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Regioselectively Modified Stereoregular Polysaccharides XIII. Polymerization of 3-Deoxygenated 1,6-Anhydroglucopyranose Derivative

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ABSTRACT: Ring-opening homo- and copolymerization of a 3-deoxygenated anhydro sugar derivative (1,6-anhydro-2,4-di-*O*-benzyl-3-deoxy-β-D-*ribo*-hexopyranose, **1**) was carried out using phosphorus pentafluoride as the initiator in dichloromethane. Homopolymerization of **1** at −60°C gave highly stereoregular polymers with α-configuration and with number average molecular weight of 12.8×10^4—2.9×10^4. The highest yield was 95.6%. The monomer reactivity ratios in copolymerization of **1** with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**2**) at −60°C were $r_1 = 1.60$ and $r_2 = 0.73$. The equilibrium monomer concentrations ($[M]_e$) of **1** and **2** were 0.029—0.042 mol l^{-1} and 0.0064 mol l^{-1}, respectively (−60°C). Hydrolysis of **1** and **2** in a solution of trifluoroacetic acid and deuterium oxide (volume ratio of 6:4) proceeded at a respective rate of 2.4×10^{-5} s^{-1} and 7.3×10^{-6} s^{-1} (60°C). Debenzylation of the homo- and copolymers using sodium in liquid ammonia yielded linear (1→6)-α-D-glucopyranans with different degree of 3-deoxygenation.

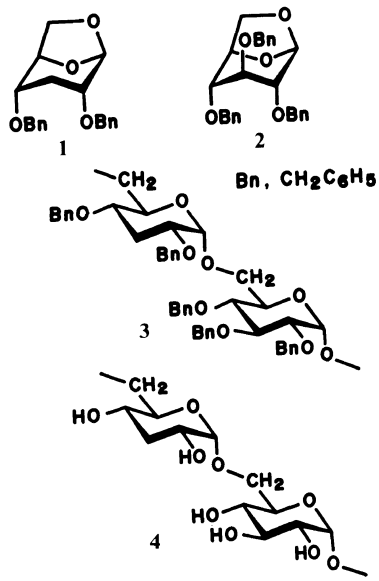
KEY WORDS Anhydro Sugar / Ring-Opening Polymerization / Synthetic Polysaccharide / Deoxygenated Polysaccharide /

Biologically important deoxysugars occur widely in nature as components of cardiac glycosides, antibiotics and antigenic determinants.[1] Recent attention has been given to synthetic deoxy oligosaccharides which serve as receptor analogues for investigating molecular recognition of enzymes, lectins, and monoclonal antibodies.[2,3] In this respect, well-defined deoxygenated polysaccharides whose structures are slightly different from naturally occuring ones are an important model system to understand the principles of the specificity of structure–function relationship. Synthesis of polysaccharides having well-defined structures have been attempted via ring-opening polymerization[4,5] and polycondensation.[6]

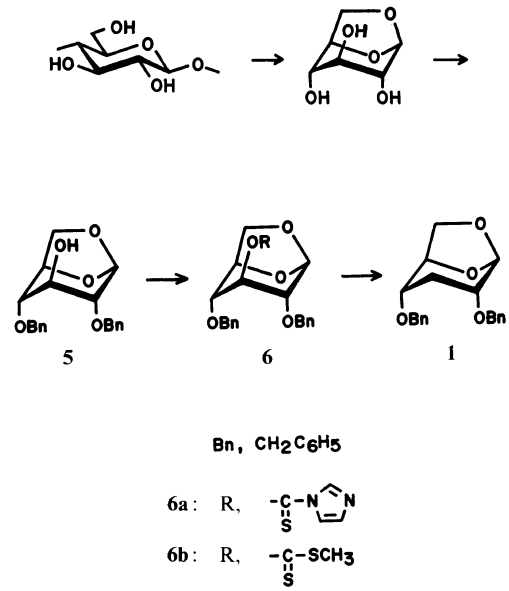
In this study, regiospecifically deoxygenated (1→6)-α-D-glucopyranans were prepared according to Scheme I: homopolymerization of 1,6-anhydro-2,4-di-*O*-benzyl-3-deoxy-β-D-*ribo*-hexopyranose (**1**)[7] and its copolymerization with 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**2**), followed by debenzylation of the resulting homo- and copolymers. The polysaccharide obtained differed from linear dextran in replacing its equatorial hydroxyl groups on C-3 carbons by hydrogen atoms.[8] The polymerization reactivity of **1** was examined for comparison with those of some related compounds.[9-15]

EXPERIMENTAL

Scheme II shows the synthetic method of 1,6-anhydro-2,4-di-*O*-benzyl-3-deoxy-β-D-*ribo*-hexopyranose (**1**) *via* four step reactions starting from microcrystalline cellulose. 1,6-Anhydro-2,4-di-*O*-benzyl-β-D-glucopyranose (**5**) was prepared by selective dibenzylation of 1,6-anhydro-β-D-glucopyranose using benzyl bromide and barium oxide in dimethylformamide according to the method of Iversen.[16]



Scheme 1. Synthesis of deoxygenated (1→6)-α-D-glucopyranans.



Scheme II. Synthesis of 1,6-anhydro-2,4-di-*O*-benzyl-3-deoxy-β-D-*ribo*-hexopyranose (**1**).

Yield, 92%; mp, 104.5—105.5°C; $[\alpha]_D^{25}$, −28.7 (*c* 1.0, chloroform) (lit.,[16] mp, 104.5—105.5°C; $[\alpha]_D^{25}$, −28.8). The free hydroxyl group of **5** was thioacylated and the resulting imidazolyl or (methylthio)thiocarbonyl intermediates **6a** and **6b** were reduced with tributylstannane.[17]

*1,6-Anhydro-2,4-di-O-benzyl-3-O-thiocarbonylimidazolyl-β-*D*-glucopyranose* (**6a**)

A mixture of **5** (4.28 g, 12.5 mmol) and *N,N'*-thiocarbonyldiimidazole (4.53 g, 25 mmol) in 1,2-dichloroethane (63 ml) was refluxed gently for 3 hr. TLC (hexane–ethyl acetate, 1:1, v/v) showed almost complete conversion of **5** (*Rf* 0.6) to **6a** (*Rf* 0.4). The solution was washed with 1 *N* HCl (63 ml), 5% aqueous $NaHCO_3$, and water (63 ml). The organic solvent was removed *in vacuo* and the residue was chromatographed on silica gel. Elution with hexane–ethyl acetate (3:7, v/v) followed by evaporation gave **6a** as a syrup (4.95 g, 88%). $[\alpha]_D^{25}$, −60.5° (*c* 1 in chloroform). ^1H NMR ($CDCl_3$) 8.21, 7.52, and 6.98 (three s, 3H, imidazolyl), ~7.29 (10H, phenyl), 5.76 (s, 1H, H-3), 5.49 (s, 1H, β-H-1), 4.77 and 4.71 (two s, 4H, benzyl CH_2), 4.57 (broad s, 1H, H-5), 3.72 (s, 2H, H-6_{exo} and H-6_{endo}), and 3.39 ppm (s, 2H, H-2 and H-4); ^{13}C NMR (CH_2Cl_2, Me_2SO-d_6 external lock, 25 MHz) 182.5 (C=S), 137.7, 128.6, 128.0 (phenyl), 137.0, 131.2, and 118.2 (imidazolyl carbon), 100.2 (C-1), 76.9, 74.6, and 74.3 (C-2, 3, 4, 5), 72.4 and 71.7 (benzyl CH_2), and 65.4 ppm (C-6). *Anal.* Calcd for $C_{24}H_{24}O_5N_2S$: C, 63.70%; H, 5.35%; N, 6.19%. Found: C, 63.42%; H, 5.42%, N, 6.07%.

*1,6-Anhydro-2,4-di-O-benzyl-3-O-(methylthio)thiocarbonyl-β-*D*-glucopyranose* (**6b**)

Sodium hydride (oil dispersion, 50%, 4.0 g) and imidazole (40 mg) was added to **5** (13.7 g, 40 mmol) in dry tetrahydrofuran (THF, 120 ml) and the mixture was stirred under nitrogen for 2 h. Carbon disulfide (14.4 g) was added and stirred for 2 h; methyl iodide (10 g) was added and stirring was continued for 1 h. Water (40 ml) was added, the solution was

concentrated *in vacuo*, and the residue was extracted with chloroform (100 ml × 2). The chloroform solution was washed with 2% hydrochloric acid (40 ml) and with saturated aqueous sodium bicarbonate (40 ml), dried over magnesium sulfate and concentrated. The crude product was chromatographed on silica gel (hexane–ethyl acetate, 2 : 1, v/v) to give **6b** as a yellow syrup. 18.1 g (~100%). *Anal.* Calcd for $C_{22}H_{24}O_5S_2$: C, 61.09%; H, 5.59%. Found: 61.08%; H, 5.60%.

*1,6-Anhydro-2,4-di-O-benzyl-3-deoxy-β-*D*-ribo-hexopyranose* **(1)**

A solution of **6a** (2.7 g, 6.0 mmol) in dry toluene (50 ml) was added dropwise over 30 min to tributylstannane (2.7 g, 9.3 mmol) in toluene (200 ml) with refluxing and stirring under nitrogen. After 2 h, tributylstannane (2.7 g) was added again. Refluxing was continued for further 12 h until TLC analysis confirmed the disappearance of **6a**. The solution was concentrated *in vacuo*, and the residue was dissolved in hexane (50 ml) and extracted with acetonitrile (30 ml × 4). The combined acetonitrile extracts were washed with hexane (50 ml) and concentrated. Crystallization from ethanol and then purification by silica gel chromatography (hexane–ethyl acetate, 2 : 1, v/v) yielded **1** as colorless crystal (1.55 g, 79%).

$[\alpha]_D^{25}$, −49.1° (*c* 1 in chloroform); mp 60—60.5°C; ^{1}H-NMR ($CDCl_3$, 200 MHz) 7.29—7.36 (10H, phenyl), 5.46 (s, 1H, β-H-1), 4.61 and 4.59 (two s, 5H, benzyl CH_2 and H-5), 3.75 (d × d, J=7 and 5 Hz, 1H, H-6_{endo}), 3.65 (d × d, J=7 and 1 Hz, 1H, H-6_{exo}), 3.3 (2 d, 2H, H-2 and H-4), 2.04 (d, J=15 Hz and t, J=2, 1H, H-3_{eq}), 1.80 ppm (d, J=15 Hz and t, J=6 Hz, 1H, H-3_{ax}); ^{13}C NMR (CH_2Cl_2, Me_2SO-d_6 external lock) 138.8, 128.5, 127.8, 127.6 (phenyl), 101.0 (C-1), 74.8 and 72.9 (C-2, 4, 5), 71.3 and 70.6 (benzyl CH_2), 65.6 (C-6), and 24.8 ppm (C-3). *Anal.* Calcd for $C_{20}H_{22}O_4$: C, 73.60%; H, 6.79%. Found, C, 73.81%; H, 6.84%.

Compound **6b** was treated in a similar way to give **1** in 91% yield.

Polymerization

1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose was prepared by complete benzylation of 1,6-anhydro-β-D-glucopyranose.

Polymerization was carried out in dichloromethane with high-vacuum techniques.[4,7-9] Phosphorus pentafluoride was generated by heating *p*-chlorobenzenediazonium hexafluorophosphate. The polymerization was terminated by added cold methanol, and the precipitated polymer was purified by reprecipitation from chloroform into methanol four times and freezed-dried from benzene.

NMR and analytical data of the stereoregular homopolymer 2,4-di-*O*-benzyl-3-deoxy-(1→6)-α-D-*ribo*-hexopyranan are as follows. ^{1}H NMR ($CDCl_3$, 9%, 60°C) 7.32 and 7.27 (2s, 10H, phenyl), 4.96 (d, J=3 Hz, 1H, α-H-1), 4.59 and 4.41 (d × d, J=4 Hz, 4H, benzyl CH_2), 3.8—3.3 (5H, H-2, 4, 5, 6_{endo}, 6_{exo}), 2.2—1.6 ppm (2H, H-3_{eq} and H-3_{ax}); ^{13}C NMR (CH_2Cl_2, 12%, Me_2SO-d_6 external lock) 139.0, 128.5, and 127.7 (phenyl), 96.4 (α-C-1), 74.7 (C-2), 71.9 and 71.2 (C-4 and C-5), 70.7 (benzyl CH_2), 65.4 (C-6), and 30.6 ppm (C-3); *Anal.* Calcd for $(C_{20}H_{22}O_4)_n$: C, 73.60%; H, 6.79%. Found: C, 73.84%; H, 6.83%.

Determination of Equilibrium Monomer Concentration

Polymerization and depolymerization were carried out in a high vacuum reaction vessel equipped with a capillary tube to determine the reaction volume. A relatively low concentration of monomer and polymer solution in dichloromethane and a large amount of initiator (PF_5) were used. The reaction was terminated with methanol, the resulting solution was concentrated, and the conversion was determined from anomeric C-1 absorptions of the monomeric and polymeric components in ^{13}C NMR spectrum.

Acid-Catalyzed Hydrolysis

1,6-Anhydro sugar compounds were dissolved in a mixture of trifluoroacetic acid and deuterium oxide (6 : 4, v/v) in an NMR sample tube (5 mmϕ) and the resulting solutions (0.29 mol l^{-1}) were kept at 60°C. The ^{13}C NMR peak intensity of the anomeric C-1 signal were followed as a function of time and the hydrolysis rate was estimated from pseudo-first-order plots.

Debenzylation

Debenzylation with sodium in liquid ammonia and work-up procedures were the same as those described previously.[7-9]

Characterization

^1H and ^{13}C NMR spectra were recorded on a Japan Electron Optics Laboratory JNM-FX-200 Fourier transform NMR spectroscopy operated at 200 and 50 MHz, respectively. Optical rotations were determined with a JASCO DIP-181 digital polarimeter by using 1-dm cell at 25°C. Melting points (uncorrected) of 1,6-anhydrosugar derivatives were determined with a Yanagimoto melting point apparatus. Thermal analysis of polymers was made with a Perkin-Elmer DSC-2 differential scanning calorimeter. Gel-permeation chromatography was carried out by using a Shodex GPC-A 80 M column (8 mm i.d. × 1000 mm) on a Hitachi 634A high-speed liquid chromatograph (solvent, chloroform). The calibration curve was made using standard samples of polystyrene. Solution viscosities were measured in Ubbelohde viscometers at 25°C. TLC was carried out on Merck silica gel 60 F_{254} coated plates, and detection was made by charring with a $Ce(SO_4)_2$ solution in 3.6 *N* sulfuric acid.

RESULTS AND DISCUSSION

Homopolymerization of 1,6-Anhydro-2,4-di-O-benzyl-3-deoxy-β-D-ribo-hexopyranose **(1)**

Crystalline compound **1** was prepared as shown in Scheme II via thioacylation of the free hydroxyl group of 1,6-anhydro-2,4-di-*O*-benzyl-β-D-glucopyranose and subsequent reduction with tributylstannane. The overall yields through intermediates **6a** and **6b** were 70% and 82%, respectively.

The polymerization of **1** was carried out under high vacuum with phosphorus pentafluoride as the initiator in dichloromethane. Table I summarizes the homopolymerization of **1** and characterization of the resulting polymers. The highest polymer yield was 95.6%. The white powdery polymer obtained was soluble in solvents such as benzene, toluene, carbon tetrachloride, chloroform, dichloromethane, 1,2-dimethoxyethane, tetrahydrofuran, pyridine, dimethyl sulfoxide, dimethylformamide, and acetone.

Figure 1 shows the ^{13}C NMR spectra of polymers obtained by the polymerization below −20°C. In the C-1 resonance regions, there appeared only one signal at 95.91 ppm (peak c). The ^1H and ^{13}C NMR spectral data in the Experimental Section confirmed the formation of stereoregular 2,4-di-*O*-benzyl-3-deoxy-(1→6)-α-D-*ribo*-hexopyranan. The high α-anomeric stereoregularity was supported by positive and large optical rotation.

The polymer (exptl. no. S18 in Table I) obtained by 40 min's polymerization at −60°C had the highest stereoregularity and highest molecular weight (1.22×10^5) among the homopolymers of **1** as judged by rotation, melting point, intrinsic viscosity, and GPC data. When polymerization was carried out at higher temperature and for a longer time, the intrinsic viscosity and estimated molecular weight of the polymer decreased. Optical rotation of the polymers, a sensitive measure of stereoregularity, was lowered with rise in polymerization temperature and prolonged time. In the ^{13}C NMR spectrum obtained by the polymerization at 0°C, there appeared several small peaks assignable to the β-configurational unit, together with α-configurational large peaks. The presence of about 6% of β-con-

Table I. Homopolymerization of 1,6-anhydro-2,4-di-*O*-benzyl-3-deoxy-β-D-*ribo*-hexopyranose (**1**)[a]

Exptl. No.	Temp °C	Time h	Yield[b] %	α-Form[c] %	$[\alpha]_D^{25}$[d] deg	mp[e] °C	$[\eta]$[f] dl g^{-1}	M_n[g] $\times 10^{-4}$
S18	−60	0.67	58.1	~100	+145.7	55—58	0.99	12.2
S5	−60	15	71.8	~100	+143.4	40—45	0.71	8.4
S27[h]	−60	24	95.6	~100	+138.9	—	0.22	2.9
S9	−40	3	67.3	~100	+141.9	54—57	0.27	3.7
S1	−20	0.67	79.6	~100	+135.3	46—50	0.18	2.0
S17	0	0.5	44.0	94	+123.7	48—51	0.08	1.4
S19	0	100	22.3	92	+127.4	50—53	0.08	1.4

[a] Monomer, 3.0 mmol; initiator, PF_5, 3.3 mol%; solvent, dichloromethane, 2 ml.
[b] Methanol insoluble polymer.
[c] Determined by ^{13}C NMR spectra of both of benzylated and debenzylated polymers.
[d] *c*, 1 g dl^{-1} in chloroform.
[e] Determined by differential scanning calorimetry.
[f] At 25°C in chloroform.
[g] Determined by gel-permeation chromatography.
[h] Monomer, 10.1 mmol; PF_5, 5.0 mol%; dichloromethane, 6 ml.

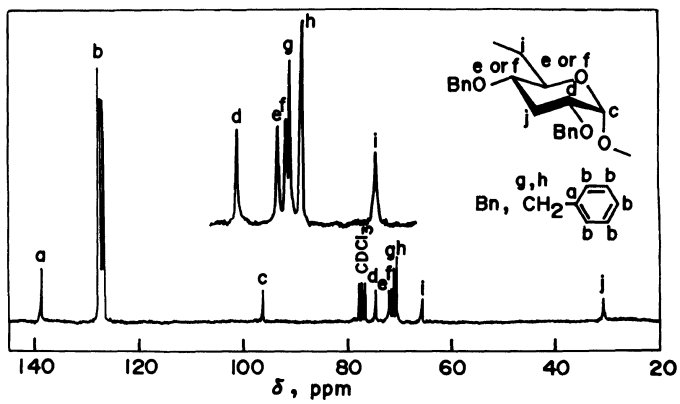


Figure 1. ^{13}C NMR spectrum of stereoregular 2,4-di-*O*-benzyl-3-deoxy-(1→6)-α-D-*ribo*-hexopyranan. Concentration, 8% in $CDCl_3$; room temp; TMS reference; 50 MHz.

figurational units and 94% of α-configurational ones in the main chains was estimated from the area ratios of the β-C-1 resonance at 105.8 ppm and the α-C-1 resonance at 96.4 ppm.

Copolymerization between 1,6-Anhydro-2,4-di-O-benzyl-3-deoxy-β-D-ribo-hexopyranose (**1**) *and 1,6-Anhydro-2,3,4-tri-O-benzyl-β-D-glucopyranose* (**2**)

The data on copolymerization between **1** and **2** at −60°C are listed in Table II. The apparent copolymerization rate was high, and the termination in 10—20 min resulted in 21—46% conversion. The copolymer composition of **1** was higher than its feed composition as plotted in Figure 2. The solid curve illustrates the instantaneous copolymer composition calculated from the reactivity ratio of $r_1 = 1.60$ and $r_2 = 0.73$ as estimated by the Kelen–Tüdős equation.[18] The reactivity of monomer **1** toward the respective growing active centers was

Table II. Copolymerization between 1,6-anhydro-2,4-di-*O*-benzyl-3-deoxy-β-D-*ribo*-hexopyranose (**1**) and 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**2**)[a]

Exptl. No.	**1**	**2**	Mol. fr. of **1**	CH_2Cl_2	Time	Yield	Mol. fr. of **1** in copolymer[b]	$[\alpha]_D^{25}$ [c]	mp[d]	$[\eta]$[e]	M_n[f]
	mmol	mmol	in feed	ml	min	%		deg	°C	dl g^{-1}	$\times 10^{-4}$
S16	0	5.0	0	4	20	79.6	0	+115.5	51—54	0.67	2.6
S11	3.0	12.0	0.20	10	12	21.1	0.26	+115.4	53—67	0.72	1.8
S22	1.8	4.2	0.30	4	12	39.0	0.38	+118.5	50—55	0.49	1.8
S3[g]	2.0	3.5	0.36	4	10	33.1	0.49[h]	+117.9	42—46	0.73	1.3
S24	7.5	7.5	0.50	10	20	45.0	0.59	+124.0	44—48	0.79	1.4
S23	3.6	2.4	0.60	4	12	37.1	0.69	+130.5	50—54	—	1.9
S10	4.2	1.8	0.70	4	13	28.6	0.78	+132.6	39—53	0.65	1.4
S25	12.0	3.0	0.80	10	20	45.5	0.87	+137.1	45—52	0.86	1.2
S26	13.6	1.5	0.90	10	18	38.8	0.96	+142.0	40—46	1.07	1.8
S18	3.0	0	1.0	2	40	58.1	1.0	+145.7	55—59	0.99	1.2

[a] Temp, −60°C; initiator, PF_5, 3.3 mol%.
[b] Determined from 50-MHz ^{13}C NMR spectra of debenzylated polymer.
[c] *c*, 1 g dl^{-1} in chloroform.
[d] Determined by differential scanning calorimetry.
[e] At 25°C in chloroform.
[f] Determined by gel-permeation chromatography.
[g] Initiator, 3.8 mol%.
[h] Determined from 25-MHz ^{13}C NMR spectrum of benzylated copolymer.

higher than that of **2**. Possibly, the replacement of electron-attractive benzyloxy substituent by hydrogen atom facilitates the approach of the monomer to growing ends owing to the enhanced nucleophilicity and reduced steric hindrance of the monomer.

The high α-anomer stereoregularity of the copolymers was suggested by the high optical rotation and also ^{13}C NMR spectrum (Figure 3). Some of the resonances in the ^{13}C NMR spectrum were split into two peaks due to crossover diad sequences between **1** and **2** units. Figure 4 shows the splittings of α-C-1 anomeric resonances whose intensities varied with copolymer composition. The separation of the signals, however, was not enough to estimate each diad content.

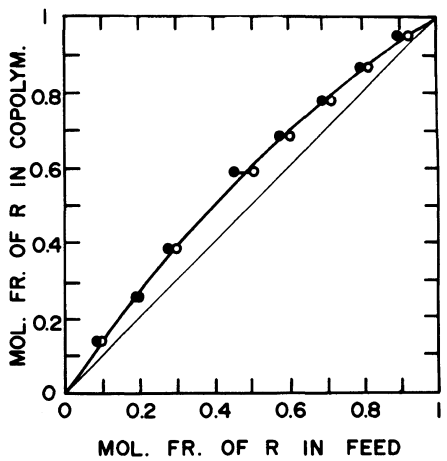


Figure 2. Composition curve for copolymerization between 1,6-anhydro-2,4-di-*O*-benzyl-3-deoxy-β-D-*ribo*-hexopyranose (**1**) and 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**2**). The initial and final monomer compositions are shown as ○ and ●, respectively. $r_1 = 1.60$ and $r_2 = 0.73$.

Etimation of Equilibrium Monomer Concentration

Equilibrium monomer concentration ($[M]_e$) was estimated from residual monomer concentrations ($[M]_r$) in polymerization and depolymerization as summarized in Table III. Both reactions were carried out at −60°C by applying low concentration of the starting compounds and a high concentration of the

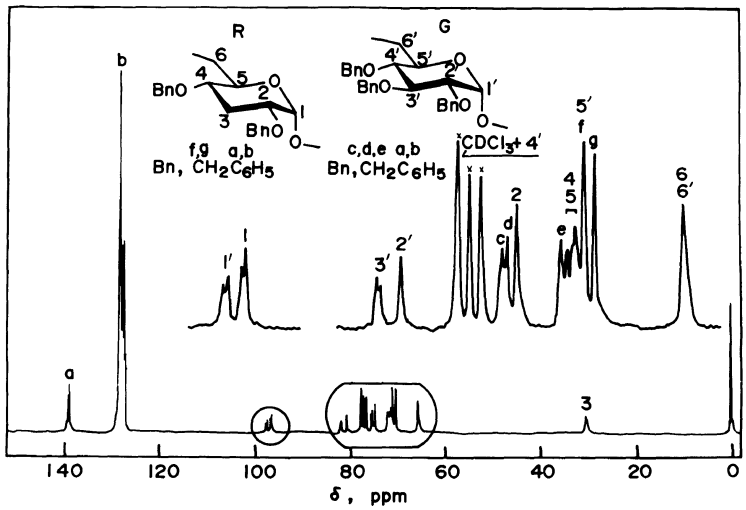


Figure 3. ^{13}C NMR spectrum of copolymer. Mole fraction of **1** in copolymer, 0.59; concentration; 9% in $CDCl_3$; 43°C; TMS reference; 50 MHz.

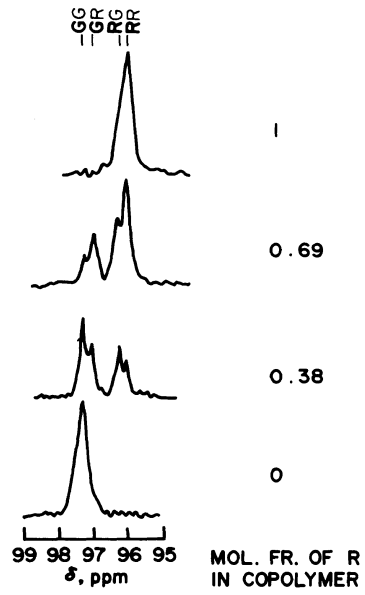


Figure 4. ^{13}C NMR spectra of anomeric carbon region of copolymers. In $CDCl_3$; TMS reference; room temp; 50 MHz.

initiator. **1**: $[M]_e = 0.028$—$0.042\,mol\,l^{-1}$; **2**: $[M]_e = 0.0064\,mol\,l^{-1}$ (at −60°C). The free energy change in polymerization of **1** calculated from the $[M]_e$ value was less negative than that of **2** (**1**, $-5.9 \pm 0.4\,kJ/mol$; **2**, $-8.9\,kJ\,mol^{-1}$ at −60°C). We assumed that the absence of the benzyloxy substituent in position 3 released a large 1,3-diaxial interactions[19] in the 1,6-anhydro form, resulting in a less favorable thermodynamic reactivity of **1**.

Acid-Catalyzed Hydrolysis

Hydrolysis rates of several bicyclic acetal using dichloroacetic acid as catalyst were compared in the literature,[5,20] but this catalytic system was not strong enough to hydrolyze **1** and **2** at measurable rates because both compounds are stabilized by an electron attractive benzyloxy group at position 2. A mixture of trifluoroacetic acid and deuterium oxide (volume ratio of 6:4) has been found to cause the acid-catalyzed solvolysis of **1** and **2** at 60°C. The rates were followed by the disappearance of the β-C-1 carbon signals. The compound **1** was hydrolyzed at a rate of $2.4 \times 10^{-5}\,s^{-1}$, and **2** of $7.3 \times 10^{-6}\,s^{-1}$. The ring-opening reactivity of **1** was 3.2-fold over that of **2**.

3-Deoxygenated (1→6)-α-D-Glucopyranan

Debenzylation of the homopolymers (**3**) using sodium in liquid ammonia is shown in Table IV. In the ^{13}C-NMR spectra of the

Table III. Determination of equilibrium monomer concentration through polymerization of **1** and **2** and depolymerization of each homopolymer[a]

Starting compound	PF_5	Time	Convn.[b]	$[M]_r$[c]
	$mol\,l^{-1}$	mol%	Day	%	$mol\,l^{-1}$
1	0.28	13	1	85.0	0.042
Homopolymer of **1**	0.076	14	6	37.7	0.029
2	0.28	13	2	97.7	0.0064
Homopolymer of **2**	0.097	20	5	6.5	0.0063

[a] At −60°C in dichloromethane.
[b] Determined by ^{13}C NMR spectroscopy.
[c] Residual monomer concentration.

Table IV. Synthesis of 3-deoxy-(1→6)-α-D-*ribo*-hexopyranan homopolymer

Exptl. No.	Weight	Na	NH_3	Toluene	DME[a]	Time	Yield	$[\alpha]_D^{25}$[b]	$[\eta]$[c]	M_n[d] $\times 10^{-4}$
	g	g	ml	ml	ml	h	%	deg	$dl\,g^{-1}$	
DS18	0.47	0.12	50	15	5	2	~100	+125	0.59	—
DS27	2.94	0.88	250	90	30	2	~100	+154	0.31	1.0
DS1	0.43	0.80	50	15	5	1.5	~100	+128	0.13	0.67
DS17	0.28	0.15	30	7.5	2.5	1.5	88	—	0.05	—

[a] 1,2-Dimethoxyethane.
[b] *c*, 1.0 in water.
[c] At 25°C in Me_2SO.
[d] Estimated by GPC (pullulan standard in water).

products of the exptl. nos. DS18 and DS27, there appeared only six resonances whose chemical shifts are listed in Table V (the spectrum was presented in the preliminary communication[7]). Table V also shows that each $^1J(^{13}C\text{-}^1H)$ coupling constant was similar to the corresponding one of (1→6)-α-D-glucopyranan except for that of the C-3 carbon. The stereoregular polysaccharide 3-deoxy-(1→6)-α-D-*ribo*-hexopyranan was soluble in water and dimethyl sulfoxide. *Anal.* Calcd for $(C_6H_{10}O_4)_n$: C, 49.31%, H, 7.09%. Found: C, 49.31%, H, 6.90%.

The polysaccharide containing 6% of the β-configurational unit in the main chain was also obtained by debenzylation of polymer S17. The NMR data (in D_2O, 70°C) of the α- and β-anomer carbons and protons are as follows: ^{13}C NMR: α-C-1, 97.80; β-C-1, 105.5. ^1H NMR: α-H-1, 4.83, $J_{1,2}=3.2$ Hz; β-H-1, 4.44, $J_{1,2}=7.3$ Hz.

Table V. Chemical shifts and ^1J (^{13}C–^1H) coupling constants of 3-deoxy-(1→6)-α-D-*ribo*-hexopyranan and (1→)-α-D-glucopyranan[a]

	3-Deoxy-(1→6)-α-D-*ribo*-hexopyranan		(1→6)-α-D-Glucopyranan	
	ppm	^1J (^{13}C–^1H) Hz	ppm	^1J (^{13}C–^1H) Hz
C-1	97.80	169.0	98.83	170.9
C-2	67.74	144.5	72.55	144.7
C-3	36.11	129.9	74.53	146.7
C-4	65.25	145.5	70.92	142.8
C-5	72.22	144.5	71.36	142.8
C-6	66.52	144.0	67.06	144.7

[a] Concentration, 10% in D_2O; temp, 70°C; TMS external reference; 50 MHz.

Debenzylation of copolymers between **1** and **2** gave high α-stereoregular copolysaccharides

Table VI. Synthesis of copolysaccharide **4**

Exptl. No.	Weight	Na	NH_3	Toluene	DME[a]	Time	Yield	$[\alpha]_D^{25}$ [b]	$[\eta]$[c]	M_n[d] $\times 10^{-4}$
	g	g	ml	ml	ml	h	%	deg	dl g^{-1}	
DS16	1.25	0.54	125	50	13	1.5	~100	+162	0.23	—
DS11	1.00	1.06	100	30	10	2.0	~100	+165	0.21	1.4
DS22	0.76	1.31	100	30	10	1.5	73	+155	0.34	2.6
DS24	2.20	0.73	200	60	20	1.7	73	+170	0.69	4.5
DS23	0.73	1.00	100	30	10	1.5	98	+161	0.35	2.2
DS10	0.41	0.49	50	15	5	1.0	96	+151	0.21	1.3
DS25	2.03	0.67	200	60	20	2.5	97	+147	0.56	3.4
DS26	1.65	0.47	200	60	20	1.5	85	+168	0.71	5.2
DS18	0.47	0.12	50	15	5	1.0	~100	+154	0.59	—

[a] 1,2-Dimethoxyethane.
[b] *c*, 1.0 in water.
[c] At 25°C in Me_2SO.
[d] Estimated by GPC (pullulan standard in water).

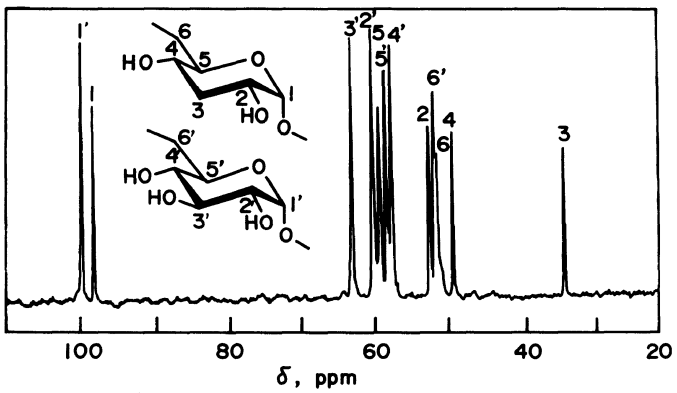


Figure 5. ^{13}C NMR spectrum of a debenzylated copolysaccharide. Mole fraction of deoxygenated unit, 0.36; concentration, 10% in D_2O; external reference, TMS; 50 MHz.

consisting of 3-deoxygenated and non-deoxygenated (1→6)-α-D-glucopyranan units (Table VI). Figure 5 represents one of their ^{13}C NMR spectra. No signal splitting due to cross-over diad sequences was observed, in contrast to the splitting of benzylated copolymers (Figures 3 and 4). The α-C-1 resonance of each structural unit was completely separated from the others, and the copolymer compositions given in Table II are those estimated from their area ratios.

Thus, well-defined (1→6)-α-D-glucopyranans with different degrees of deoxygenation have been prepared. Enzymatic hydrolysis using an endo-acting dextranase suggests that the deoxygenated sequences are bound to the enzyme but not hydrolyzed.[21] The data will be given elsewhere.

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