 (1990).
33. B. Marciniec, *Comprehensive Handbook on Hydrosilylation*, Pergamon, Oxford, 1992, p. 122.
34. H. F. Lamoreaux, US Patent, US 3220972.
35. B. Grüning and G. Koerner, *Tenside Surf. Det.* **26**, 312 (1989).
36. F. W. Lichtenthaler, *Zahnärztl. Z.* **37**, 46 (1982).
37. Ref. 33, p. 126.
38. R. Wersig, G. Sonnek and C. Niemann, *Appl. Organomet. Chem.* **6**, 701 (1992).
39. H. Hagemann and D. Klamann, *Houben-Weyl* E14a13, G. Thieme Verlag, Stuttgart, 1992, p. 777.
40. H.-J. Kollmeier, R.-D. Langenhagen and K. Hoffmann, German Patent DE 3422268.
41. H.-O. Kallinowski, S. Berger and S. Braun, *^{13}C-NMR Spektroskopie*, G. Thieme Verlag, Stuttgart, 1984, p. 403.
42. H. Röger, PhD Thesis, Technical University of Braunschweig, 1987, p. 88.