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# PREPARATION OF UNSUBSTITUTED 6-ALDEHYDOCELLULOSES BY PHOTOLYSIS OF 6-AZIDO-6-DEOXYCELLULOSES*

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## ABSTRACT

A general method for the selective oxidation of celluloses to unsubstituted 6-aldehydocelluloses (**4**) and 6-carboxycelluloses is described. 6-Chloro-6-deoxycelluloses (**1**), prepared by treating celluloses with methanesulfonyl chloride in *N*,*N*-dimethylformamide, were converted into the corresponding 6-azido-6-deoxy derivatives (**3**) which, upon photolysis and mild hydrolysis, yielded **4**. The degree of substitution by aldehyde is determined by the proportion of chlorine introduced in the preparation of **1**. The 6-aldehydocelluloses were characterized by reduction to celluloses (**6**), by oxidation to 6-carboxycelluloses (**7**), by copper number, and by a deuteration–mass spectrometry method. Viscometry was used to monitor the effect of the chemical transformations upon the degree of polymerization of the cellulose derivatives.

## INTRODUCTION

Oxidation of some of the primary hydroxyl groups in cellulose to aldehyde groups is thought to be one of several possible reactions that initiate the oxidative degradation of cellulosic material during aging, bleaching, and other technical processes[1,2]. A useful contribution to cellulose chemistry and technology would be the preparation, and studies on the stability, of celluloses selectively oxidized at C-6 to the 6-aldehydo derivatives, but otherwise unsubstituted. Strictly, such products are β-D-(1→4)-linked copolymers of D-*gluco*-hexodialdo-1,5-pyranose and D-glucose residues, but the trivial name 6-aldehydocellulose is used here. In one of our laboratories, as shown with methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-α-D-glucopyranoside, photolysis of a primary azide, with subsequent, mild hydrolysis of the resultant product, provides an excellent route to the corresponding ω-aldehyde[3]. The reaction

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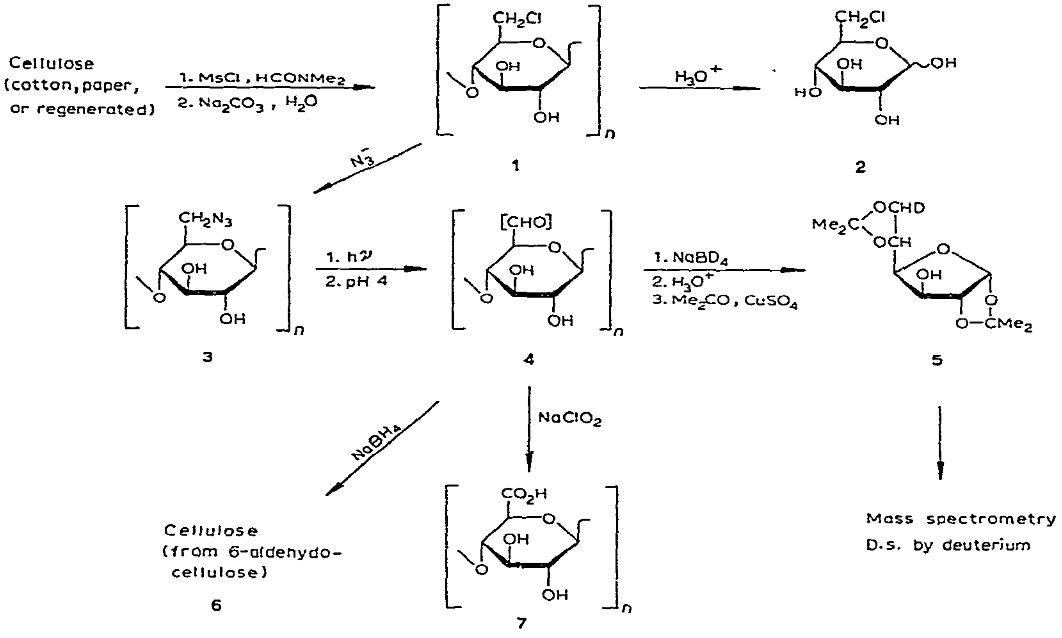
is effective with unprotected as well as with acetylated[4] glycosides, and has been applied for preparation of 6-aldehydo analogs of starch[5] and cellulose 2,3-diacetate[6], and with sugar derivatives having configurations other than D-*gluco*[7]. The reaction is also effective when aromatic aglycons are present[4], and has been exploited for the preparation of 5'-aldehyde analogs of nucleosides[8]. The present article describes extension of the method of photolysis of azides to the preparation of the 6-aldehydo derivatives of cellulose in such fibrous forms as cotton linters and filter paper, and to regenerated forms of cellulose. Because of the nature of cellulose, and the lability of 6-aldehydo derivatives to β-elimination under basic conditions[4,9], these 2,3-unsubstituted analogs cannot be prepared from 6-aldehydocellulose 2,3-diacetate[6].

## RESULTS AND DISCUSSION

*Chlorination of celluloses at C-6.* — A prerequisite for specific oxidation at a primary hydroxymethyl group by the azide photolysis method is the selective introduction of a suitable leaving-group at this primary position. For preparing a cellulose derivative having a leaving group substituted specifically at C-6, no method has been recorded that does not require the protection of the secondary hydroxyl groups at some point in the synthesis[10]. In previous work on the preparation of 6-aldehydo derivatives of D-glucopyranosides[3,4], methanesulfonyl chloride in *N*,*N*-dimethylformamide, a reagent introduced by Long and co-workers[11,12], was successfully used for introducing chlorine (a good leaving-group) at C-6, without the need for prior protection of the secondary hydroxyl groups. We now describe the preparation of 6-chloro-6-deoxycelluloses (**1**) by use of this reagent, and the successful use of **1** as an intermediate in the preparation of 6-aldehydocelluloses (**4**). Other workers have prepared nonspecifically chlorinated chlorodeoxycelluloses[10] by use of thionyl chloride dissolved in pyridine[13], chloroform or carbon tetrachloride[14], or *N*,*N*-dimethylformamide[15,16]. For the chlorodeoxycelluloses prepared in *N*,*N*-dimethylformamide, 60–75% of the chlorine content was reported to be displaceable by nucleophiles[15,16].

In the transformation of cellulose into the 6-aldehydo derivative, the reaction conditions were optimized to minimize side-reactions, color formation, and depolymerization. Changes in the degree of polymerization (d.p.) of the cellulose during modification was monitored by viscometry[17] in cadmium ethylenediamine hydroxide (Cadoxen), a cellulose solvent that does not permit occurrence of oxidative depolymerization.

Scheme 1 shows the overall reaction-sequence used for the synthesis and characterization of the 6-aldehydocelluloses (**4**). The first reaction investigated was the chlorination of cotton-linters cellulose. Cotton linters were presoaked in *N*,*N*-dimethylformamide for several hours at 80°, and then treated with an excess of a 10% solution of methanesulfonyl chloride in *N*,*N*-dimethylformamide for various lengths of time and at several temperatures. The results from these experiments, expressed in terms of chlorine incorporation, depolymerization, and color formation are given in



Scheme 1

Table I. The data indicate that the incorporation of chlorine varies according to the temperature and the time of reaction, and that there is gradual depolymerization and color formation at extended times and high temperatures. Similar experiments with filter-paper cellulose showed that chlorine could be introduced without disintegration of the paper sheet. Traces of sulfur were found, and the proportion thereof increased, with concomitant degradation, at the higher temperatures and extended reaction times. Reaction appears to take place primarily on the surface and in the amorphous regions of the cellulose fiber. For some reason not yet understood, some of these products were not completely soluble in Cadoxen; repeat experiments gave reproducible results. The slight increase in d.p. at the beginning of the reaction in certain examples could indicate that some cross-linking had occurred.

To obtain products having higher contents of chlorine, the chlorination of regenerated celluloses was explored. The results from these experiments are given in Table II. Several methods for regenerating the cellulose were used, in an attempt to obtain cellulose in a form the most accessible to chemical reagents. Celluloses that had been precipitated from cupriethylenediamine solutions by stirring into water, and then swollen in *N*,*N*-dimethylformamide, were more reactive than fibrous samples. However, the maximum degree of substitution (d.s.) by chlorine that was obtained with these samples was still only ~0.5. Freeze-drying of the precipitated cellulose before reaction appeared to decrease the accessibility somewhat. A more accessible product was obtained by precipitating the cellulose directly into *N*,*N*-dimethylfor-

TABLE I

EFFECT OF REACTION TIME AND TEMPERATURE ON THE PREPARATION OF FIBROUS 6-CHLORO-6-DEOXYCELLULOSES[a]

| *Cellulose type* | *Reaction temp. (degrees)* | *Reaction time (hours)* | *Color of product* | *Chlorine (%)* | *D.s.* | *D.p.* | *%S* |
|---|---|---|---|---|---|---|---|
| Cotton linters A | | | | | | 1,584 | |
| | 62 | 5 | White | 0.65 | 0.03 | 1,853 | |
| | | 16 | White | 1.68 | 0.07 | 1,350 | 0.72 |
| | | 48 | White | 2.38 | 0.11 | (200)[b] | 1.63 |
| | 80 | 5 | White | 1.70 | 0.07 | (232)[b] | |
| | | 24 | White | 2.70 | 0.12 | (985)[b] | |
| | | 48 | Light tan | 3.41 | 0.15 | (130)[b] | 1.77 |
| | 97 | 1.5 | White | 1.45 | 0.06 | 1,622 | |
| | | 4 | White | 1.92 | 0.085 | 1,339 | |
| | | 8 | Light tan | 2.42 | 0.11 | 916 | |
| | | 24 | Tan | 4.40 | 0.20 | 286 | |
| | | 48 | Brown | 3.70 | 0.17 | 280 | |
| | | 72 | Dark brown | 2.60 | 0.12 | 270 | 2.95 |
| Cotton linters B | | | | | | 4,098 | |
| | 75 | 48 | White | 3.44 | 0.15 | (313)[b] | 1.63 |
| Filter paper | | | | | | 2,657 | |
| | 60 | 16 | White | 1.30 | 0.06 | 2,478 | 0.39 |
| | 90 | 2 | White | 1.96 | 0.09 | 1,378 | |

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[a] Cellulose (1–2 g) per 100 ml of 10% solution of methanesulfonyl chloride in *N*,*N*-dimethylformamide (the yields were 90–100%). [b] Product not completely soluble in Cadoxen.

mamide. Under the most favorable reaction-conditions, a d.s. of 0.83 was achieved with such a sample. Celluloses regenerated from 82% phosphoric acid were found to be less reactive than samples regenerated from cupriethylenediamine, and generally gave products of poorer quality. Cellophane could be chlorinated without losing its general physical characteristics.

Chlorination at 90° for shorter times was found to be more efficient than reaction at 60° for longer periods. Some bound sulfur was again detected in the products. From the limited data available, it appears that, as expected, the regenerated celluloses were depolymerized more rapidly than the fibrous samples. Products having a chlorine content greater than ~8% were insoluble in Cadoxen, and some samples having chlorine contents of 6–7% were only partially soluble.

The i.r. spectra of the chlorinated celluloses (both fibrous and regenerated) isolated directly from the reaction mixtures showed ester-group absorption at 1730 cm$^{-1}$. By analogy with the products of chlorination of glycosides[11,12] obtained with methanesulfonyl chloride in *N*,*N*-dimethylformamide, and by the thionyl chloride–*N*,*N*-dimethylformamide method of preparing chlorodeoxycellulose[18], this absorption was assigned to the formyl group. The formyl groups were conveniently saponified by soaking the products in aqueous sodium carbonate at room

TABLE II

EFFECT OF REACTION TIME AND TEMPERATURE ON THE PREPARATION OF 6-CHLORO-6-DEOXYCELLULOSES FROM REGENERATED CELLULOSES[a]

| *Cellulose type* | *Type of regeneration*[b] | *Reaction temp. (degrees)* | *Reaction time (hours)* | *Color of product* | *Chlorine (%)* | *D.s.* | *D.p.*[c] | *%S* |
|---|---|---|---|---|---|---|---|---|
| Cotton linters A | Precipitated | | | | | | 1,400 | |
| | from CED into | 62 | 5 | White | 2.3 | 0.10 | 679 | 0.62 |
| | water | | 16 | White | 6.5 | 0.30 | 381 | |
| | Freeze-dried | 62 | 48 | Tan | 11.4 | 0.55 | NS | 2.27 |
| | sample | 90 | 4 | White | 8.04 | 0.40 | NS | 1.83 |
| | Precipitated | 62 | 2 | White | 2.55 | | 1,267 | 2.65 |
| | from CED into | | 20 | White | 14.0 | 0.67 | NS | 0.48 |
| | $HCONMe_2$ | 90 | 1 | White | 12.82 | 0.63 | NS | 1.82 |
| | | | 3 | White | 16.46 | 0.83 | NS | 1.23 |
| | Precipitated | | | | | | 700 | |
| | from 82% $H_3PO_4$ | 62 | 20 | White | 13.7 | 0.67 | NS | 3.23 |
| | into $HCONMe_2$ | 95 | 4 | White | 13.7 | 0.67 | NS | 1.89 |
| | | | 21 | Tan | 14.9 | 0.74 | NS | 6.14 |
| Cotton linters B | Precipitated | | | | | | 4,000 | |
| | from CED into | 62 | 6.5 | White | 4.2 | 0.19 | (566)[d] | |
| | water | | 16.5 | White | 7.8 | 0.37 | NS | |
| | | 85 | 2 | White | 6.05 | 0.28 | (120)[d] | |
| Cellophane | | | | | | | 320 | |
| | | 62 | 16 | Colorless (more brittle) | 3.5 | 0.15 | 183 | |

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[a] Cellulose (1 g) per 100 ml of *N*,*N*-dimethylformamide and 10 ml of methanesulfonyl chloride (yield 80–90%). [b] CED, cupriethylenediamine. [c] NS, not soluble in Cadoxen. [d] Not completely soluble in Cadoxen.

TABLE III

EXTENT OF DISPLACEMENT OF CHLORINE BY AZIDE IN THE PREPARATION OF 6-AZIDO-6-DEOXYCELLULOSES (3)

| *Cellulose type* | *Solvent* | *Time (hours)* | *Temp. (degrees)* | *Yield (%)* | *Color of product*[a] | *% of Chlorine* | | *%N* | *D.s.* | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | *Before* | *After* | | *By Cl before* | *By $N_3$ after* |
| Cotton linters | $HCONMe_2$ | 72 | 105 | ~95 | W | 1.68 | 0.10 | 1.16 | 0.07 | 0.05 |
| Filter paper | $H_2O$ | 72 | 100 | ~100 | W | 1.30 | 0.10 | 1.19 | 0.06 | 0.05 |
| | $Me_2SO$ | 12 | 100 | ~100 | W | 1.96 | 0.18 | | | |
| Cellophane | $H_2O$ | 72 | 100 | ~100 | W | 3.50 | 0.28 | | | |
| Regenerated celluloses | $HCONMe_2$[b] | 72 | 105 | 80 | W | 3.10 | 0.21 | 3.31 | 0.14 | 0.13 |
| | $HCONMe_2$[b] | 72 | 103 | 89 | W | 2.80 | 0.09 | 3.28 | 0.12 | 0.13 |
| | $HCONMe_2$[b] | 96 | 110 | 62 | T | 7.80 | 0.44 | 6.63 | 0.37 | 0.27 |
| | $HCONMe_2$[b] | 96 | 105 | 70 | LT | 13.6 | 0.49 | 10.72 | 0.67 | 0.44 |
| | $Me_2SO$ | 48 | 100 | 80 | W | 16.5 | 1.02 | | | |

[a] Color of product: LT, light tan; T, tan; W, white. [b] Reactions performed by method *B*; other reactions, by method *A*.

temperature. Dilute ammonium hydroxide was also used, in some examples, with regenerated celluloses.

Hydrolysis of the 6-chloro-6-deoxycelluloses (**1**) in 72% sulfuric acid, followed by analysis by t.l.c., proved convenient for qualitatively monitoring the d.s. level; the presence of 6-chloro-6-deoxy-D-glucose (**2**) was shown by comparison with an authentic sample. Hydrolysis of **1** on a larger scale permitted isolation of crystalline **2**, further characterized as the known 1,2,3,4-tetra-*O*-acetyl-6-chloro-6-deoxy-α-D-glucopyranose[12]. T.l.c. analysis also revealed in the hydrolyzates of some samples of **1** traces of other components having $R_F$ values greater, and less, than that of **2**. These components appeared in samples prepared under the more-vigorous reaction-conditions, and became progressively more significant as the degradation of the cellulose derivative increased.

*6-Azido-6-deoxycelluloses* (**3**). — The data in Table III show that the 6-chloro-6-deoxycelluloses (**1**) can be converted heterogeneously into the corresponding 6-azido-6-deoxycelluloses (**3**) by treatment with solutions of sodium azide in any one of several solvents. Initially, *N*,*N*-dimethylformamide was explored as a solvent for this reaction. Although most of the chlorine was replaced and there was little color formation, some depolymerization was detected. Chlorinated filter-paper underwent disintegration when *N*,*N*-dimethylformamide was used. To obtain more information on the displacement reaction, a sample of **1** from regenerated cellulose was treated with an excess of sodium azide at 100° in three different solvents, namely, *N*,*N*-dimethylformamide, water, and methyl sulfoxide. The results in Table IV indicate that the latter two solvents cause less depolymerization, and that methyl sulfoxide is the most efficient. Water or methyl sulfoxide can be used for the reaction with chlorinated filter-paper without causing disintegration of the paper. The i.r. spectra of the 6-azido-6-deoxycelluloses (**3**) showed characteristic absorption at 2070 $cm^{-1}$ for the azido group. The intensity of this band was used for qualitative estimation of azide incorporation, and nitrogen analysis provided a quantitative measure of the d.s. by azide. These d.s. values were observed to correspond closely to the d.s. values of the corre-

TABLE IV

COMPARISON OF SOLVENTS FOR THE AZIDE-DISPLACEMENT REACTION CONDUCTED FOR 72 HOURS AT 100°

| *Solvent*[a] | *Chlorine remaining*[b] (%) | *D.p.*$_w$ | *Color of product* |
|---|---|---|---|
| $HCONMe_2$ | 0.9 | 153 | Tan |
| $H_2O$ | 1.2 | 448 | White |
| $Me_2SO$ | 0.27 | 463 | White |

[a] Reactions performed by method *A*. [b] Starting material was 6-chloro-6-deoxycellulose from regenerated cellulose: Cl, 4.2%; D.p.$_w$ 566.

TABLE V

DATA FOR CHARACTERIZATION OF 6-ALDEHYDOCELLULOSES (4) AND THE CORRESPONDING REDUCED (6) AND OXIDIZED (7) PRODUCTS

| *Cellulose type* | *6-Aldehydocellulose* | | | | *Reduced product* (6) | | *Oxidized product* (7) | | *Uronic acid* (%) |
|---|---|---|---|---|---|---|---|---|---|
| | *Yield* (%) | *Nitrogen* (%) | *Copper no.*[a] | *D.s. by deuteration method* | *Yield* (%) | *Copper no.*[a] | *Yield* (%) | *Copper no.*[a] | |
| Cotton linters | ~100 | — | 14.0 | 0.030 | 100 | 0.4 | ~100 | 1.6 | 1.73 |
| Filter paper | ~100 | 0.39 | 13.4 | 0.028[b] | 100[b] | 0.2 | ~100[b] | 0.7 | 1.35 |
| Cellophane | ~100 | — | 46.4 | 0.091[b] | 100[b] | 3.5 | ~100[b] | 6.5 | 10.5 |
| Regenerated | 90 | 0.60 | 36.4 | 0.05 | 90 | 2.2 | 82 | 3.3 | 5.88 |
| | 80 | — | 43.8 | 0.08 | 90 | — | 90 | — | — |
| | 70 | 0.10 | 46.9 | 0.08 | 70 | 1.5 | 90 | 4.3 | 11.5 |
| | 63 | 0.12 | 155 | 0.38 | 65 | 14 | 65 | 10.6 | 48.9 |
| | | | | 0.45[b] | 60[b] | 9.9 | | | |

[a] Copper numbers are expressed as g of copper per 100 g of sample. Reference copper numbers[22]: cellulose (0–0.1); methyl β-D-glucopyranoside (~5); methyl 6-*aldehydo*-α-D-*gluco*-hexodialdo-1,5-pyranoside (~150); D-glucose (~200). [b] Reactions conducted by method *B*. All other reactions were performed by method *A*.

sponding 6-chloro-6-deoxycellulose (1) precursors. All of the azide-displacement reactions were heterogeneous, except for the reaction in methyl sulfoxide with **1** having a d.s. of 0.83; in this example, the reactant dissolved during the course of the reaction. An attempt to prepare **3** directly from a regenerated sample of **1** that still contained formyl groups resulted in rapid development of color. Attempts to hydrolyze samples of **3** with 72% sulfuric acid resulted in much color-formation, and no 6-azido-6-deoxy-D-glucose was detected by t.l.c. The azide group has been reported to be unstable in strong acid[19].

*6-Aldehydocelluloses* (**4**). — In previous work, the azido derivatives of sugars have been photolyzed in solution[3–8]. Because of the solubility characteristics of the cellulose analogs (**3**), photolysis under heterogeneous conditions was explored as a means of generating the aldehydo group. Two types of photochemical reactor were used (see Experimental section for details), and several techniques were investigated for the different physical forms of the 6-azido derivative **3**. The filter-paper and cellophane forms of **3** were photolyzed directly, either by wrapping them around the window of the photolysis lamp or by suspending them in polyethylene bags inside the photolysis apparatus. Regenerated forms of **3** were photolyzed as suspensions in 2-methoxyethanol or in 4:1 2-methoxyethanol–benzene, the former being found the more satisfactory. In media containing benzene, some polymeric material is produced, presumably from the photo-condensation of benzene; this oily material adheres to the product, and requires washing of the product with an organic solvent (such as ethyl acetate) for its removal. The cotton-linter form of **3** was photolyzed either in suspension or by spreading the linters around the window of the photolysis lamp. The aldimine presumed to be formed initially by photolysis was hydrolyzed with dilute acetic acid at room temperature. After such treatment, little nitrogen remained in the product (see Table V). The d.s. by aldehyde groups present in **4** was estimated by a copper-number method[20] and by the borodeuteride–mass spectrometry technique previously used[5,6] with 6-aldehydoglucans. The copper numbers [grams of copper(II) reduced per 100 grams of sample], although non-stoichiometric, give a general estimation of the reducing capacity of the 6-aldehydo derivatives **4**. Table V also records the copper numbers of some reference compounds. The deuteration method for determining the d.s. by aldehyde groups in the polymer was the general procedure already described[5,6]. The polymer was reduced with sodium borodeuteride, the 6-deuteriocellulose obtained was hydrolyzed, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose-*6-d* (**5**) was prepared from the resultant mixture of D-glucose and D-glucose-*6-d*, and the extent of deuterium incorporation at C-6 of **5** was determined by mass spectrometry. In the present work, this method was refined by using a combination of g.l.c.–mass spectrometry; this improvement allowed the analysis to be performed on 10–15 mg of **4**. Two methods were used for the borodeuteride reduction of **4**, namely, by reduction in 0.2M borate buffer for 16 h, or by reduction in water for 3 days. The d.s. values recorded in Table V are the average of values calculated from the pairs of deuterated and nondeuterated fragments (*m/e* 246, 245; 188, 187; and 102, 101) that contain the C-6 moiety. A comparison, for samples of **4**, of copper numbers

TABLE VI

SUMMARY OF D.S. AND D.P. VALUES IN THE PREPARATION AND CHARACTERIZATION OF 6-ALDEHYDOCELLULOSES (4)

| | *Cotton linters* | | *Filter paper* | | *Cellophane* | | *Regenerated celluloses* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | *D.s.* | *D.p.* | *D.s.* | *D.p.* | *D.s.* | *D.p.* | *D.s.* | *D.p.* | *D.s.* | *D.p.* | *D.s.* | *D.p.* | *D.s.* | *D.p.* |
| Cellulose | | 1,584 | | 2,651 | | 317 | | 1,400 | | 4,000 | | 4,000 | | 1,400 |
| 6-chloro-6-deoxy- (2) | 0.06 | 1,421 | 0.06 | 2,479 | 0.15 | 183 | 0.14 | 740 | 0.19 | 566 | 0.30 | Insoluble | 0.67 | Insoluble |
| 6-azido-6-deoxy- (3) | 0.05 | 835 | 0.05 | 1,676 | | 174 | 0.14 | 155 | 0.16 | 448 | 0.27 | Insoluble | 0.44 | Insoluble |
| 6-aldehydo- (4) | | (185) | | (270) | | (23) | | (40) | | (38) | | (32) | | |
| Reduced (6) | 0.03 | 231 | 0.028 | 483 | 0.09 | 35 | 0.06 | 66 | 0.08 | 79 | 0.08 | 50 | 0.45 | 15 |
| Oxidized (7) | 0.017 | 247 | 0.014 | 476 | 0.10 | 32 | 0.06 | 54 | | 70 | 0.12 | 43 | 0.49 | 7 |

with the d.s. values determined by the deuterium method indicated a progressive increase in copper number as the d.s. level increased.

The i.r. spectra of the 6-aldehydocelluloses (4) did not show any carbonyl absorption in the region 1950–1600 cm$^{-1}$, indicating that, as expected, the aldehyde groups exist as hemiacetals, as hydrates, or as both.

The 6-aldehydocellulose (4) of highest d.s. was hydrolyzed in 0.5M sulfuric acid at 100°. The presence of D-*gluco*-hexodialdose was detected by electrophoretic comparison with an authentic sample thereof. In previous work with 6-aldehydo-amylose, D-*gluco*-hexodialdose was isolated and characterized definitively as tetra-*O*-acetyl-D-*gluco*-hexodialdose tetraethyl bis(dithioacetal). Much color formation and a black precipitate accompanied the hydrolysis of **4**. Similar behavior has been noted[5,6] during the hydrolysis of other 6-aldehydoglucans. Treatment of D-*gluco*-hexodialdose under the same hydrolytic conditions likewise resulted in color development and formation of a precipitate[21]. Production of color during the hydrolysis of supposedly reduced 6-aldehydocelluloses was used to indicate incomplete reduction and/or incomplete photolysis of the azido groups.

It was expected that, under strongly basic conditions, 6-aldehydocelluloses (4) would be degraded by β-elimination. To permit measurement of the d.p. by viscometry in Cadoxen, the 6-aldehydocelluloses (4) were converted into the corresponding celluloses (6) and 6-carboxycelluloses (7) by reduction with sodium borohydride, and by oxidation with sodium chlorite[23] in acetic acid, respectively. Copper numbers (see Table V) were determined for these products, to provide an estimate of the extent of reduction or oxidation. The reductions were performed under the two sets of conditions used in the deuteration method for determining the d.s. Oxidations with chlorite were performed for 16 and 72 h. From the data obtained on the oxidized products, and from general observation[5], it was concluded that some of the aldehyde groups had not reacted, even after 72 h. The i.r. spectra of the 6-carboxycelluloses (7) showed carboxyl-group absorption at 1700 cm$^{-1}$.

The uronic acid content of the 6-carboxycelluloses (7) was determined by the semi-micro procedure of Bylund and Donetzhuber[24], in which the uronic acids are decarboxylated by the action of concentrated hydriodic acid. The carbon dioxide released is absorbed into a solution of barium hydroxide, the conductivity of which is continuously recorded. The values in Table V give the percentage of uronic acid in the samples; division of these values by 100 gives an approximate measure of the d.s. by carboxyl group in **7**.

Table VI summarizes the d.s. and d.p. values measured for the intermediates and products in the preparation and characterization of the various forms of 6-aldehydocelluloses (4). Except for the sample of **4** of high d.s., there is a sharp decrease in the d.s. level on proceeding from the 6-azido derivatives **3** to the aldehydes **4**. The following facts help to explain this observation. Water-soluble fragments of high reducing-capacity were detected in the wash solutions and in the hydrolysis media during the isolation of **4**. This loss of material is also reflected in the decrease of weight-yields as the d.s. level increases (see Table V). Some product is also lost during the reduction of **4**, as evidenced by the yields of **6**. Some potential aldehyde groups might have been lost by a side-reaction leading to formation of amino groups during photolysis of the azido derivative.

In the series of highest d.s., the 6-aldehydo (**4**) and 6-carboxy (**7**) derivatives were soluble in water to the extent of ~60 and 100%, respectively. The soluble fraction of **4** had a higher copper number than the insoluble fraction, and exhibited a weak absorption in the u.v. Solutions of **4** and **7** showed levorotation comparable to that of cellulose itself. The more-highly degraded products are more appropriately termed derivatives of cello-oligosaccharides ("cellodextrins").

Theoretically, the reduced (**6**) and oxidized (**7**) products from **4** should have the same d.p. values as the precursor 6-azido-6-deoxycelluloses (**3**) if no glycoside bonds were cleaved during these transformations. However, in no case were these values reached. Generally, reduction gave products having d.p. values slightly higher than for those obtained by oxidation. These data provide further evidence indicating that some glycosidic bonds are cleaved during preparation, reduction, and oxidation of **4**. Incomplete reduction and oxidation of **4** would also lead to lower d.p. values for **6** and **7**.

Dissolution of the 6-aldehydocelluloses (**4**) in Cadoxen is accompanied by formation of a yellow color that fades rapidly. Other evidence, to be published later, also indicates that *β*-elimination does occur very rapidly when **4** is dissolved in Cadoxen. Therefore, the d.p. values recorded for **4** in Table VI are a measure reflecting regions in the cellulose polymer where there is little or no substitution. Only in the case of the 6-chloro-6-deoxycellulose (**1**) prepared from cellulose regenerated directly into *N*,*N*-dimethylformamide does it appear that substitution is reasonably uniform along the cellulose chain. It should also be noted that no viscosity–molecular weight relationship has been determined for celluloses of d.p. lower than ~200. Values below 200 in Table VI should be considered to be very approximate only.

In summary, this report describes a method for selectively oxidizing the primary hydroxyl groups of unsubstituted cellulose to aldehyde groups and to carboxyl groups. Other studies are in progress on these 6-aldehydocelluloses in an attempt to define more precisely the role that the 6-aldehydo group may play in color development, and its effect on the stability of cellulosic materials in aqueous media over the pH range of 1–12.

## EXPERIMENTAL

*Materials.* — Cellulose samples were either cotton linters (A) (Hercules type HXV 20); cotton linters (B) (Peter Temming Company, Gluckstadt, quality 4425/150); Whatman No. 1 filter paper for paper chromatography; or cellophane (untreated). Pure-grade *N*,*N*-dimethylformamide (min. 99%, b.p. 152–155°) was used for swelling the cellulose samples, and was stored over molecular sieves. Reagent-grade *N*,*N*-dimethylformamide was used in the chlorination reactions. Methanesulfonyl chloride (min. 95%) was used without further purification for the chlorination reactions. Commercial cupriethylenediamine (1.0M Cu) was used for regeneration of the cellulose. Cadmium ethylenediamine hydroxide (Cadoxen) was prepared by the procedure of Donetzhuber[25].

*General methods.* — Solutions were evaporated under diminished pressure below 45°. T.l.c. was performed on Silica Gel G, with 4:1 ethyl acetate–methanol (solvent *A*) or 4:1:1 butanol–acetic acid–water (solvent *B*) as eluants. Paper chromatography was conducted with solvent *A*. Bisulfite buffer[26] (pH 4.7) was employed at 50° for electrophoresis. Chromatograms were visibilized with 50% sulfuric acid, silver nitrate–sodium hydroxide, *p*-anisidine, or a 1% solution of ninhydrin in ethanol. Column chromatography was performed on Silica Gel 7734 (70–325 mesh ASTM, Merck). Melting points were measured with a Mettler FP2 automatic, melting-point apparatus. I.r. spectra for potassium bromide pellets were recorded with a Perkin–Elmer Model 237 i.r. spectrophotometer. Optical rotations were measured in a 1-dm tube with a Perkin–Elmer Model 141 polarimeter. Mass spectra were recorded with a Perkin–Elmer Model 270 spectrometer at an accelerating potential of 2 kV, an ionizing potential of 70 eV, and a source temperature of 200°. G.l.c. separations were effected on 3% ECNSS-M (a cyanoethyl silicone polymer, Applied Science Laboratories, State College, Pennsylvania) in a glass column.

Irradiations were conducted in a 1-liter, Hanovia photochemical reactor (Engelhard Hanovia Lamps, Slough, England) with unfiltered light from a medium-pressure mercury lamp of ~100 watts fitted with a high-purity, synthetic quartz envelope, or in a Rayonet Model RPR-208 preparative photochemical reactor (The Southern New England Ultraviolet Company, Middletown, Conn.) equipped with a lamp producing maximal radiation at 300 nm.

Elemental analyses were performed by W. N. Rond and by the Analytical Department, Swedish Forest Products Laboratory, who also performed the cuprimetric and uronic acid determinations. A powerful pulp-dispersion stirrer was used in the regeneration of the cellulose samples, and for other dispersions of the cellulose derivatives. Filtrations were conducted on Büchner funnels, and the process was greatly facilitated by using filter discs cut from commercial paper-bed sheets.

*Swelling of samples of fibrous cellulose.* — The cotton linters or filter paper were soaked in *N,N*-dimethylformamide for 2 h at 80°, and the excess liquid was filtered off. The samples were washed once with fresh *N,N*-dimethylformamide, and then used in the reactions.

*Regeneration of celluloses*[27]. — *Method* A. Cellulose was regenerated from solution in cupriethylenediamine by the standard method. The cellulose was added in small amounts, with stirring, to cupriethylenediamine at 10–15° under nitrogen. A cellulose–cupriethylenediamine ratio of 4 g and 2 g per 100 ml was used for cotton linters A and B, respectively. After being stirred for 30 min, the viscous solutions were diluted with an equal volume of water. For a cellulose sample of medium accessibility, the cellulose solution was poured slowly, with vigorous stirring, into ice–water kept acidic by the addition of M hydrochloric or sulfuric acid. The cellulose precipitated was filtered off, and washed consecutively with cold water (to remove copper ions), cold 0.1M sodium hydrogen carbonate, and water. The wet mass was transferred to a beaker, and allowed to swell in cold *N,N*-dimethylformamide with vigorous stirring. The excess liquid was filtered off, and the swelling process was repeated twice more.

For cellulose samples of high accessibility, the diluted cellulose solution was poured slowly, with vigorous stirring, into cold *N,N*-dimethylformamide, neutralization being effected by suitable addition of cold acetic acid. The precipitated cellulose was filtered off, and washed four times by stirring vigorously with *N,N*-dimethylformamide in a beaker, with subsequent filtration. The addition of some acetic acid in the first washing helped in removing most of the copper ions. Residual traces of copper ions, evident from the pale-blue color, did not appear to hinder the chlorination reaction. Some samples of the swollen cellulose were stored in the cold for several days before use. In some preparations, the solution of cellulose in cupriethylenediamine was filtered by suction through a fine-mesh, wire screen (to remove undissolved particles) before precipitation of the cellulose. This refinement produced a more uniform product.

*Method* B. A solution of cotton linters A (2 g/100 ml) in 82% phosphoric acid was kept for 2 days at 5°. The cellulose was precipitated by pouring into either cold water or cold *N,N*-dimethylformamide, with vigorous stirring. The cellulose precipitates were washed by the techniques described in method *A*.

*6-Chloro-6-deoxycelluloses* (**1**). — *Method* A. The cellulose (cotton linters, filter paper as 4-cm discs, or cellophane) was placed in a stoppered flask with a 10% v/v solution of methanesulfonyl chloride in *N,N*-dimethylformamide (100 ml). The flask and contents were heated in a bath of poly(ethylene glycol) for the time and at the temperature indicated in Tables I and II. The product was filtered off, washed with water, and then soaked for 4 h in an aqueous solution (pH 9–10) of sodium carbonate. The product was filtered off, washed well with water, and dried under a heat lamp. In experiments where the incorporation of chlorine and change in d.p. were determined as a function of time and temperature, small amounts of material were removed periodically from the flask, treated with base, dried, and submitted for analysis. When filter paper was used, care was taken not to tear the sheets.

*Method* B. Methanesulfonyl chloride was slowly added from a dropping funnel to a stirred suspension of the regenerated cellulose in *N,N*-dimethylformamide in a two- or a three-necked, round-bottomed flask. The mixture was heated and stirred for the duration of the reaction (see Table II). The resultant mixture was poured into ice–water (in a hood). After 30–60 min, the precipitated product was filtered off, transferred to a beaker, and stirred with aqueous sodium carbonate at pH 9–10 for 16 h. An alternative treatment with base consisted in gently shaking the product in 5% aqueous ammonium hydroxide for 16 h. The product was collected by centrifugation, transferred to a dialysis bag, dialyzed against tap water for 16–30 h, filtered off, and freeze-dried. Washing by dialysis was found to be more efficient than washing in a centrifuge tube or on a filter.

In both methods *A* and *B*, the reactions were performed with a ratio of 1–2 g of cellulose (dry weight) per 100 ml of *N,N*-dimethylformamide and 10 ml of methanesulfonyl chloride. During the reactions, a yellow color usually developed, but this disappeared when the reaction mixture was poured into water. The yields of chlorinated products were approximately equal to the weights of cellulose used. The products were characterized by analysis for chlorine and sulfur, and, in some examples, nitrogen. The values for d.s. by chlorine were determined from the chlorine analyses, and are not corrected for small proportions of moisture or sulfur that may have been present. These data, together with a visual estimate of the extent of color development, are given in Tables I and II. Before treatment with base, the products (**1**) showed i.r. absorptions at 1730 $cm^{-1}$ (formyl group); no such absorption was evident after treatment.

*Hydrolysis of 6-chloro-6-deoxycelluloses* (**1**). — The cellulose derivative (20–30 mg) was stirred with 72% sulfuric acid (7 drops) in a glass-stoppered test-tube at ~25° until dissolution was complete (7–16 h). The solution was diluted with water (4 ml), heated for 6–10 h at 100°, cooled, its pH brought to 5–6 by addition of saturated barium hydroxide solution, and the resulting suspension briefly heated on a steam bath, and then centrifuged. The supernatant liquor was decanted, and concentrated to small volume. T.l.c. (solvent systems *A* and *B*) showed products having the characteristics of D-glucose ($R_F$ 0.30 in *A*, 0.26 in *B*), 6-chloro-6-deoxy-D-glucose (**2**) ($R_F$ 0.45 in *A* and 0.49 in *B*), and, in some samples, traces of other compounds having $R_F$ values greater, and less, than those of **2**.

*Isolation and characterization of 6-chloro-6-deoxy-*D*-glucose* (**2**). — A sample of **1** (150 mg, Cl 14%) was hydrolyzed with 72% sulfuric acid (1 ml) as just described. The resulting syrup (125 mg) was chromatographed on silica gel with 8:1 ethyl acetate–methanol as the eluant. The fractions containing **2** were collected, and evaporated to a syrup (72 mg) that eventually crystallized. Recrystallization from 9:1 ether–ethanol gave **2** having m.p. 135° (lit.[12] m.p. 135°). Acetylation with acetic anhydride in the presence of perchloric acid at 100° gave 1,2,3,4-tetra-*O*-acetyl-6-chloro-6-deoxy-α-D-glucose, m.p. 163°, $[\alpha]_D^{23}$ +119° (*c* 1, chloroform) [lit.[12] m.p. 164°, $[\alpha]_D^{23}$ +120° (in chloroform)].

*6-Azido-6-deoxycelluloses* (**3**). — *Method* A. The 6-chloro-6-deoxycellulose (**1**) from cotton linters, filter paper, cellophane, or regenerated cellulose was kept, without stirring, in a stoppered flask with sodium azide and the solvent for the indicated time and at the specified temperature (see Table III). Fibrous products were collected by filtration, washed well with water, and dried under a heat lamp. With samples of regenerated cellulose, the reaction mixture was transferred to a dialysis bag, dialyzed for at least 16 h, and the product filtered off and freeze-dried. When methyl sulfoxide was used as the solvent, the flask was purged with nitrogen before being stoppered. Some of the products obtained with methyl sulfoxide were dark colored.

*Method* B. The procedure was the same as that of method *A*, except that the reaction mixture was stirred. An excess of sodium azide was used in each preparation.

The following general ratios of reactants were used: 1 g of **1**, 2 g of sodium azide, and 100 ml of *N*,*N*-dimethylformamide; 1 g of **1**, 10 g of sodium azide, and 20 ml of water; and 1 g of **1**, 4 g of sodium azide, and 100 ml of methyl sulfoxide.

To determine the optimal time for maximal displacement of the chlorine, the reactions were monitored by i.r. spectrometry, the increasing intensity of the azido-group absorption at 2070 $\mathrm{cm}^{-1}$ being observed. All reactions were performed heterogeneously, except for some of those in methyl sulfoxide that employed, as reactants, samples of 6-chloro-6-deoxycelluloses (**1**) of high d.s. The products were characterized by nitrogen analysis (to determine the extent of substitution by azide), by chlorine analysis (to determine how much chlorine had not been displaced), and by viscosity (to determine the extent of depolymerization). These data, together with the extent of color development, are recorded in Tables III and IV.

*Hydrolysis of 6-azido-6-deoxycelluloses* (**3**). — When the 6-azido derivatives were hydrolyzed by the procedure described for **2**, a dark suspension resulted. After being rendered neutral, the resultant colored solution contained (according to t.l.c. and paper chromatography with solvents *A* and *B*) a complex mixture in which were chromatographically detected components identical with glucose and 6-amino-6-deoxyglucose, but 6-azido-6-deoxyglucose was absent. Treatment of the 6-azido-6-deoxycelluloses with 72% sulfuric acid without heating at 100° resulted in less color formation, but no 6-azido-6-deoxyglucose was detected.

*6-Aldehydocelluloses* (**4**). — *Method* A. A suspension of the 6-azido-6-deoxycellulose (**3**, ~1 g) in 4:1 2-methoxyethanol–benzene (1 liter) was prepared by vigorous stirring, and was transferred to a Hanovia photochemical reactor. The product was maintained in suspension by magnetic stirring, and was photolyzed until a sample no longer showed i.r. absorption for the azido group (2–5 h). The product was filtered off, washed three times by shaking for 15 min with ethyl acetate (100 ml), shaken with 5% acetic acid for 20 min, and the suspension transferred to a dialysis bag and dialyzed against running, distilled water for 16 h. The product was filtered off and freeze-dried. In those examples where regenerated cellulose had been used, the total contents of the dialysis bag were freeze-dried. The photolysis solution, the wash liquid, and the solution passing through the dialysis membrane, all gave positive tests with the Somogyi reagent, indicating that reducing sugars were present. Analysis of these solutions by t.l.c. (solvents *A* and *B*) gave components at the base line that gave positive tests to sulfuric acid, $\mathrm{AgNO_3}$–NaOH, and *p*-anisidine sprays.

*Method* B. The 6-azido-6-deoxycellulose (**3**) (from cotton linters, filter paper, or cellophane) was moistened with the photolysis solvent (4:1 2-methoxyethanol–benzene), and placed around the window of the lamp of the Hanovia apparatus. The samples were held in place by wrapping aluminum foil around the lamp. Samples were photolyzed for 1 h on each side. For cellophane, because of its transparency, photolysis for only 1 h was sufficient. The samples were well washed with ethanol, soaked in 2% acetic acid for 3 h, washed with water, and air-dried at room temperature.

*Method* C. The 6-azido-6-deoxycellulose (**4**) from filter-paper discs was placed in polyethylene bags which were suspended in the Rayonet photochemical reactor and photolyzed for 1.5 h with 300-nm radiation. The discs were soaked in 2% acetic acid for 3 h, washed with water, and air-dried.

*Method* D. The 6-azido-6-deoxycellulose (**3**, 500 mg) from regenerated cellulose was suspended in 2-methoxyethanol (100 ml), and the suspension was sealed, with a magnetic stirring-bar, in a polyethylene bag (3.5 × 15 cm) after purging the bag with nitrogen. The mixture was stirred and photolyzed for 3–4 h in the Rayonet apparatus with 300-nm radiation. After treatment with acetic acid, the product was isolated by the techniques described in method *A*.

Yields, copper numbers, and d.s. data for the products are recorded in Table IV. The i.r. spectra of the "aldehyde" **4** did not show, in the region 1800–1600 cm$^{-1}$, any absorptions assignable to a free carbonyl group.

The 6-aldehydocellulose (**4**) of highest d.s. (100 mg) was hydrolyzed in 0.5M sulfuric acid (20 ml) for 8 h at 100°. The dark solution containing some suspended material was made neutral with saturated barium hydroxide as described before. T.l.c. and electrophoresis showed a principal component indistinguishable from an authentic sample of *gluco*-hexodialdose.

The 6-aldehydocellulose of highest d.s. was suspended in water (10 ml), stirred for 1 h, and then centrifuged. The slightly yellow liquid was decanted, and both the liquid and the solid were freeze-dried. The solid (75 mg) had copper number 128, whereas the product from the water phase (125 mg) had copper number 185. The soluble fraction had relative viscosity 1.05 at 25° (*c* 6.6 mg/ml), $[\alpha]_D^{25}$ $-20°$ (*c* 0.5, water), $\lambda_{max}$ 250 nm (weak; *c* 250 mg/liter).

*Preparation of celluloses* (**6**) *by reduction of 6-aldehydocelluloses* (**4**). — *Method* A. To a suspension of the 6-aldehydocellulose (**4**, 200 mg) in 0.2M borate buffer (20 ml) of pH 8.8 was added sodium borohydride (200 mg) in small portions, with magnetic stirring, during 2 h. After 6 h, sodium borohydride (200 mg) was added, and the suspension was stirred for 16 h, during which time the pH rose to ~9.8. The product was filtered off, and washed with water, 1% acetic acid, and water. Fibrous products were dried under a heat lamp, and products from regenerated celluloses were freeze-dried. In the series of high d.s., the reaction mixture was dialyzed for 16 h, and the contents of the dialysis sac were freeze-dried.

*Method* B. The 6-aldehydocellulose (**4**, 100 mg) was suspended in water (10 ml), and sodium borohydride (100 mg) was added in small portions during 1 h. The suspension was kept for 16 h without stirring, sodium borohydride (100 mg) was added, and the suspension was kept for a further 48 h. The product was isolated as described in method *A*. The resultant celluloses (**6**) were characterized by copper number and d.p. (see Table V).

*6-Carboxycelluloses* (**7**). — *Method* A. A suspension of the 6-aldehydocellulose (**4**) (100–200 mg) in 20% acetic acid (25 ml) containing sodium chlorite (400 mg) was shaken gently for 16 h in a stoppered flask. The product was filtered off, washed with water, and dried. In those preparations employing cellulose of high accessibility, the reaction mixture was transferred to a dialysis sac, dialyzed for 16 h, and the contents of the sac freeze-dried. The product was almost completely water-soluble and had relative viscosity 1.11 at 25° (*c* 6.6 mg/ml); $[\alpha]_D^{25}$ $-32°$ (*c* 0.5, water).

*Method* B. The oxidation reactions were conducted as in method *A*, except that shaking was not employed and the reaction time was extended to 72 h.

The products were characterized by copper number and d.p. The uronic acid content was determined by the method of Bylund and Donetzhuber[24] (see Table V). When the content of uronic acid was sufficiently high, the i.r. spectrum of **6** indicated carboxyl-group absorption at 1700 $cm^{-1}$.

*Estimation of the degree of polymerization of the cellulose derivatives by viscometry.* — The cellulose derivative (20 mg) was dissolved in Cadoxen (5 ml) by shaking, and the solution was diluted with water (5 ml). In those examples where dissolution was incomplete, the suspension was clarified by centrifugation. Viscosities were measured at 25° in an Ubbelohde type of viscometer. The intrinsic viscosities and degrees of polymerization were calculated by use of the equations of Henley[28]. For a comparison of these weight-average, d.p. values with other d.p. relationships, the paper by Treiber[29] should be consulted. A reference solution prepared from filter-paper cellulose had $[\alpha]_D^{25}$ $-22°$ (*c* 0.5, water).

*Determination of copper numbers.* — A semi-micro modification of the Braidy method[20] was used. Because of the large proportion of reducing groups present, only 5–10 mg of sample (equilibrated in air) was used for each analysis.

*Reduction of 6-aldehydocelluloses* (**4**) *with sodium borodeuteride, and measurement, by mass spectrometry, of the position and extent of incorporation of deuterium.* — *Method* A. In a glass-stoppered test-tube, the 6-aldehydocellulose (**4**) was suspended in 0.2M borate buffer (2 ml, pH 8.8) by means of magnetic stirring at room temperature. Sodium borodeuteride (10 mg) was added in small portions during 2 h, the suspension was stirred for 5 h, a further 10 mg of sodium borodeuteride was added, the suspension was stirred for 16 h, water (5 ml) was added, and the solid was centrifuged off. The supernatant liquor was decanted off, and the solid was washed with 1% acetic acid, twice with water, and once with ethanol, and dried *in vacuo*. In the preparations having a high d.s., the reaction mixture was dialyzed for 16 h, and the contents of the dialysis sac were freeze-dried.

In a glass-stoppered test-tube, each sample of reduced cellulose was stirred with one drop of 72% sulfuric acid for 2–3 h, ensuring that all of the material had dissolved. The solution was diluted with water (3 ml), and the tube was stoppered, and heated for 6 h at 100°. The clear to slightly yellow solution was made neutral with barium hydroxide as described for the hydrolysis of **1**. After removal of the barium sulfate, the solution was evaporated to a syrup. To the residue of D-glucose plus D-glucose-*6-d* were added acetone (3 ml), anhydrous copper(II) sulfate (50 mg), and a trace of sulfuric acid, and the suspension was stirred magnetically for 16 h. The stirring bar was removed, the solid was centrifuged off, the solution was decanted into another tube, and an excess of Dowex-3 ($OH^-$) was added (to neutralize the sulfuric acid). The solution containing 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose-*6-d* was filtered from the resin, concentrated to a smaller volume, and analyzed by g.l.c.–mass spectrometry. The d.s. values recorded in Table V are the average of the d.s. values, calculated as previously described[6], from the pairs of deuterated and nondeuterated fragments (*m/e* 246, 245; 188, 187; and 102, 101) that contained the C-6 moiety.

*Method* B. Water was used instead of borate buffer. The second amount of sodium borodeuteride was added after 16 h, and the total reaction-time was extended to 3 days. Otherwise, the procedure was identical with method *A*.

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