Poly(1,4-anhydro-D-glucitols) by Regioselective Reductions of Amylose or Cellulose[1]

All of the chemical transformations of the 1,4-anhydro-D-glucose polymers amylose (**1a**) and cellulose (**1b**), which involve the acetal groupings, result in cleavages of the exocyclic acetal linkages (glycosidic bonds) so that degradations occur.[2,3] Well-known examples of such degradations are the acid-catalyzed or enzymic hydrolyses and the acid-catalyzed acetolyses. Nondegrading transformations involving the acetal groupings obviously necessitate that only the endocyclic carbon–oxygen bonds are cleaved. Hitherto no transformations at the acetalic centers of polysaccharides with retention of the polymer backbone have been described.

During our investigations on the reductions of *O*-ethylboron protected glycosides with alkyldiboranes(6) in the presence of catalysts such as 9-[(methylsulfonyl)oxy]-9-borabicyclo[3.3.1]nonane (MSBBN),[4a] it was found that endocyclic C–O hydroborations frequently occurred. Thus, for example, 4-*O*-(1-deoxy-D-glucit-1-yl)-D-glucitol could be prepared from both maltose and cellobiose. Below we report on the high-yield conversions of amylose (**1a**) and cellulose (**1b**) to the novel poly(1,4-anhydro-D-glucitols) (**4a** and **4b**).

In order to achieve regioselective acetal hydroborations of amylose (**1a**) and cellulose (**1b**), it is necessary to convert them to their per-*O*-diethylboryl derivatives **2a** and **2b** by reaction with activated triethylborane.[5] **2a** can also conveniently be obtained from starch by the efficient *O*-diethylborylation separation procedure giving hydrocarbon-soluble **2a** and the insoluble amylopectin component which can easily be filtered off.[5,6] In contrast to the heptane soluble **2a**, the higher molecular weight **2b** is insoluble in all the common organic solvents. Quantitative total reductions of both **2a** and **2b** are then realized by using ethyldiboranes(6) in the presence of catalytic amounts of MSBBN at 120 °C in toluene.[4b] Complete reduction of **2a** occurs in 4 h in the presence of only 0.1 equiv of catalyst, whereas 14 h and ≈0.5 equiv of MSBBN are required for the total reduction of **2b**.

The course of the reductions was easily followed as thick gels were formed, which then gradually gave easily stirred mixtures as the reactions neared completion. After they were concentrated in vacuo, poly[2,3:5,6–bis-*O*-(ethylboranediyl)-1,4-anhydro-D-glucitols] **3a** and **3b**, respectively, were obtained as amorphous, colorless, solids in quantitative yields (Scheme I).

3a and **3b** have identical ^{13}C NMR spectra (Figure 1). The key signals are the low-field doublet for C-4 at 82.2 ppm and the triplets for C-1 and C-6 at 75.3 and 67.0 ppm. No signals due to end groups were observed in the ^{13}C NMR spectra of **3a** or **3b**, indicating that only minor amounts of low molecular weight degradation products could have been formed in this remarkably clean reaction.

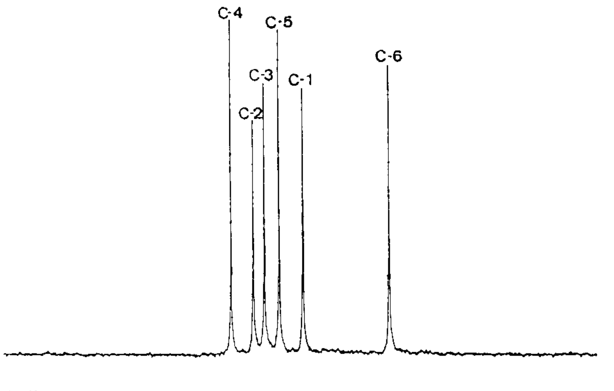
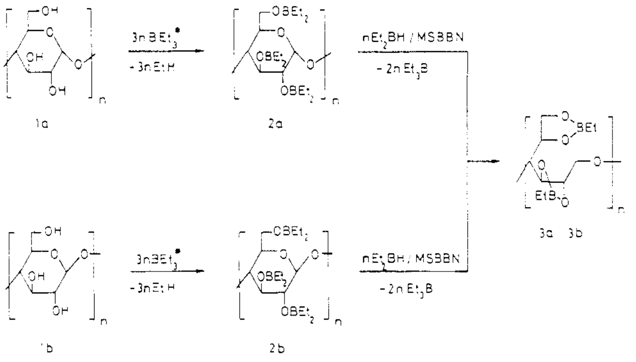
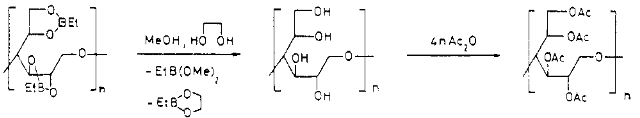


Figure 1. 75.5-MHz ^{13}C NMR spectrum of **3b** measured in C_6D_6 (H_5C_2B signals omitted, assignments for C-2, C-3, and C-5 may be interchanged).

Scheme I
Synthesis of Poly[2,3:5,6-bis-*O*-(ethylboranediyl)-1,4-anhydro-D-glucitols] (3a,b) from Amylose (1a) and Cellulose (1b)



Scheme II
Deboronation of 3 and O-Acetylation to Poly(1,4-anhydro-D-glucitols) (4) and Their O-Acetates 5



3a and **3b** were easily deboronated by repeated treatments with methanol/ethylene glycol giving the glassy solid poly(1,4-anhydro-D-glucitols) **4a** and **4b** in quantitative yields. A base such as pyridine, or preferably triethylamine, should be added to the ethylene glycol to ensure nonacidic conditions. The bath temperature must not exceed ≈80 °C when pyridine is the chosen base, as

Table I
^{13}C NMR Chemical Shifts (δ, ppm), Melting Points, and Optical Rotations of 3a–5a and 3b–5b

compd	C-1	C-2	C-3	C-4	C-5	C-6	other signals	mp, °C	$[\alpha]^{20}_D$ (*c*, solvent)
3a[a]	75.3	77.5[c]	79.0[c]	82.2	80.0[c]	67.0	2.9, 3.1 (BCH_2)	~160	-18.4° (0.5, $CHCl_3$)
3b[a]							7.9, 8.1 (BCH_2CH_3)	~180	-24.4° (1, $CHCl_3$)
4a[b]	74.0	71.8[c]	70.7[c]	82.2	70.3[c]	62.5		115–120	19.2° (0.5, DMSO)[d]
4b[b]								135–140	6.8° (0.5, DMSO)
5a[a]	71.0	71.5[c]	70.8[c]	78.4	70.8[c]	62.9	170.4, 170.2, 170.1, 169.9 ($COCH_3$)	~100	50° (1, $CHCl_3$)
5b[c]							20.8, 20.76, 20.6, 20.4 ($COCH_3$)	~92	28.8° (0.7, $CHCl_3$)

[a] In C_6D_6. [b] In DMSO-d_6. [c] Assignments may be interchanged. [d] **4a** contained ~10 wt% ethylene glycol.

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slow degradation to 1,4-anhydro-D-glucitol occurs above this temperature.

After per-O-acetylating **4a** and **4b** with acetic anhydride in pyridine, the poly(2,3,5,6-tetra-*O*-acetyl-1,4-anhydro-D-glucitols) **5a** and **5b** were isolated as foamy solids (Scheme II). Crude **5a** and **5b** have number-average molecular weights of 3800 and 4600 ($\overline{\mathrm{DP}}_n$ = 11.4 and 13.9., respectively), as determined by vapor pressure osmometry in pyridine at 60 °C (Table I).

Although these molecular weights are relatively low, it should be noted that the reduction, deboronation, and acetylation steps were all realized in essentially quantitative yields and that no purifications or separations were undertaken. The $\bar{M}_n$ of crude **5a** and **5b** indicate that >90% regioselectivity in favor of endocyclic C–O hydroborations of **2a** and **2b** had occurred.

Hence, for the first time, transformations at the acetalic centers of polysaccharides have been realized with (at least) partial retentions of the polymer backbone. Work is in progress to apply this methodology to other polysaccharides and also to achieve partial reductions.

References and Notes

(1) Organoboron Polysaccharides 2. For part 1 see: A preliminary account of this work was presented at the XIII International Carbohydrate Symposium, Cornell University, Ithaca, NY, 1986; Abstr p 28.

(2) *Methods in Carbohydrate Chemistry*; Whistler, R. L., Ed.; Academic Press: New York, 1963; Vol. III, Section IV.

(3) *Methods in Carbohydrate Chemistry*; Whistler, R. L., Ed.; Academic Press: New York, 1964; Vol. IV, Section V.

(4) (a) Köster, R.; Penades-Ullate, S.; Dahlhoff, W. V. *Angew. Chem.* **1985**, *97*, 508; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 519. (b) Typical procedure. Poly[2,3:5,6-bis-*O*-(ethylboranediyl)-1,4-anhydro-D-glucitol] (**3a**) from per-*O*-(diethylboryl)amylose (**2a**): MSBBN (0.4 g, 1.85 mmol) and toluene (20 mL) were added to **2a** (5.13 g, 14 mmol) followed by the dropwise addition of ethyldiboranes(6) (5.1 g with 11.5‰ H$^-$, ≈58.6 mmol of >BH). The stirred mixture was heated to 120 °C (bath temp) for 4 h and then all the volatile components were removed in vacuo (10^{-3} Torr, bath temp 60–100 °C) to give colorless, glasslike **3a** (3.3 g, 98%) with mp ≈ 160 °C, $[\alpha]^{20}_{\mathrm{D}}$ −18.4° (*c* 0.5, CHCl$_3$). Similarly, **2b** (4.64 g, 12.7 mmol) gave **3b** (3.05 g, 100%) on heating for 14 h with ethyldiboranes(6) (2.88 g with 11.5‰ H$^-$, ≈33.1 mmol) in the presence of MSBBN (1.22 g, 5.65 mmol).

(5) Köster, R.; Amen, K.-L.; Dahlhoff, W. V. *Justus Liebigs Ann. Chem.* **1975**, 752.

(6) Köster, R.; Dahlhoff, W. V. *ACS Symp. Ser. 1977, No.* 39, 1.

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