Regioselectively Modified Stereoregular Polysaccharides. 2. Synthesis of 3-*O*-Methyl-(1→6)-α-D-glucopyranan

Kazukiyo Kobayashi* and Hiroshi Sumitomo

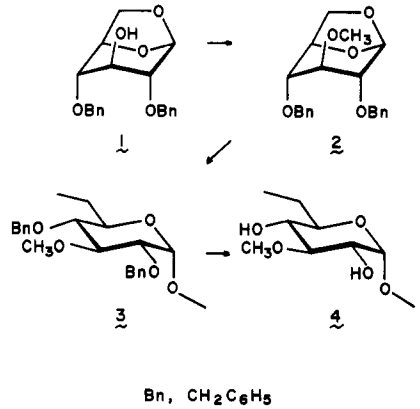
Faculty of Agriculture, Nagoya University, Chikusa, Nagoya 464, Japan.
Received October 9, 1980

ABSTRACT: The regioselectively substituted polysaccharide 3-*O*-methyl-(1→6)-α-D-glucopyranan (**4**) was synthesized by ring-opening polymerization of 1,6-anhydro-2,4-di-*O*-benzyl-3-*O*-methyl-β-D-glucopyranose (**2**) in the presence of PF_5 catalyst at −60 °C followed by removal of the protecting benzyl groups. As a control experiment, a natural dextran was partially methylated and the distribution of methoxyl groups was determined by ^{13}C NMR spectroscopy.

Natural dextrans, (1→6)-α-D-glucopyranans with different degrees of branching, are commercially important as blood plasma substitutes and molecular sieves in a modified form.[1] Stereoregular linear dextran obtained by chemical synthesis has been used as their model compounds for the investigations in the fields of allergy, enzymology, and immunology.[2] In a series of studies,[3-6] we feel that regioselectively well-defined modifications of the linear dextran are indispensable in elucidating relations between the structure and functionality and in developing useful polysaccharides with novel properties. Chemical modifications of polysaccharides, however, are usually not regioselective because the three hydroxyl groups of a sugar unit have similar reactivities. Therefore, we have been attempting ring-opening polymerization of 1,6-anhydro sugar derivatives which are substituted regioselectively by two different types of blocking groups.[7] Some desired polysaccharides are obtained by subsequent chemical reactions of the resulting polymers.[8]

In the present paper, stereoregular 3-*O*-methyl-(1→6)-α-D-glucopyranan (**4**) was synthesized according to Scheme I. Polymerization of 1,6-anhydro-2,4-di-*O*-benzyl-3-*O*-methyl-β-D-glucopyranose (**2**), followed by debenzylation of the product **3**, gave the selectively 3-O-methylated linear dextran. It may be a model system for clinical dextrans with (1→3)-linked sugar residues.[8] On the other hand, it has been reported that *O*-methyl sugars occur in some biologically important polysaccharides. For example, methylglucose-containing lipopolysaccharides isolated from *Mycobacterium smegmatis* were shown to stimulate the fatty acid synthetase complex isolated from the same origin.[9] Recently, several mono-*O*-methyl sugars, including 3-*O*-methyl- and 4-*O*-methyl-D-glucoses, were identified in polysaccharides from slow-glowing strains of *Rhizobium* isolated from the root nodules of legumes.[10-12] In these respects, the selectively 3-O-methylated polysaccharide **4** as well as a cyclodextrin analogue[13] will be made available for physicochemical and physiological studies on the role of methyl substituents.

Scheme I
Synthesis of 3-*O*-Methyl-(1→6)-α-D-glucopyranan



Bn, $CH_2C_6H_5$

Experimental Section

Characterization. ^{13}C NMR spectra were recorded with Japan Electro-Optic Laboratory JNM-FX-100 Fourier transform NMR spectrometers. Optical rotations were determined in a JASCO DIP-181 digital polarimeter by using a 1-dm cell. UV spectra were recorded with a JASCO UVIDEC-1 digital double-beam spectrophotometer. Gel permeation chromatography was carried out by using a Shodex 802A column (8-mm i.d. × 1000 mm) on a Hitachi 634A high-speed liquid chromatograph (solvent, chloroform). Solution viscosities were measured in chloroform and dimethyl sulfoxide (Me_2SO) in Ubbelohde viscometers at 25 °C.

Polymerization. 1,6-Anhydro-2,4-di-*O*-benzyl-3-*O*-methyl-β-D-glucopyranose (**2**) was prepared from 1,6-anhydro-2,4-di-*O*-benzyl-β-D-glucopyranose (**1**)[14] according to the method of Hakomori[15] and purified by silica gel chromatography with 1:1 (v/v) hexane–ethyl acetate as solvent. A colorless syrup was obtained in an 89% yield: $[\alpha]^{25}_D$ −35.2° (*c* 1.0 in chloroform); ^{13}C NMR ($CDCl_3$)[16] δ 137.9, 137.8, 128.2, 127.7, and 127.6 (aromatic), 100.4 (C-1), 79.0 (C-3), 76.7 (C-2), 76.3 (C-4), 74.2 (C-5), 71.6 and 71.0 (benzyl CH_2), 65.2 (C-6), 57.8 (CH_3). 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose was prepared and purified according to the method previously described:[3,20] mp 91–92.5 °C (lit. mp 89.5–91.0,[8] 90–91.5 °C[21]); $[\alpha]^{25}_D$ −31.5° (*c* 1.0 in chloroform) (lit. $[\alpha]^{25}_D$ −30.8,[20] −31.6°[21]). Methylene chloride and *p*-chlorobenzenediazonium hexafluorophosphate were purified in the usual manner.

The high-vacuum polymerization technique was similar to that previously adopted,[3,4,7,20] except that an improved reaction vessel was used to dry the liquid monomer thoroughly. Thus a 100-mL round-bottomed flask, attached to a polymerization tube through a glass filter, was connected to a high-vacuum system. In the flask, a mixture of the prescribed amount of **2** and excess methylene chloride was dried over calcium hydride and degassed under vacuum. After the vessel was sealed, the monomer solution was passed through the filter to the polymerization tube. The excess solvent was returned to the first flask by vacuum distillation until the prescribed monomer concentration was attained. The tube was sealed and the catalyst break seal was broken.

The polymerization was carried out in a thermostat-controlled refrigerator at −60 °C with occasional shaking and terminated by adding a cold mixture of methanol and petroleum ether. The precipitated polymer was purified by reprecipitation from chloroform solution into petroleum ether three times and isolated by freeze-drying from benzene: UV (chloroform) λ_{max} 258.8 nm (ϵ_{max} 400); ^{13}C NMR ($CDCl_3$) δ 138.7, 128.2, 127.6, and 127.1 (aromatic), 97.3 (C-1), 83.6 (C-3), 80.0 (C-2), 77.0 (C-4), 74.7 and 71.9 (benzyl CH_2), 70.6 (C-5), 65.7 (C-6), 60.9 (CH_3). Anal. Calcd for $(C_{21}H_{24}O_5)_n$: C, 70.76; H, 6.79. Found: C, 70.23; H, 6.77.

Debenzylation. Debenzylation of the polymers was carried out in a 3:1 (v/v) mixture of toluene and dimethoxyethane with sodium–liquid ammonia at −33 °C.[4,20] The debenzylated polymer was washed with methylene chloride, dialyzed with water, concentrated, and freeze-dried from water. Anal. Calcd for $(C_7H_{12}O_5)_n$: C, 47.72; H, 6.87. Found: C, 47.89; H, 7.08.

0024-9297/81/2214-0250$01.25/0

Table I
Polymerization of 1,6-Anhydro-2,4-di-O-benzyl-3-O-methyl-β-D-glucopyranose (2)[a]

expt	monomer, mmol	monomer, mol/L	catalyst, mol %	time, min	yield, %	$[\alpha]^{25}_D$,[b] deg	$[\eta]$[c]	$M_n \times 10^{-4}$ [d]	$M_w \times 10^{-4}$ [d]
101	2.8	1.12	3.5	60	81	134.2	0.48	4.3	13
103	5.3	0.88	1.9	60	86	133.9	1.15	7.9	23
105[e]	5.1	0.68	2.0	7	27[f]	123.1	0.65	6.4	15

[a] Catalyst precursor, p-chlorobenzenediazonium hexafluorophosphate, 0.1 mmol; solvent, methylene chloride; temperature, −60 °C. [b] Determined in chloroform (1 g/100 mL). [c] Determined in chloroform at 25 °C. [d] Estimated from the GPC retention time-molecular weight relationship derived for standard polystyrenes. [e] Copolymerization with 1,6-anhydro-2,3,4-tri-O-benzyl-β-D-glucopyranose; mole fraction of 2 in the feed, 0.50. [f] Mole fraction of 3 in the copolymer, 0.57 (determined from the ^{13}C NMR spectrum) and 0.56 (determined from the UV spectrum).

Partial Methylation of Natural Dextran. The dextran with an M_n of 1.6×10^4 and a reducing sugar content of 1.36% was obtained from Meito Sangyo Co. (lot. no. XM-5350). Sodium hydride oil suspension (55%, 0.025 mol) was washed with pentane and treated with 12 mL of dried Me_2SO at 50 °C for 4 h.[15] The resulting solution of methylsulfinyl carbanion was added to a solution of dextran (4.0 g, 0.025 mol of glucose units) in 50 mL of Me_2SO at 50 °C with vigorous stirring. Soon, the reaction mixture became gel, but it gradually turned to solution. The stirring was continued at room temperature for 2 h. Methyl iodide (0.048 mol) was added to the reaction mixture with external cooling. The solution was stirred at room temperature for 0.5 h. Then, 50 mL of water was added to the solution and the solvents were removed under reduced pressure at 70–80 °C. The residue was dissolved in water, dialyzed with water, and freeze-dried from water. The yield was 3.36 g (77%).

Results and Discussion

Polymerization of 1,6-Anhydro-2,4-di-O-benzyl-3-O-methyl-β-D-glucopyranose (2). The liquid monomer 2 was thoroughly dried over calcium hydride in a modified reaction vessel. The polymerization was carried out under high vacuum at −60 °C in anhydrous methylene chloride. The polymerization conditions and results are summarized in Table I. Experiments 101 and 103 are the homopolymerization of 2. The polymerization was rapid: the polymerization solution became gel in less than 10 min even with use of a low catalyst concentration of 1.9 mol % PF_5. After 1 h, homopolymers with high intrinsic viscosities were obtained in high yields. Number- and weight-average molecular weights (M_n and M_w, respectively) were estimated from the gel permeation chromatograms by using a calibration curve of standard polystyrenes. If the molecular size could be estimated from a viscosity-number average molecular weight relationship derived for corresponding 2,3,4-tri-O-benzyl-(1→6)-α-D-glucopyranan,[22] an intrinsic viscosity of 1.15 would correspond to an M_n value of about 4.5×10^5. The other M_n values in Table I are also smaller than those expected from the viscosities.

The high positive optical rotations of the homopolymers are suggestive of high proportions of α-anomer linkage. The high stereoregularity was proved by the ^{13}C NMR spectrum of 3, in which no observable β-anomeric carbon signal appeared. The assignment of the spectrum is described in the Experimental Section. A characteristic relationship proposed in the previous paper[7] also holds for the ^{13}C NMR chemical shifts of the present monomer 2 and the corresponding polymer 3.

Experiment 105 is the copolymerization of 2 with 1,6-anhydro-2,3,4-tri-O-benzyl-β-D-glucopyranose in a 0.50:0.50 molar composition. The copolymerization was terminated at 27% conversion. The mole fraction of 3 in the copolymer was determined by ^{13}C NMR and UV spectroscopies. The pyranose carbons in position 3 of both structural units appeared as two isolated signals at rather low magnetic fields. Their area ratio gave a value of 0.56 for the mole fraction of 3. An independent value of 0.57 was obtained on the basis that the UV absorbance at 258.8 nm of each homopolymer was proportional to the number of phenyl groups in a glucose unit.

Table II
Synthesis of 3-O-Methyl-(1→6)-α-D-glucopyranan (4)[a]

expt	starting polymer, g	Na, g	time, min	yield, %	$[\alpha]^{25}_D$,[b] deg	$[\eta]$[c]
101D	0.574	0.35	90	~100	191.7	0.24
103D	0.537	0.14	80	~100	200.3	0.63
105D	0.524	0.20	110	91	194.7	0.40

[a] Solvent, liquid ammonia (50 mL) and 3:1 (v/v) toluene-dimethoxyethane (20 mL). [b] Determined in Me_2SO (1 g/100 mL). [c] Determined in Me_2SO at 25 °C.

The higher copolymer composition indicates that the monomer 2 is more reactive than 1,6-anhydro-2,3,4-tri-O-benzyl-β-D-glucopyranose. The reactivity of 2 seems comparable to that of 3-O-crotylated monomer, 1,6-anhydro-2,4-di-O-benzyl-3-O-but-2-enyl-β-D-glucopyranose, which was studied in detail by Ito and Schuerch.[8] This result is consistent with the mechanistic model previously proposed.[3,8] Since each 3-O-methyl and 3-O-crotyl monomer has a smaller substituent on C-3, the monomer is more easily accessible to the propagating cation and the conformational change from the chairlike to the boatlike form may require less energy.

Synthesis of 3-O-Methyl-(1→6)-α-D-glucopyranan (4). Debenzylation was carried out with sodium in liquid ammonia, using a mixed solvent of toluene and dimethoxyethane. The product was isolated by dialysis, freeze-drying from water, and further drying under reduced pressure at room temperature. As listed in the Experimental Section, a satisfactory elemental analysis was obtained for a polymer sample which was thoroughly dried in vacuo at 50 °C for 40 days. It took so long to dry the polymer that the yields and physical properties of the polysaccharides are reported without correction for retained water (Table II).

The debenzylated polymers were soluble in water and Me_2SO. The intrinsic viscosity of polymer 103D determined in Me_2SO was 0.63. This value is among the highest (0.64) thus far reported for synthetic dextrans in water.[21] The specific rotations of the homopolymers were high and similar to those of stereoregular (1→6)-α-D-glucopyranans.[4,8,20-22]

The completion of debenzylation was ascertained by IR, ^1H NMR, and ^{13}C NMR spectra, in which no absorptions due to benzyl groups were detected. Figures 1 and 2 show the ^{13}C NMR spectra of the homopolymer of 3-O-methyl-(1→6)-α-D-glucopyranan and the copolymer consisting of 3-O-methyl and unsubstituted units, respectively. The absence of a β-anomeric carbon signal proved that complete debenzylation proceeded without anomeric

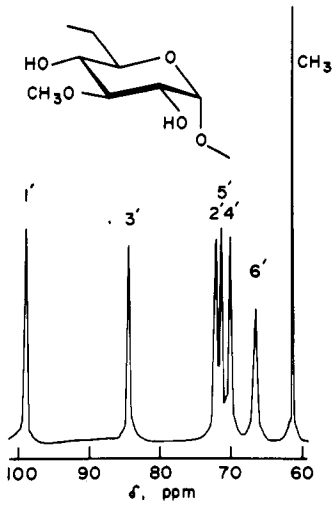


Figure 1. 25-MHz ^{13}C NMR spectrum of 3-*O*-methyl-(1→6)-α-D-glucopyranan (4) in D_2O, concentration 11%.

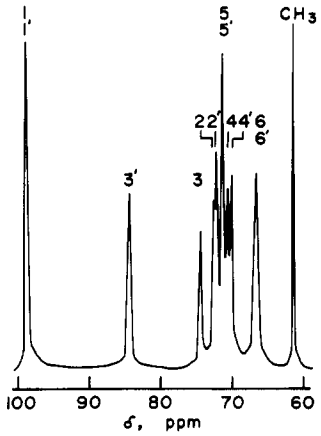


Figure 2. 25-MHz ^{13}C NMR spectrum of the debenzylated copolymer (no. 105D) consisting of 3-*O*-methyl- and unsubstituted (1→6)-α-D-glucopyranose residues in D_2O, concentration 10%. Primes designate the pyranose carbons of the 3-O-methylated unit.

Table III
^{13}C NMR Chemical Shifts (δ) of (1→6)-α-D-Glucopyranan, 4, and Their Copolymer in D_2O

polymer	C-1	C-2	C-3	C-4	C-5	C-6	CH_3
(1→6)-α-D-glucopyranan	98.9	72.5	74.6	70.7	71.3	66.7	
4	98.9	72.2	84.5	70.1	71.5	66.6	61.6
		72.5	74.5	70.7			
copolymer	98.9				71.4	66.7	61.5
		72.2	84.5	70.1			

change. All peaks of the copolymer were superimposable on peaks of one or the other homopolymers.[4,8,23,24] These spectra could be assigned by assuming the 3-O-methylation had little effect on the chemical shifts of the C-1, C-5, and C-6 signals but promoted a strong downfield shift of 10 ppm for the directly attached C-3 and a weak upfield shift of 0.3–0.6 ppm for the adjacent C-2 and C-4.[24] The assignments are given in the figures; primes are used to distinguish the 3-O-methylated unit from the unsubstituted one. Table III summarizes the chemical shifts of each homopolymer and their copolymer. It is worth noting that α-(1→3) branching of dextrans caused little observable shift of C-2 and C-4 signals, in contrast to these signals of the 3-O-methylated dextran. These observations are suggestive of the validity of the present assignment, although there is a different view as to the assignment of C-4 and C-5.[23] In addition, the mole fraction of the 3-O-methylated unit in the copolymer could be calculated from the intensity of the peaks 3′ and 3. The obtained value of 0.59 is in good agreement with those for the benzylated copolymer.

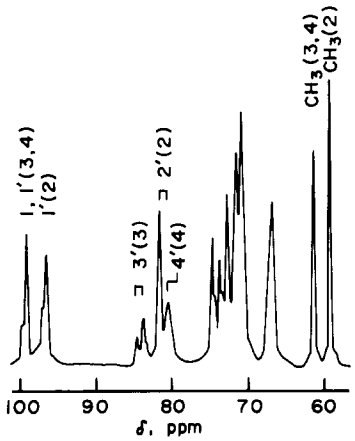


Figure 3. 25-MHz ^{13}C NMR spectrum of partially methylated dextran in D_2O, concentration 13%. The numbers in parentheses designate the methylated position.

Partial Methylation of Natural Dextran. Complete permethylation of complex polysaccharides, followed by hydrolysis, has proved invaluable for their structural analysis.[15,25] Another line of research is partial methylation to determine selectivity of hydroxyl groups in carbohydrates.[26,27] In the present paper, partial methylation of a natural dextran was attempted to demonstrate the difficulty in controlling the methylation regioselectively and to utilize the product as a reference sample of the selectively methylated polysaccharide. Treatment of dextran with equimolecular amount of methylsulfinyl carbanion in Me_2SO and subsequently with methyl iodide gave a product having a degree of substitution (DS) of about 1.0. Figure 3 gives its well-resolved ^{13}C NMR spectrum. The assignments were made on the basis of comparisons with 4, permethylated dextran,[28] and monomethylglucoses.[24] The location and content of the substituent groups were determined as follows. As an approximation, branching of the dextran could be neglected in the calculation.

The 2-*O*-methyl signal at δ 59.3 was found at higher field than the overlapping signals of the 3-*O*- and 4-*O*-methyls at δ 61.3. The relative intensity was 55 (2-*O*-methyl):45 (3-*O*- and 4-*O*-methyls). The position of highest substitution is at O-2. Resonances of the pyranose carbons of O-methylated positions exhibited large downfield shifts to the region between δ 80.6 and 84.7. The relative intensity of C-3 to C-2 and C-4 was 25:75. On the other hand, there appeared two isolated C-1 signals at δ 96.4 and 99.0. The former signal was assignable to the 2-O-methylated unit but the latter signal was larger, suggesting that there still remained an unsubstituted glucose unit which should have the chemical shift corresponding to the latter signal. The presence of disubstituted units was also suggested by the splitting of the above-mentioned C-3 resonance into two signals at δ 84.7 and 83.7. The lower field signal corresponded closely in chemical shift to that of C-3 in the selectively 3-O-methylated dextran (4), and the higher field signal was assignable to C-3 of 2,3-di-O- and 3,4-di-O-methylated units. These findings have made possible estimation of the content of disubstituted glucose units and unsubstituted ones.

The results are summarized in Table IV, showing that the reactivities of the hydroxyl groups of dextran are 2-OH > 3-OH ≥ 4-OH. It is also shown that a rather large amount of unsubstituted and disubstituted glucose units

Table IV
Partial Methylation of Natural Dextran

	substd hydroxyl group, %			substd glucose unit, %		
DS	2-OH	3-OH	4-OH	unsubstd	monosubstd	disubstd
~1.0	55	25	20	~20	~60	~20

is present in the polymer sequence. The substitution pattern of partially methylated dextran is slightly different from that determined by paper and gas chromatography of its hydrolysate,[27] but follows the same pattern reported for partial O-acetylation of dextran.[29]

References and Notes

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Simulation of Reactions with Lignin by Computer (SIMREL). 6. Interpretation of Primary Experimental Analysis Data ("Analysis Program")†

W. G. Glasser,* H. R. Glasser, and N. Morohoshi

Department of Forest Products, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061. *Received June 18, 1980*

ABSTRACT: A computer program is described which converts primary lignin analysis data obtained from multiple experimental procedures into information pertaining to the composition of unifying phenylpropane (C_9) lignin substructures. Quantitative information on average phenylpropane units concerns interunit linkages and functionality. The input data converted by the "analysis program" include elemental composition, methoxy, total hydroxy, and carbonyl groups, impurities in the form of ash and hydrolyzable sugars, and gas and gel permeation chromatography data obtained with the permanganate oxidation product mixtures of unaltered and oxidatively depolymerized lignin preparations. Repeatability of all primary analysis data is assessed and evaluated in relation to the determination of specific structural features of the average C_9 unit, in terms of both functionality and interunit linkages.

Introduction

The analysis of polymeric lignin preparations is faced with the interpretation of a multitude of observations from analytical laboratory experiments in terms of a common structure of the statistical polyphenolic polymer. Such correlations between chemical structures and analytical behaviors are most suitably performed by computer techniques. Prior papers in this series have reported on the development of a linear computer program that simulates the formation of lignin on a structural level from a mixture of precursors.[1,2] In later papers, the predictive capabilities of this model were tested with regard to analytical features.[3,4] With this technique, several lignin model structures were obtained which satisfied the input parameters relating to polymerization mechanisms and which approximated closely prominent analytical data obtained experimentally.[5] In general, the distinction between "good models" and "bad models" must be made on the grounds that good models satisfactorily reflect primary analytical observations. Given the development of a computer program which permits the formulation of lignin's structure on the basis of several analytical features, the acquisition

† Part of the results have been presented in a paper given at the Spring Annual Meeting of the American Chemical Society, held in Honolulu, Hawaii, April 2–6, 1979. Previous paper: Glasser, W. G.; Glasser, H. R.; Nimz, H. H. H. *Macromolecules* **1976**, *9*, 866–7. The authors are Professor of Wood Chemistry, Computer Programmer, and Associate Professor of Wood Chemical Technology (on leave from Tokyo University of Agriculture and Technology, Fuchu, Japan), respectively.

0024-9297/81/2214-0253$01.25/0