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Analysis of cationic starches: determination of the substitution pattern of *O*-(2-hydroxy-3-trimethylammonium)propyl ethers

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Abstract

A method was developed to determine the substitution pattern of *O*-(2-hydroxy-3-trimethylammonium)propyl ethers of starch. As model compounds cationic cyclomaltoheptaose and cyclomaltooctaose were prepared. After cleavage of the glucosidic linkages by methanolysis und subsequent permethylation, the positively charged substituents were transformed to the neutral *O*-(2-methoxy)-2-propenyl ethers. These compounds could directly be separated by capillary GLC or after mild hydrolysis as the more stable *O*-(2-oxo)propyl derivatives. To halve the number of degradation products, the methyl glucosides could be reduced to the corresponding 1,5-anhydroglucitols. Results for two model compounds [degree of substitution (ds) 0.33 and 0.46] and three cationic starches (ds 0.02-0.05) are given.

Keywords: Polysaccharide derivatives; Cationic starch; Substitution pattern

1. Introduction

Cationic starches have found large-scale use in the paper industry as wet-end additives, surface sizes, and coating binders. In addition, they are applied as warp sizing agents in textile manufacture, as flocculants, and in detergents and cosmetics [1]. Commercial cationic starches for the paper industry have a low degree of substitution (ds) of max. 0.05. They are prepared in a heterogeneous process under alkaline conditions ("wet" or "dry" modified), or in a more homogeneous reaction ("paste"

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modified) [2]. Homogenous cationization of cellulose in DMAc–LiCl to a high ds was also reported [3]. The total ds is usually calculated from the content of nitrogen (Kjeldahl), by polyelectrolyte titration, or by ^{1}H NMR spectroscopy [2,4,5]. Beside the ds, the substitution pattern strongly influences the properties. A detailed analytical characterization is therefore of great interest. Roberts and Rowland [6] investigated diethylaminoethylcellulose and determined the positions of the tertiary alkyl amino groups after hydrolysis and trimethylsilylation. In the analysis of the substitution pattern of neutral polysaccharide derivatives by standard methylation analysis or the reductive cleavage method, the use of the high separation efficiency of capillary GLC is a key step [7–13]. From our experience in this field and the fact that tetraalkylammonium groups easily eliminate trialkylamines, we were encouraged to convert the cationic residues to neutral species, which should be compatible with GLC and GLC–MS analysis. We now report on the method development and first applications to different *O*-(2-hydroxy-3-trimethylammonium)propyl starch ethers, probably the most popular cationic ether.

2. Results and discussion

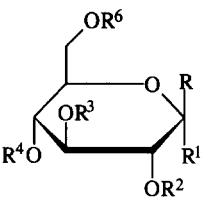
Synthesis of model compounds.—For method development cyclomaltoheptaose and cyclomaltooctaose (β- and γ-cyclodextrin) were cationized with 2,3-epoxypropyltrimethylammonium chloride in aqueous alkaline solution. The ds was determined by elemental analysis. In the ^{1}H NMR spectra only the H-1 resonance of the 2-*O*-substituted anhydroglucose units is shifted downfield to 5.22 ppm, while the H-1 signal of the non-, 3- and 6-*O*-substituted units appears at 5.08 ppm [14]. Together with the integral of the methine proton resonance of the substituent at 4.42 ppm, the ratio of 2-*O*- to (3-*O* + 6-*O*)-substitution could be estimated (Table 1). With increasing number of equivalents of NaOH per sugar hydroxy group, etherification at the primary O-6 is favoured.

Strategy of analysis (Scheme 1).—Owing to the very low ds values in commercial starches, the charged fraction was separated from the unsubstituted methyl glucosides, obtained after methanolysis of the cyclodextrin derivatives, by anion exchange (OH^- form), which was superior to cation-exchange chromatography. Charged methyl glucosides (**1–3a,b**) eluted prior to neutral compounds. The identity of the products could be confirmed by FABMS ($M^+ = 310$).

Table 1
Dependence of the ratio of 2-*O*- to 6-*O*-substitution on the equivalents of NaOH used in the cationization reaction of β-cyclodextrin

Equiv NaOH per OH of β-CD	ds		Ratio of 2-: (3 + 6)-*O*-substitution
	Elemental analysis	^{1}H-NMR	
0.16	0.79	0.82	6:4
1.08	0.58	0.63	3:7
3.78	0.45	0.46	1:9

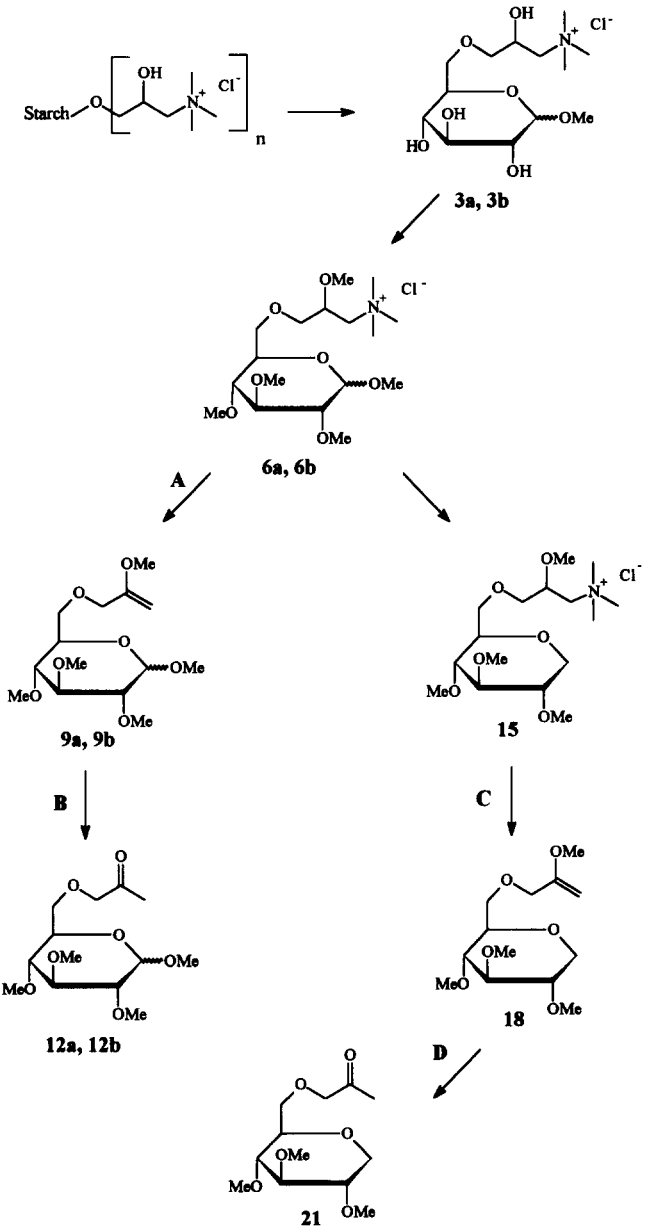
	R	R^1	R^2	R^3	R^4	R^6
1a	H	OMe	X1	H	H	H
1b	OMe	H	X1	H	H	H
2a	H	OMe	H	X1	H	H
2b	OMe	H	H	X1	H	H
3a	H	OMe	H	H	H	X1
3b	OMe	H	H	H	H	X1
4a	H	OMe	X2	Me	Me	Me
4b	OMe	H	X2	Me	Me	Me
5a	H	OMe	Me	X2	Me	Me
5b	OMe	H	Me	X2	Me	Me
6a	H	OMe	Me	Me	Me	X2
6b	OMe	H	Me	Me	Me	X2
7a	H	OMe	X3	Me	Me	Me
7b	OMe	H	X3	Me	Me	Me
8a	H	OMe	Me	X3	Me	Me
8b	OMe	H	Me	X3	Me	Me
9a	H	OMe	Me	Me	Me	X3
9b	OMe	H	Me	Me	Me	X3
10a	H	OMe	X4	Me	Me	Me
10b	OMe	H	X4	Me	Me	Me
11a	H	OMe	Me	X4	Me	Me
11b	OMe	H	Me	X4	Me	Me
12a	H	OMe	Me	Me	Me	X4
12b	OMe	H	Me	Me	Me	X4
13	H	H	X2	Me	Me	Me
14	H	H	Me	X2	Me	Me
15	H	H	Me	Me	Me	X2
16	H	H	X3	Me	Me	Me
17	H	H	Me	X3	Me	Me
18	H	H	Me	Me	Me	X3
19	H	H	X4	Me	Me	Me
20	H	H	Me	X4	Me	Me
21	H	H	Me	Me	Me	X4



X1 = $CH_2CHOHCH_2N^+(Me)_3\ Cl^-$
X2 = $CH_2CHOMeCH_2N^+(Me)_3\ Cl^-$
X3 = $CH_2COMe{=}CH_2$
X4 = CH_2COCH_3

After permethylation the positively charged derivatives (**4–6a,b**) were submitted to Hofmann elimination (Scheme 1, path **A**). The resulting methyl *O*-(2-methoxy)-2-propenyl-*O*-methyl-α,β-D-glucosides (**7–9a,b**) could be identified by GLC–MS. Fig. 1 shows the gas chromatogram of compounds **7–9a,b** obtained from substituted γ-cyclodextrin with a ds of 0.33. The 2-*O*- and the 3-*O*-substituted β-anomers **7b** and **8b** co-eluted, but the relative ratios of 2-:3-:6-*O*-substitution could be calculated on the premise that the α:β-ratio is similar for similarly monosubstituted methyl glucosides. About 6% of disubstituted methyl glucosides could be detected for the γ-cyclodextrin (results not shown). Their substitution pattern was deduced from the EI mass spectra and showed preferred 2,6-di-*O*-substitution. No characteristic fragments for oligoether formation of the substituent were observed [11].

The enol ethers **7–9a,b** were hydrolysed to the more stable *O*-(2-oxo)propyl ethers **10–12a,b** (Scheme 1, path **B**). Fig. 2 shows the gas chromatogram of these methyl glucoside derivatives obtained from the γ-cyclodextrin derivative. The position of the substituents was located by GLC–MS analysis. Again, the 2-*O*- and the 3-*O*-substituted β-anomer (**10b** and **11b**) coelute.



Scheme 1.

Reduction.—To halve the number of compounds to be separated, the methyl glucosides **4–6a,b** were reduced to give the corresponding 1,5-anhydro-D-glucitol derivatives **13–15**. Subsequent Hofmann elimination yielded the corresponding enol ethers **16–18** (Scheme 1, path **C**). After mild acid hydrolysis, the expected 2-oxopropyl ether

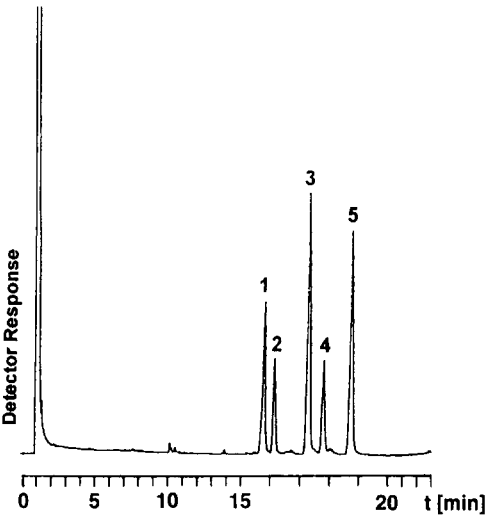


Fig. 1. Gas chromatogram of the degradation products from cationic γ-cyclodextrin obtained according to Scheme 1, path **A**. 1, **7b** and **8b**; 2, **9b**; 3, **7a**; 4, **8a**; 5, **9a**.

derivatives **19–21** were obtained (Scheme 1, path **D**). Figs 3 and 4 show the gas chromatograms of the 1,5-anhydro-D-glucitol derivatives obtained from the γ-cyclodextrin model compound.

Quantitative results.—The method was successfully applied to cationic starches from wet- or paste-modification processes. In Table 2 the quantitative results are summarized. The γ-cyclodextrin prepared with low alkali concentration showed a similar ds for

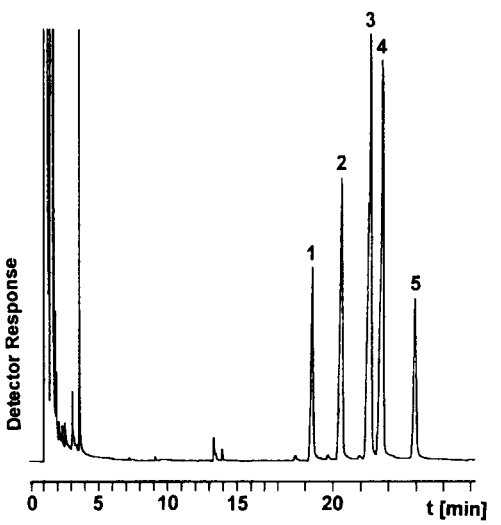


Fig. 2. Gas chromatogram of the degradation products from cationic γ-cyclodextrin obtained according to Scheme 1, path **B**. 1, **12b**; 2, **10b** and **11b**; 3, **10a**; 4, **12a**; 5, **11a**.

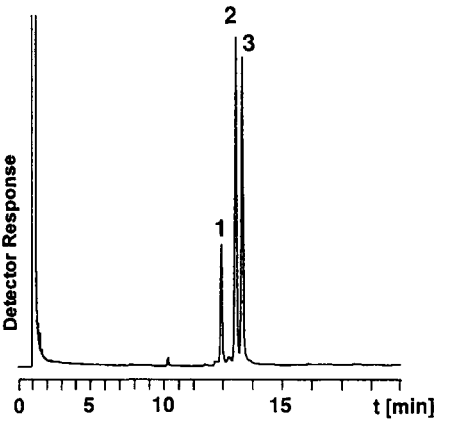


Fig. 3. Gas chromatogram of the degradation products from cationic γ-cyclodextrin obtained according to Scheme 1, path **C**. 1, **17**; 2, **16**; 3, **18**.

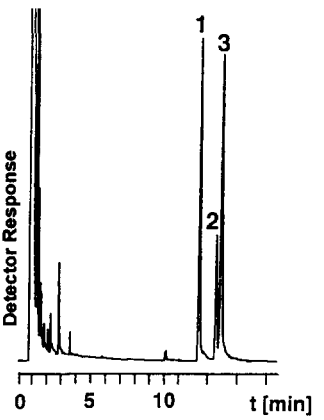


Fig. 4. Gas chromatogram of the degradation products from cationic γ-cyclodextrin obtained according to Scheme 1, path **D**. 1, **21**; 2, **20**; 3, **19**.

Table 2
Relative distribution (%) of substituents in the monosubstituted glucose fraction obtained from cationic ether derivatives of α-D-glucans

Sample:	γ-CD				β-CD		Starch 1		Starch 2		Starch 3	
Modification:	– [a]				– [a]		"Wet"		"Wet"		"Paste"	
Method [b]:	A	B	C	D	A	B	A	B	A	B	A	B
Position	ds [c] = 0.33				ds [c] = 0.46		ds [c] = 0.02		ds [c] = 0.05		ds [c] = 0.041	
2-	46.2	45.6	42.8	46.6	10.9	10.1	86.7	85.6	84.4	83.7	80.2	78.2
3-	15.6	15.1	15.7	15.2	2.4	2.5	8.0	8.0	9.5	8.8	13.4	13.1
6-	38.2	39.2	41.5	38.2	86.7	87.3	5.3	6.3	6.1	7.5	6.4	8.5

[a] See Experimental.
[b] See Scheme 1.
[c] Calculated from ^{1}H NMR (cyclodextrins) or from Kjeldahl-N (starches).

Table 3
Mass spectral data for the degradation products derived from *O*-(2-hydroxy-3-trimethylammonium)propyl-substituted α-D-glucans according to Scheme 1, paths **A**, **B**, **C**, and **D**

Compound	*m/z* (rel. int. (%))
	Methyl *O*-methyl-*O*-(2-methoxy)-2-propenyl-α,β-D-glucosides [a]
7	41 (48), 45 (70), 71 (100), 72 (11), 73 (14), 75 (49), 84 (10), 85 (17), 88 (28), 89 (17), 101 (62), 115 (29), 125 (6), 144 (8), 157 (37), 158 (3), 159 (1), 169 (1), 187 (4), 205 (1), 211 (0.3), 218 (0.7), 219 (0.8), 229 (0.2), 232 (0.3), 243 (0.5), 306 (M^+, 2), 307 (0.3)
8	41 (35), 45 (50), 71 (100), 72 (17), 73 (13), 75 (24), 85 (15), 88 (20), 101 (61), 102 (7), 115 (25), 127 (9), 131 (24), 144 (8), 145 (13), 169 (1), 187 (2), 197 (0.4), 203 (1), 211 (0.7), 229 (0.6), 246 (0.6), 274 (0.5), 306 (M^+, 2)
9	41 (18), 45 (16), 71 (22), 72 (10), 73 (10), 75 (40), 88 (100), 89 (12), 101 (37), 131 (9), 187 (1), 205 (0.7), 211 (0.2), 218 (0.2), 219 (0.3), 243 (1), 244 (0.2), 274 (0.2), 275 (0.1), 306 (M^+, 5), 307 (0.7)
	Methyl *O*-methyl-*O*-(2-oxo)propyl-α,β-D-glucosides [b]
10	41 (16), 43 (29), 45 (80), 57 (25), 59 (10), 61 (21), 71 (46), 73 (31), 74 (11), 75 (87), 87 (37), 88 (33),89 (16), 101 (78), 117 (16), 130 (100), 143 (62), 159 (1), 173 (2), 187 (1), 191 (0.3), 197 (0.2), 201 (0.3), 203 (0.1), 215 (0.5), 217 (0.1), 218 (4), 219 (0.5), 229 (0.4), 247 (0.1)
11	41 (12), 43 (20), 45 (57), 57 (16), 61 (12), 71 (49), 73 (19), 75 (29), 87 (24), 88 (23), 101 (85), 117 (36), 130 (100), 143 (16), 145 (12), 153 (1), 155 (2), 159 (3), 173 (2), 187 (4), 191 (1), 197 (0.1), 201 (0.1), 203 (0.3), 215 (1), 218 (0.2), 219 (0.1), 229 (0.3)
12	43 (12), 45 (18), 71 (12), 73 (14), 75 (38), 87 (10), 88 (100), 101 (44), 191 (4), 192 (0.4), 205 (0.1)
	1,5-Anhydro-*O*-methyl-*O*-(2-methoxy)-2-propenyl-D-glucitols [c]
16	41 (45), 45 (44), 59 (14), 71 (100), 72 (28), 73 (11), 88 (13), 89 (10), 101 (26), 102 (7), 115 (6), 125 (8), 157 (12), 167 (2), 189 (2), 199 (2), 231 (1), 232 (0.1), 244 (0.2), 276 (M^+, 4), 277 (0.5)
17	41 (63), 43 (16), 45 (75), 58 (19), 59 (23), 69 (11), 71 (100), 72 (35), 73 (14), 75 (21), 89 (27), 101 (28), 102 (7), 113 (6), 115 (12), 125 (12), 157 (13), 167 (1), 189 (2), 199 (2), 231 (0.4), 276 (M^+, 3), 277 (0. 4)
18	41 (84), 42 (14), 43 (26), 45 (71), 57 (10), 58 (21), 59 (49), 69 (18), 71 (100), 72 (79), 73 (29), 75 (50), 85 (13), 87 (23), 88 (45), 89 (26), 97 (12), 99 (44), 101 (86), 102 (9), 111 (7), 113 (8), 114 (8), 115 (22), 116 (5), 125 (9), 143 (13), 157 (12), 172 (1), 174 (1), 175 (2), 188 (8), 189 (6), 244 (0.3), 245 (0.1), 276 (M^+, 14), 277 (2)
	1,5-Anhydro-*O*-methyl-*O*-(2-oxo)propyl-D-glucitols [c]
19	41 (16), 43 (20), 45 (32), 57 (15), 71 (100), 72 (13), 87 (18), 88 (18), 101 (58), 102 (33), 111 (10), 115 (10), 117 (13), 127 (6), 143 (50), 156 (5), 161 (2), 173 (3), 185 (12), 186 (1), 217 (1), 230 (1), 231 (0.2), 262 (M^+, 0.2)
20	41 (24), 43 (37), 45 (75), 57 (27), 58 (22), 59 (20), 69 (15), 71 (100), 73 (11), 75 (56), 85 (11), 87 (20), 89 (37), 101 (65), 102 (13), 113 (16), 114 (9), 115 (21), 125 (9), 127 (6), 130 (5), 143 (33), 157 (11), 158 (7), 173 (5), 185 (8), 188 (3), 189 (3), 217 (2), 262 (M^+, 0.3)
21	41 (45), 43 (52), 45 (70), 57 (22), 58 (36), 59 (28), 69 (21), 71 (97), 73 (22), 75 (65), 85 (11), 87 (100), 88 (56), 89 (14), 99 (24), 101 (78), 102 (5), 111 (8), 115 (15), 125 (6), 131 (6), 143 (30), 156 (6), 157 (7), 172 (2), 173 (2), 174 (1), 175 (12), 176 (1), 187 (3), 188 (9), 189 (2), 199 (1), 230 (0.7), 262 (M^+, 0.3)

[a] Values of $m/z < 100$ are given with a relative intensity > 10%, m/z 100-160 > 5%, m/z 160-190 > 1%, and $m/z > 190 > 0.1\%$.
[b] Values of $m/z < 150$ are given with a relative intensity > 10%, m/z 150-190 > 1%, and $m/z > 190 > 0.1\%$.
[c] Values of $m/z < 100$ are given with a relative intensity > 10%, m/z 100-160 > 5%, m/z 160-220 > 1%, and $m/z > 220 > 0.1\%$.

positions 2 and 6 and also a significant substitution in the less reactive position 3. In contrast, the β-cyclodextrin derivatives prepared with the highest excess of sodium hydroxide (see Table 1) showed preferred etherification in position 6 of the glucose units, which is in agreement with the NMR data. The starch samples are marked by highly preferred 2-*O*-substitution. Interestingly, a higher ds is observed for position 3 than for the more reactive and sterically less hindered primary 6-OH. About 5% of these groups are blocked by branching in the waxy corn starch used. The selectivity of 2-*O*-substitution was influenced by the type of modification (''wet'' or ''paste''). Disubstituted glucose units (1%) could only be detected for the starch with a ds of 0.05.

Mass spectra.—All degradation products could be identified from their mass spectra. The EI mass spectra of all methoxypropenyl ether derivatives (**7–9** and **16–18**) showed significant ions for $M^{\cdot+}$ at m/z 306 and 276, respectively, and for the oxopropyl ethers traces of the molecular ion of the anhydroglucitols at m/z 5 262 are detected. The molecular masses of all compounds were confirmed by CI–MS. The position of the substituents was deduced from characteristic fragment shifts (56 mass units for methoxypropenyl or 42 mass units for oxopropyl ethers) compared with the permethylated methyl glucosides [15] or analogous 1,5-anhydroglucitol derivatives [11]. The mass spectral data for compounds **7–12** and **16–21** are listed in Table 3.

3. Conclusion

The reaction sequence of methanolysis, permethylation, and Hofmann elimination combined with GLC and GLC–MS analysis was shown to be an efficient method for determining the substitution pattern of *O*-(2-hydroxy-3-trimethylammmonium)propyl starches and cyclodextrins. Mild hydrolysis or reduction prior to Hofmann elimination can be included to obtain more stable degradation products or only one compound per substitution pattern of an anhydroglucose unit.

4. Experimental

General.—Cyclomaltoheptaose and cyclomaltooctaose (β- and γ-cyclodextrin) were purchased from Wacker Chemie (Munich, Germany), 2,3-epoxypropyltrimethylammonium chloride, triethylsilane, BF_3 etherate, and dioxane from Fluka (Neu-Ulm, Germany), dimethyl sulfoxide, MeI, Me_3SiOSO_2Me, MeOH (p.a.) and acetyl chloride from E. Merck (Darmstadt, Germany), Sephadex LH20 from Pharmacia (Uppsala, Sweden), and the anion-exchange resin AG 1-X4, 50–100 mesh, from Bio-Rad. Cationic β- and γ-cyclodextrin derivatives and the commercial cationic starches (ds 0.02, 0.041, and 0.05) were submitted to the same analytical procedure.

Cationization of γ-cyclodextrin.—γ-Cyclodextrin (10 g) was dissolved in 60 mL of 3.45 M NaOH and the solution was cooled to 0°C. 2,3-Epoxypropyltrimethylammonium chloride (14.5 g) in 45 mL of H_2O were added dropwise. The mixture was stirred overnight, neutralized with concd HCl and evaporated to a viscous residue. After

redissolving in 100 mL of abs MeOH, NaCl was filtered off. The white solid (770 mg) obtained after evaporation was dialysed against H_2O (Spectra/Por CE membrane, M_r cut-off 3500), and after removing the solvent a colourless solid was obtained (330 mg); ds = 0.33 by ^1H NMR, 0.32 by elemental analysis. ^1H NMR: δ (ppm) 3.2 (s, ds · 9 H, $N(CH_3)_3$), 3.4–4.1 (6 H, H-2–H-6a,b; ds · 4 H, 2 × CH_2, substituent), 4.42 (m, ds · H, CH, substituent), 5.08 (H-1), 5.22 (H-1 of the 2-*O*-substituted glucose units).

Cationization of β-cyclodextrin.—β-Cyclodextrin (3 g) was dissolved in 20 mL of 10.5 M NaOH and the solution was cooled to 0°C. 2,3-Epoxypropyltrimethylammonium chloride (6 g) in 15 mL of H_2O were added dropwise. Dialysis was carried out as described. Yield, 2.3 g; ds = 0.46 by ^1H NMR and 0.45 by elemental analysis (see Table 1).

Methanolysis.—To 300 mg of cationic cyclodextrin derivative or cationic starch in a V-Vial, 4.5 mL of 1.5 M MeOH–HCl was added and the mixture was stirred at 100°C for 4 h. After evaporation to dryness, the remaining HCl was removed in vacuo.

Anion-exchange chromoatography.—The charged monomers (**1–3a,b**) were isolated by means of anion-exchange chromatography (15 × 280 mm, OH^- form). Elution was carried out with H_2O at a flow-rate of 3 mL/min. The charged fraction was neutralized and evaporated to dryness. FABMS: $m/z = 310$ (M^+).

Permethylation.—The charged methyl glucosides (**1–3a,b**) were dissolved in Me_2SO. Powdered NaOH (3 equiv per OH group) and MeI (4 equiv per OH group) were added and the mixture was stirred for 1.5 h at room temperature. After addition of H_2O the solution was neutralized with 3 M HCl. The charged, permethylated methyl glucosides (**4–6a,b**) were isolated by Sephadex LH-20 chromatography (20 × 25 mm) with MeOH as the eluent, to obtain a colourless solid after evaporation. FABMS: $m/z = 366$ (M^+).

Reduction.—The charged permethylated methyl glucosides **4–6a,b** (27 mg) derived from cationic γ-cyclodextrin were dissolved in CH_2Cl_2 (1 mL) and 20 equiv Et_3SiH, 5 equiv $BF_3 \cdot OEt_2$, and 5 equiv Me_3SiOSO_2Me were added. After stirring overnight at room temperature and neutralization with $NaHCO_3$, the corresponding 1,5-anhydro-D-glucitol derivatives **13–15** were isolated by Sephadex LH-20 chromatography.

Hofmann elimination.—The permethylated products (**4–6a,b** or **13–15**) were converted to the free bases by treatment with an anion-exchange resin (OH form). The solution was concentrated by freeze-drying and then heated to 80°C in a small distillation apparatus in vacuo for 30 min. The enol ethers (**7–9a,b** or **16–18**) were extracted with diethyl ether. The extract was concentrated and solid $CaCO_3$ was added to prevent acid hydrolysis. The enol ethers were analysed by GLC and GLC–MS.

Acid hydrolysis.—The enol ethers (**7–9a,b** or **16–18**) were evaporated and 400 μL of dioxane and 100 μL of 0.05 M HCl were added. After stirring for 25 min at room temperature, 1 mL of H_2O was added and the *O*-(2-oxo)propyl derivatives (**10–12a,b** or **19–21**) were extracted with 1 mL of CH_2Cl_2. The organic phase was dried and analysed by GLC and GLC–MS.

GLC.—GLC was carried out on a Carlo Erba Fractovap 4160 gas chromatograph, equipped with an on-column injection system, a CP-Sil 8 CB capillary column (25m × 0.25 mm) and a 2 m retention gap, a flame ionization detector, and a Merck-Hitachi D-2500 Chromatointegrator. Hydrogen was used as the carrier gas. Temperature programme: 70°C (1 min), then increased at 20°C/min to 160°C (14 min isothermal), at

20°C/min to 290°C (**A**, **C**, and **D**) or 70°C (1 min), then at 20°C/min to 140°C, at 1°C/min to 160°C, and again at 20°C/min to 290°C (**B**).

Physicochemical analysis.—Mass spectra (GC–MS) were obtained with a VG Analytical VG/70-250S instrument. For CI–MS ammonia was used as reactant gas. FAB mass spectra were recorded on a VG Analytical VG/70-250S instrument with a xenon gun and *m*-nitrobenzyl alcohol as matrix. ^{1}H NMR (400 MHz) spectra were obtained for D_2O solutions using a Bruker WM 400 instrument.

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