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The preparation of *O*-methyl- and *O*-ethyl-celluloses having controlled distribution of substituents

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ABSTRACT

O-Methyl- and *O*-ethyl-celluloses having controlled distributions of substituents were prepared by alkylation of 6-*O*-triphenylmethyl ("trityl") cellulose in dimethyl sulfoxide (Me_2SO) and subsequent detritylation of the alkylated products. Water-free alkylation reactions failed to give complete substitution of the hydroxyl groups at both the C-2 and C-3 positions. The addition of a small amount of water to the tritylcellulose solution in Me_2SO improved the efficiency of the alkylations, yielding 2,3-di-*O*-substituted-6-*O*-tritylcelluloses which in turn gave 2,3-di-*O*-alkylcelluloses on detritylation with HCl gas. Repeated further alkylation of the 2,3-di-*O*-alkylcelluloses in Me_2SO furnished products with high degrees of substitution at the C-6 position. The distribution of substituents in the alkyl cellulose ethers was determined by acid hydrolysis, reduction, and gas-chromatographic separation of the partially alkylated alditol acetates. The distribution of methyl and ethyl groups in the polymers prepared by repeated alkylation systematically changed with each alkylation step.

INTRODUCTION

O-Alkylcelluloses such as *O*-methylcellulose and *O*-ethylcellulose have received considerable attention industrially. The distribution of alkyl groups in the anhydroglucose units as well as along the chain is considered to influence strongly physical properties such as solubility, crystallization, gel formation, liquid-crystal formation, and resistance to enzymatic degradation. The precise determination and control of the distribution of substituents in the synthesis of cellulose ethers is important in clarifying the correlation between the physical properties of these derivatives and their chemical structure.

The distribution of substituents in *O*-alkylcellulose derivatives has been extensively examined by paper chromatography[1,2], g.l.c.[3–6], and ^{13}C-n.m.r.[7–11] techniques. However, only a few reports[12–14] have related physical properties to the distribution of substituents in cellulose ethers and esters. This lack of correlative effort is due to the difficulty of preparing alkylcellulose derivatives having a controlled distribution of substituents.

In a previous paper[15], a facile method for the preparation of tri-*O*-alkylcelluloses

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was reported. It was found that a small amount of water added to the reaction mixture improved the reactivity of the hydroxyl groups, especially at the C-3 position. In this report, *O*-triphenylmethyl ("trityl") cellulose, in which the C-6 hydroxyl is selectively substituted[16,17], was used as a starting material, since the trityl group can be easily removed by exposing the *O*-tritylcellulose derivatives to acidic conditions[18-20]. This allows the preparation of cellulose derivatives that are specifically substituted at the C-2 and C-3 positions[20,21].

The beneficial effect of added water on the preparation of cellulose triethers also facilitated the preparation of *O*-methyl- and *O*-ethyl-celluloses that were completely substituted at the C-2 and C-3 positions. These products have been characterized by hydrolysis, reduction, and g.l.c. of the resulting alditol acetates, F.t.-i.r., and ^{13}C-n.m.r. These polymers would appear to be ideal samples for determining a correlation between physical properties and the distribution of substituents in alkylcellulose derivatives.

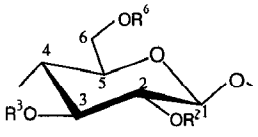
EXPERIMENTAL

Materials. — Commercial cellulose acetate samples were provided by Eastman (acetyl content 39.9%, ASTM viscosity 27). The samples were completely deacetylated in aqueous 15% ammonium hydroxide for 14 days at room temperature. The dimethyl sulfoxide (Me_2SO) and pyridine were dehydrated over type 3A molecular sieves. Reagent grade solvents and reagents (Aldrich Gold Label) were used without further purification. Powdered sodium hydroxide was prepared by grinding NaOH pellets in a domestic coffee grinder.

Preparation of 6-O-(triphenylmethyl)cellulose ("tritylcellulose"). — The preparative method followed that previously described[17,21]. The completely deacetylated cellulose (32.5 g) was added to 300 mL of dry pyridine, which was then heated for 3 h at 80° and filtered off, in order to remove water. This procedure was repeated three times. The cellulose was added to 500 mL of anhydrous pyridine and 142.0 g of triphenylmethyl chloride (2.5 moles per mole of hydroxyl groups) in a 1000 mL three-necked round-bottom flask equipped with a condenser, stirrer, and drying tube. The mixture was heated for 26 h at 95°, then cooled to room temperature and poured into methanol. The precipitate was isolated and washed in methanol for 12 h. After a second washing, the precipitate was filtered off and dried at 100° under vacuum. The yield of product was 95% and the degree of substitution with trityl groups was 1.07 by ^{1}H-n.m.r. measurements.

Preparation of tri-O-methyl- and tri-O-ethyl-celluloses. — The preparative route to these derivatives has been presented in a previous report[15].

Preparation of cellulose partially alkylated at the C-2 and C-3 positions (Fig. 1, mixture of S_0, S_2, S_3, and S_{23}). — Tritylcellulose (1.0 g) completely dissolved in 60 mL of Me_2SO on stirring for 1 h at 60°. The solution was cooled to room temperature, and 2.0 g of powdered NaOH was dispersed in it. Following 1 hour's stirring under a nitrogen atmosphere, the alkyl iodide (3.1 mL of methyl iodide or 4.0 mL of ethyl iodide) was added dropwise to the solution. The amounts of powdered NaOH and alkylating agents



	R^2	R^3	R^6	
1	H	H	H	$=S_0$
2	Alkyl	H	H	$=S_2$
3	H	Alkyl	H	$=S_3$
4	Alkyl	Alkyl	H	$=S_{23}$
5	Alkyl	Alkyl	Alkyl	$=S_{236}$

Fig. 1. The structures of five of the possible types of glucose residues found in cellulose ethers.

were adjusted to 10 moles per mole of hydroxyl group in tritylcellulose. The mixture was stirred under a nitrogen atmosphere for 1 h, kept at 40° for 1 h, at 50° for 1 h, and at 60° for 2 h, then cooled to room temperature and poured into 95% methanol. The precipitate was dissolved in chloroform, the chloroform layer was extracted with water three times, and then evaporated under reduced pressure at 60° to a syrup. The products (MTC1 for methylation and ETC1 for ethylation) were precipitated from the syrup by the addition of methanol, filtered off, and dried under vacuum at 65°. The yield was 90%.

As the alkylation procedure did not result in complete substitution at both the C-2 and C-3 positions it was repeated three times. For the second alkylation, the procedure was as follows: One gram of MTC1 or ETC1 was added to 60 mL of Me_2SO, and following stirring for 1 h at 60° the turbid solution was cooled to room temperature. The same amount of powdered NaOH as used to prepare MTC1 and ETC1 was added to the solution. After the mixture was stirred for 1 h, 3.1 mL of methyl iodide or 4.0 mL of ethyl iodide was added dropwise. Following 30 min stirring under a nitrogen atmosphere at room temperature, the temperature was raised to 70° and kept there for 3 h. The reaction mixture was then cooled to room temperature, and the product precipitated and purified according to the procedure given above.

After a total of four alkylations the hydroxyl groups at C-2 and C-3 were still only partially substituted. Samples of methylated trityl cellulose (MTC1–MTC4) and ethylated trityl cellulose (ETC1–ETC4) were isolated after each of the alkylation steps, and each of these samples was detritylated by treating 4.5 g of the polymer in 150 mL of dichloromethane with hydrogen chloride gas for 4 min[18]. The detritylated mixture was poured into 500 mL of acetone. The products (MC1–MC4 for the four methylated celluloses and EC1–EC4 for the four ethylated celluloses) were isolated by centrifugation, washed with acetone, filtered, and dried under vacuum at 65°. The yields of the detritylated products were approximately 85%.

*Preparation of 2,3-di-*O*-alkylcellulose (Fig. 1, S_{23}).* — Our method[15] for the preparation of tri-*O*-alkylcelluloses was applied to the preparation of 2,3-di-*O*-alkylcelluloses. Thus, 2.5 g of powdered NaOH was dispersed in a solution of tritylcellulose (1.0 g) in Me_2SO (60 mL) containing 1 mL of water. Following 1 hour's stirring under a nitrogen atmosphere, two thirds of the total amount of alkyl iodide (2.2 mL of methyl

iodide or 2.8 mL of ethyl iodide) was added dropwise to the solution. At 2, 3, and 4 h after the first addition of alkyl iodide, one third of the remaining alkyl iodide (0.3 mL of methyl iodide or 0.4 mL of ethyl iodide) was added dropwise. Following the last addition of alkyl iodide to the solution, still under a nitrogen atmosphere, the temperature was raised to 70° and kept there for 20 h. The mixture was cooled to room temperature and the product was isolated and purified as described above. The yield was 90%. Following alkylation the products were detritylated and the samples (2,3-diMC for 2,3-di-*O*-methylcellulose and 2,3-diEC for 2,3-di-*O*-ethylcellulose, respectively) were isolated by the same method as described in the previous section.

*Preparation of 2,3-di-*O*-alkyl-6-*O*-partially alkylated cellulose (Fig. 1, mixture of S_{23} and S_{236}).* — 2,3-Di-*O*-alkylcelluloses were treated in Me_2SO by the same method as described for the first alkylation in the methylation or the second alkylation in the ethylation of tritylcelluloses. In this reaction, the hydroxyl groups at the C-6 position were expected to be alkylated. After the alkylation the reaction mixture was extracted with 100 mL each of water and methylene chloride. The methylene chloride layer was separated, washed with water, and evaporated under reduced pressure at 40° to yield a syrup. The product was precipitated from the syrup by the addition of aqueous 50% acetone. The filtered product was dried first in air then under vacuum at 65°. The alkylation step was repeated three times. A sample (2,3-diMC1–2,3-diMC4 for methylation and 2,3-diEC1–2,3-diEC4 for ethylation) was isolated after each alkylation step.

Characterization. — The distribution of methyl and ethyl groups in the MC and EC samples was determined by acid hydrolysis and analysis of the components as partially alkylated alditol acetates by gas-liquid chromatography[3,22]. The sample (50 mg) was dissolved in 3 mL of 72% sulfuric acid, kept at room temperature for 1 h, then diluted into 3% sulfuric acid and heated at 120° for 1 h. The hydrolyzate was neutralized to pH 5.5 with barium hydroxide and the precipitated barium sulfate was removed by centrifugation. The partially alkylated glucoses thus obtained were reduced with $NaBH_4$ and then acetylated. The alditol acetates were dissolved in $CHCl_3$ and analyzed with a Hewlett–Packard Model 5890A gas-liquid chromatograph equipped with a Hewlett–Packard Model 3392A integrator, a flame-ionization detector, and a J. and W. Scientific DB-1 fused-silica capillary column (0.25 mm × 30 m, silicone film thickness 0.25 μm). The average area percent in triplicate analyses was adopted as the area percent of each peak. The temperature was increased from 190° to 210° at 1°/min.

I.r. spectra were obtained with a Mattson Cygnus F.t.-i.r. spectrophotometer using photoacoustic detection. ^{13}C-N.m.r. spectra were obtained with a Varian XL 200 spectrometer operating at 50.4 MHz, on samples dissolved in deuterated chloroform ($CDCl_3$) or pyridine-d_5 (C_5D_5N). Chemical shifts were measured from the solvent signal (δ_C 77.01 for $^{13}CDCl_3$) and from internal Me_4Si, respectively.

Size exclusion chromatograms in chloroform and tetrahydrofuran were obtained with a refractive index detector and 10^5, 10^4, 10^3, 500, and 100 Å μ-Styragel columns in series. The columns were calibrated with a series of poly(styrene) standards.

RESULTS AND DISCUSSION

F.t.-i.r. and ^{13}C-n.m.r. analyses of the products. — Cellulose samples partially alkylated at the C-2 and C-3 positions were prepared from alkylated tritylcellulose. Repeating the alkylation in dry Me_2SO solutions increased the degree of substitution of the OH groups. However, the i.r. spectra of Figs. 2 and 3 show that the OH stretching bands around 3400 cm^{-1} decrease with repeated alkylation, but do not disappear. In other words, neither 2,3-diMTC nor 2,3-diETC could be prepared by this procedure. On the other hand, after alkylation of tritylcellulose in Me_2SO solution containing a small amount of water, the hydroxyl stretching band almost disappeared for the methylated sample (Fig. 2, trace 6), and was absent from the spectrum of the ethylated sample (Fig. 3, trace 5), suggesting that 2,3-di-*O*-alkyl-6-*O*-tritylcelluloses were prepared in one step.

Significant depolymerization of the product did not occur during alkylation. The size-exclusion chromatograms show no significant change with number of alkylation steps (Fig. 4), so serious chain degradation does not result at this stage. Following alkylation the samples were detritylated with HCl gas, all under identical conditions. All the alkylcellulose samples thus prepared should have had almost the same degree of polymerization even if some acid-catalyzed degradation of the cellulose did occur.

The 50.4 MHz ^{13}C-n.m.r. spectra of 2,3-di-*O*-ethylcellulose (2,3-diEC) and 2,3-di-*O*-ethyl-6-tritylcellulose (2,3-diETC) are shown in Figs. 5a and 5b, respectively. The signal appearing at 16.5 p.p.m. is assigned to the methyl carbons of the ethyl substituents. The signals for the methylene carbons in the ethyl substituents are located

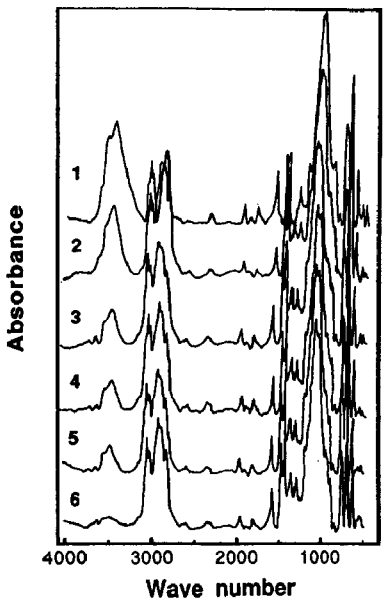


Fig. 2. The change in the i.r. spectrum of *O*-tritylcellulose with repeated methylation. 1, *O*-tritylcellulose; 2–5, methylated *O*-tritylcelluloses with increasing methylation; 6, 2,3-di-*O*-methyl-6-*O*-tritylcellulose.

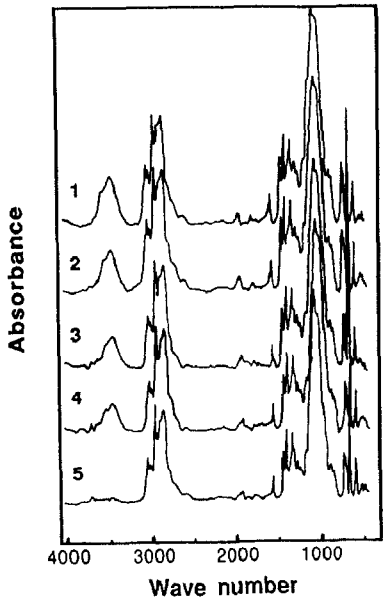


Fig. 3. The change in the i.r. spectrum of *O*-tritylcellulose with repeated ethylation. 1–4, ethylated *O*-tritylcelluloses with increasing ethylation; 5, 2,3-di-*O*-ethyl-6-*O*-tritylcellulose.

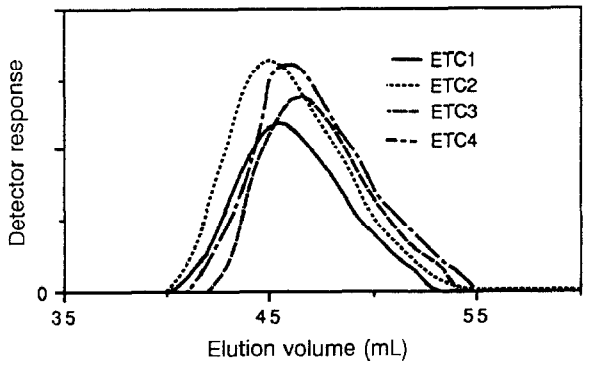


Fig. 4. Size exclusion chromatograms of *O*-tritylcellulose samples after one (ETC1) to four (ETC4) ethylation reactions.

around 67 and 69 p.p.m. in the respective spectra. The signal for C-6 appears at 62 p.p.m.[8]. Carbon atoms substituted by ethoxy groups (C-2, C-3) give a broad signal around 84 p.p.m. in 2,3-diETC, and two signals, at 84.4 and 83.6 p.p.m., in 2,3-diEC. The signals of carbon atoms bearing ethoxy substituents exhibited about 9 p.p.m. of downfield shift relative to the corresponding carbons of cellulose itself[7,8,23,24]. Signals for C-4 and C-5 appear around 77–79 p.p.m., and the signal at 103.8 p.p.m. is assigned to C-1. The aromatic trityl carbon signals appear at 128.5, 129.5, and 144 p.p.m. (c, d, and b) in Fig. 5b and the signal at 86.8 p.p.m. can be assigned to the quaternary carbon of the trityl group[25,26]. The solvent signals appear around 77.0 for $CDCl_3$, and 149.9, 135.5, and

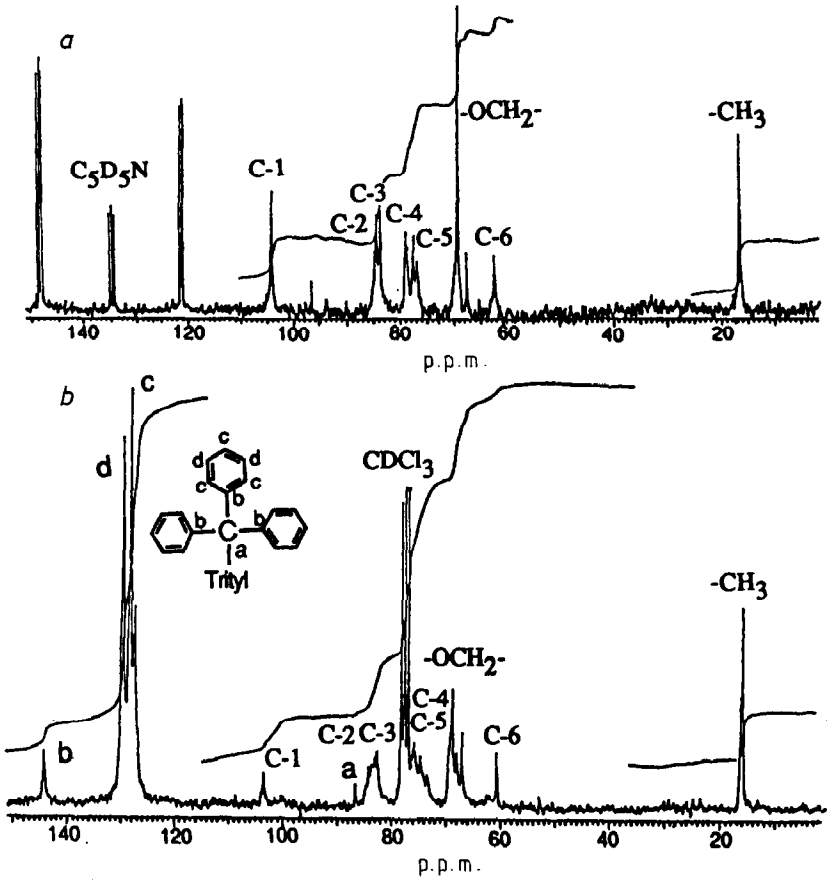


Fig. 5. ^{13}C-N.m.r. spectra of: *a*, 2,3-di-*O*-ethylcellulose (2,3-diEC, Table II) in C_5D_5N at 30°; *b*, 2,3-di-*O*-ethyl-6-*O*-tritylcellulose (sample 5, Fig. 3) in $CDCl_3$ at 30°.

123.5 p.p.m. for C_5D_5N. Comparing spectra *a* and *b* in Fig. 5, signals are sharper in *a* and no trityl signals appear there. This suggests that the HCl treatment successfully removed the trityl groups from 2,3-diETC to yield 2,3-diEC, but some depolymerization may have occured during the reactions, resulting in sharper ^{13}C signals. The n.m.r. results were supported by the F.t.-i.r. spectra showing trityl groups (1600, 1490, and 1450 cm^{-1}) before and hydroxyl groups (around 3400 cm^{-1}) after the HCl treatment. The F.t.-i.r. spectra of the detritylated products had no trityl bands.

Distribution of substituents in O-*methyl- and* O-*ethyl-cellulose.* — Tables I and II show the results of g.l.c. analyses of the substituent distribution for the *O*-methylcellulose and *O*-ethylcellulose samples, respectively. The mol fractions X_2, X_3 and X_6 were calculated from the molar percentages of glucitol (S_0) and its mono-, di-, and tri-*O*-alkyl derivatives (S_2–S_{236}, Fig. 1) which were present in the hydrolyzates of the polymer:

$$\begin{aligned} X_2 &= (S_2 + S_{23} + S_{26} + S_{236})/100 \\ X_3 &= (S_3 + S_{23} + S_{36} + S_{236})/100 \\ X_6 &= (S_6 + S_{26} + S_{36} + S_{236})/100 \\ \text{d.s.} &= X_2 + X_3 + X_6 \end{aligned} \qquad (I)$$

TABLE I

Distribution of substituents in *O*-methylcellulose samples

Sample	*Overall d.s.*[a]	*Alkylated glucitols by hydrolysis and reduction*[b] *(mol%)*								*D.s. at individual positions*[c]		
		S_0	S_2	S_3	S_6	S_{23}	S_{36}	S_{26}	S_{236}	X_2	X_3	X_6
MC1	1.29	13.7	31.8	12.5	0	42.0	0	0	0	0.74	0.55	0
MC2	1.48	7.9	26.3	9.6	0	56.2	0	0	0	0.82	0.66	0
MC3	1.57	6.2	21.1	9.7	0	63.0	0	0	0	0.84	0.73	0
MC4	1.56	6.8	20.0	9.8	0	63.4	0	0	0	0.83	0.73	0
2,3-diMC	1.77	2.0	10.6	10.0	0	75.0	0	0	2.4	0.88	0.87	0.02
2,3-diMC1	2.87	0	0	0	0	11.6	1.2	1.0	86.3	0.99	0.99	0.89
2,3-diMC2	2.89	0	0	0	0	8.5	1.0	0.9	89.6	0.99	0.99	0.92
2,3-diMC3	2.96	0	0	0	0	2.9	0	0.9	96.2	1.00	0.99	0.97
2,3-diMC4	2.97	0	0	0	0	2.4	0	0.8	96.7	1.00	0.99	0.98
Tri-*O*-MC	3.00	0	0	0	0	0	0	0	100.0	1.00	1.00	1.00

[a] Equals $X_2 + X_3 + X_6$. [b] Determined by g.l.c. [c] X_n is the mol fraction of glucitol derivatives substituted on the OH of C_n (n = 2, 3, and 6). For example, $X_2 = (S_2 + S_{23} + S_{26} + S_{236})/100$

TABLE II

Distribution of substituents in *O*-ethylcellulose samples

Sample	*Overall d.s.*[a]	*Alkylated glucitols by hydrolysis and reduction*[b] *(mol%)*								*D.s. at individual positions*[c]		
		S_0	S_2	S_3	S_6	S_{23}	S_{36}	S_{26}	S_{236}	X_2	X_3	X_6
EC1	1.13	22.3	34.0	11.1	0	30.6	0	0	2.0	0.67	0.44	0.02
EC2	1.37	14.5	29.2	7.6	0	45.5	0	0	3.2	0.78	0.56	0.03
EC3	1.65	6.0	20.9	5.9	0	62.9	0	0	4.3	0.88	0.73	0.04
EC4	1.61	7.7	21.6	5.0	0	63.5	0	0	2.1	0.88	0.71	0.02
2,3-diEC	1.93	0	8.8	5.7	0	77.2	0	0	8.3	0.94	0.91	0.08
2,3-diEC1	2.57	0	1.6	0.5	0	32.9	1.3	2.5	61.2	0.98	0.96	0.65
2,3-diEC2	2.80	0	0	0	0	16.7	0	2.9	80.4	1.00	0.97	0.83
2,3-diEC3	2.85	0	0	0	0	12.3	0	3.1	84.6	1.00	0.97	0.88
2,3-diEC4	2.88	0	0	0	0	9.7	0	2.0	88.3	1.00	0.98	0.90
tri-*O*-EC	3.00	0	0	0	0	0	0	0	100.0	1.00	1.00	1.00

[a,b,c] See Table I.

These values of X_n give the distribution of substituents at each position (C-2, C-3, and C-6) of the ring and hence indicate the relative reactivities of the hydroxyl groups.

For samples MC1–MC4 and EC1–EC4 in Tables I and II, the main glucitol residues are S_0, S_2, S_3, and S_{23}, since trityl substituents were used as protective groups, and hence the OH groups at the C-6 position of the products should be free. According to Hearon and coworkers[17], under moderate conditions trityl chloride reacts 13.8 times faster with the primary hydroxyl at the C-6 position as with the secondary hydroxyls at the C-2 and C-3 positions. This results in degrees of tritylation of approximately 1.0, with 90% substitution at the primary position. In our procedure, the unreacted hydroxyl groups in the tritylcellulose were almost completely substituted by the alkylation reactions, as the i.r. spectra for 2,3-diMTC and 2,3-diETC (Fig. 2, trace 6, and Fig. 3, trace 5, respectively) showed very small hydroxyl absorption bands at 3400 cm^{-1}. (In the case of the complete ethylation of tritylcellulose, there was no OH band around 3400 cm^{-1} and hence complete substitution.) Since the d.s. with respect to ethyl groups of this 2,3-diETC is 1.93, corresponding to the result for 2,3-diEC in Table II, the d.s. of tritylcellulose should be 1.07. This value agreed with ^{1}H-n.m.r. measurements. The values of the mol percentages of S_2, S_3, S_{23}, and S_{236} from 2,3-diEC in Table II should also be equal to the substitution ratios of *trityl* groups at C-3 plus C-6, C-2 plus C-6, C-6, and nonsubstituted positions, respectively. Thus it may be inferred on the basis of Eq. *1* that tritylation occurred with 92% substitution of the primary hydroxyl group on C-6, 9% substitution of the secondary hydroxyl on C-3, 6% substitution at the C-2 position, and no substitution of 8% of the units. The order of reactivity is thus O-6 > > O-3 > O-2.

With the alkylation steps yielding MC1–MC3 and EC1–EC3 the values of total d.s. and the mole percent of S_{23} increased, while S_2 and S_3 decreased. After three alkylation steps the distribution patterns did not change, suggesting that alkylation does not proceed further.

Repeated alkylations in dry Me_2SO of samples 2,3-diMC and 2,3-diEC gave as major products the glucitol residues S_{23} and S_{236} (Tables I and II). The mol percent of S_{23} decreased instead of increasing after each alkylation step, indicating that the hydroxyl groups at the C-6 positions of S_{23} were being substituted to yield S_{236}. When 2,3-diMC and 2,3-diEC were alkylated in Me_2SO containing a little water, they gave the trisubstituted ethers Tri-*O*-MC and Tri-*O*-EC.

In summary, as the alkylation level increased from MC1 to 2,3-diMC4 and from EC1 to 2,3-diEC4, the hydroxyl groups at the C-2 and C-3 positions were substituted progressively to give, after detritylation, 2,3-di-*O*-alkylcelluloses having free hydroxyl groups at the C-6 position. These free OH groups were then further alkylated to give nearly completely trisubstituted cellulose ethers. Addition of a limited amount of water allowed virtually complete alkylation of unprotected hydroxyl groups in a single step.

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REFERENCES

1 I. Croon and B. Lindberg, *Sven. Papperstidn.*, 60 (1957) 843–849.
2 I. Croon, *Sven. Papperstidn.*, 61 (1958) 919–921.
3 O. Ramnäs, *Acta Chem. Scand.*, 27 (1973) 3139–3146.
4 A. Isogai, A. Ishizu, and J. Nakano, *Sen'i Gakkaishi*, 40 (1984) T504–T511; *Chem. Abstr.*, 102 (1985) 151 095k.
5 A. J. D'Ambra, M. J. Rice, S. G. Zeller, P. R. Gruber, and G. R. Gray, *Carbohydr. Res.*, 177 (1988) 111–116.
6 K.-G. Rosell, *J. Carbohydr. Chem.*, 7 (1988) 525–536.
7 A. Parfondry and A. S. Perlin, *Carbohydr. Res.*, 57 (1977) 39–49.
8 S. Takahashi, T. Fujimoto, B. M. Barua, T. Miyamoto, and H. Inagaki, *J. Polym. Sci., Polym. Chem. Ed.*, 24 (1986) 2981–2993.
9 J. Reuben, *Carbohydr. Res.*, 157 (1986) 201–213.
10 J. Reuben, *Carbohydr. Res.*, 161 (1987) 23–30.
11 Y. Tezuka, Y. Imai, M. Oshima, and T. Chiba, *Macromolecules*, 20 (1987) 2413–2418.
12 S. Takahashi, T. Fujimoto, T. Miyamoto, and H. Inagaki, *J. Polym. Sci., Polym. Chem. Ed.*, 25 (1987) 987–994.
13 K. Kamide and M. Saito, *Eur. Polym. J.*, 20 (1984) 903–914.
14 K. Kamide, K. Okajima, K. Kowsaka, and T. Matsui, *Polym. J.*, 19 (1987) 1405–1412.
15 T. Kondo and D. G. Gray, *J. Appl. Polym. Sci.*, in press.
16 B. Helferich and K. Koester, *Ber.*, 57 (1924) 587–589.
17 W. M. Hearon, G. D. Hiatt, and C. R. Fordyce, *J. Am. Chem. Soc.*, 65 (1943) 2449–2452.
18 D. Horton and E. K. Just, *Carbohydr. Res.*, 30 (1973) 349–357.
19 M. Yalpani, *Tetrahedron*, 41 (1985) 2957–3020.
20 K. Kageyama, A. Isogai, K. Iiyama, and J. Nakano, *Mokuzai Gakkaishi*, 31 (1985) 274–279; *Chem. Abstr.*, 103 (1985) 23 925g.
21 B. R. Harkness and D. G. Gray, *Macromolecules*, 23 (1990) 1452–1457.
22 H. G. Johns, *Methods Carbohydr. Chem.*, 6 (1972) 25–53.
23 A. Isogai, A. Ishizu, and J. Nakano, *J. Appl. Polym. Sci.*, 31 (1986) 341–352.
24 A. S. Perlin, B. Casu, and H. J. Koch, *Can. J. Chem.*, 48 (1970) 2596–2606.
25 *The Sadtler Standard Spectra*, Carbon-13 NMR Spectra, 82 (1984) 16 300.
26 I. Flétier, A. LeBorgne, and N. Spassky, *Polym. Bull.*, 24 (1990) 349–353.