

The Availability of Hydroxyl Groups in Native and Mercerized Cotton Celluloses

J. L. BOSE,* E. J. ROBERTS, and S. P. ROWLAND, *Southern Regional Research Laboratory, Southern Marketing and Nutrition Research Division, Agricultural Research Service, U.S. Department of Agriculture, New Orleans, Louisiana 70179*

Synopsis

The accessibilities of the hydroxyl groups of the D-glucopyranosyl units of slack mercerized grey yarn and of the same yarn restretched to its original length are compared with those of the original grey yarn, a purified printcloth, and a hydrocellulose. The study involved reactions of the celluloses with N,N-diethylaziridinium chloride under conditions which ensure minimum conversion of the reagent by hydrolysis to 2-hydroxyethyldiethylamine. Amylose was taken as a reference material in which the hydroxyl groups are assumed to be completely accessible. Selective accessibilities of the hydroxyl groups at C-6 and C-3 relative to those at C-2 were determined with the same reagent by a method whose development has been described earlier. The results of this study are expressed as fractions of the hydroxyl groups at C-2, C-3, and C-6 that are accessible to the reagent.

INTRODUCTION

Reactions of cotton cellulose are limited to those hydroxyl groups that are accessible to the reagents under the specific conditions employed for reaction. Under conditions most commonly involved in the chemical finishing of cotton or blend fabrics, there is little or no change in the crystallinity of the cotton, i.e., there is no penetration into or disruption of the crystalline regions.

From recent studies, a generally clear but incomplete concept of the accessibility of purified native cotton fibers (lattice I) has evolved. Approximately 40% of the D-glucopyranosyl units in the cotton fiber lie in regions which are potentially accessible without disruption of crystalline order.¹ Substantially less than 40% of the D-glucopyranosyl units is readily accessible.^{1,2} The accessible D-glucopyranosyl units are those on the surfaces of crystalline elementary fibrils having cross-sectional dimensions of 8×10 cellulose chains or $40 \times 50 \text{ \AA}$.^{2,3} The hydroxyl groups at the C-2, C-3, and C-6 positions of the D-glucopyranosyl units are selectively accessible, those at C-2 and C-3 being most and least accessible, respectively.⁴

* NRC-ARS Postdoctoral Research Associate.

This report is concerned with an estimation of actual accessibilities of the individual hydroxyl groups at C-2, C-3, and C-6 in the D-glucopyranosyl units of grey yarn, mercerized yarns, purified cotton printcloth, and hydrocellulose. These samples were chosen arbitrarily, but for both practical and fundamental perspective regarding differences among these types of cotton celluloses. The samples are interrelated as follows: the grey yarn was mercerized slack and slack with restretching to provide two samples; the purified cotton printcloth was hydrolyzed with 2.5*N* hydrochloric acid at reflux for 40 min to produce the hydrocellulose. The hydrocellulose is, in fact, "exemplar hydrocellulose" (EHC), which has been shown to possess a higher degree of lateral order than that of hydrocelluloses obtained in shorter or longer periods of hydrolysis.^{5,6}

EXPERIMENTAL

Materials

The grey yarn employed in this study was combed 40/2 yarn. It was slack mercerized with 23% sodium hydroxide at 30°C. A portion of the yarn was restretched to 100% of its original length before washing and drying.

The printcloth used was desized, scoured, and bleached 80 × 80 printcloth.

The exemplar hydrocellulose⁵ was obtained from Wiley-milled printcloth (20 mesh) by refluxing it with 2.5*N* hydrochloric acid for a period of 2/3 hr.

The reagent, *N,N*-diethylaziridinium chloride,⁴ was prepared by placing 2-chloroethyldiethylamine hydrochloride (17.2 g, 0.1 mole) in a 100-ml volumetric flask and making the volume up to the mark with 10% sodium hydroxide. The liberated free base rising to the top was immediately withdrawn and dissolved in water, whereupon it converts to the actual reagent required.

Reaction of *N,N*-Diethylaziridinium Chloride with Celluloses

The sample of cellulose to be reacted, 1 g, was chopped, where necessary, in a Wiley mill to pass through a 20-mesh sieve and suspended in 5 ml of a freshly prepared 0.5*M* solution of *N,N*-diethylaziridinium chloride, and filtered through a millipore filter to the point of 100% pick-up. The wet cake was suspended in 10 ml of sodium hydroxide solution of the required normality and allowed to react for 45 min. The detail has been described earlier.⁴

Hydrolysis of 2-Diethylaminoethyl Celluloses

The chemically modified cellulose (0.75 g) was dissolved in 72% sulfuric acid (7 ml) and hydrolyzed during stepwise dilution of the acid as described in detail earlier.⁷ The mixture of glucose and *O*-2-diethylaminoethyl-D-glucoses was isolated as "anhydrous" freeze-dried solids.

Removal of Glucose from 2-Diethylaminoethyl-D-Glucoses

The mixture of glucose and substituted glucoses obtained above was dissolved in water and subjected to fermentation as described previously.⁸ The fermentation was completed in 16–18 hr. The fermented solution was immediately filtered through celite to remove the yeast and was freeze dried overnight.

Distribution of Substituents in *O*-(2-Diethylaminoethyl)-D-Glucoses

The freeze-dried solid product from above was taken up in 2 ml of dry pyridine and allowed to reach equilibrium between the anomeric forms in 16 to 20 hr. A portion (0.5 ml) of the equilibrated pyridine solution was withdrawn and silylated by the method of Sweeley et al.⁹ and analyzed by gas-liquid chromatography according to the method described by Roberts and Rowland.¹⁰ The sample should be analyzed within a few hours or kept in a freezer and analyzed within a few days. The limitations of time indicated in the above experiments should be strictly followed to avoid the decomposition of the 6-*O*-isomer.

Kinetic Study of the Reaction Between Cellulose and the Aziridinium Form of Diethylaminoethyl Chloride

Series 1: 0.05M N,N-Diethylaziridinium Chloride and 0.1N NaOH

Four samples each of 0.81 g of cellulose (or amylose) were taken in 100-ml glass-stoppered conical flasks. Each sample was moistened (the process of moistening was facilitated with the help of a glass rod whenever necessary) with 5 ml of water and left for 1/2 hr for swelling. To each of these flasks was then added 20 ml of a solution prepared by mixing 50 ml of 0.2N NaOH and 10 ml of freshly prepared 0.5M N,N-diethylaziridinium chloride and making up to 80 ml with water. (This makes finally 0.05M N,N-diethylaziridinium chloride and 0.1N NaOH in the reaction mixture.) The flasks were shaken in a Warburg apparatus at 30°C for periods of 2/3 hr, 2 hr, 4 hr, and 6 hr., respectively. After the specified periods the flasks were taken out and immediately treated with 50 ml of ethanolic acetic acid (0.2N), filtered through a millipore filter (5.0 μ), washed with ethanol, and dried in air.

Series 2: 0.10M, N,N-Diethylaziridinium Chloride and 0.1N NaOH

The same procedure as in series 1 was followed, except that to each of the four flasks was added 20 ml of a solution prepared by mixing 50 ml of 0.2N NaOH and 20 ml of freshly prepared N,N-diethylaziridinium chloride and making up to 80 ml with water. (This makes finally 0.1M, N,N-diethylaziridinium chloride and 0.1N NaOH in the reaction mixture.)

RESULTS AND DISCUSSION

Accessibilities of the Hydroxyl Groups

The estimation of the accessibility of hydroxyl groups in various forms of cotton cellulose to *N,N*-diethylaziridinium chloride was based on the extent of reaction that occurred in the cotton cellulose compared to that which occurred in amylose. It is assumed that the hydroxyl groups of amylose are completely accessible.

In a 16-hr period, 1% of *N,N*-diethylaziridinium chloride is converted to 2-hydroxyethyldiethylamine by hydrolysis in an aqueous system. In the presence of base, which is essential for the reaction of *N,N*-diethylaziridinium chloride with cellulose in aqueous media, the formation of 2-hydroxyethyldiethylamine is substantially higher: 39% in a 16-hr period in 0.1*N* sodium hydroxide, 57% in 0.5*N*, 64% in 1.0*N*, 73% in 2.0*N*, 76% in 4.0*N*, and 85% in 6.0*N*. Thus, the reactions of *N,N*-diethylaziridinium chloride with celluloses were conducted in 0.1*N* sodium hydroxide and were limited to a 6-hr period of reaction.

To limit the extent of reactions of *N,N*-diethylaziridinium chloride with the various cotton celluloses to low levels, *N,N*-diethylaziridinium chloride was employed at 0.05*M* and 0.10*M* initial concentrations. These reactions introduced sufficient nitrogen for reliable analysis, and yet the highest extents of reaction for the celluloses and for the amylose have involved only about 2% and 8%, respectively, of the total hydroxyl groups of the polysaccharides. Thus, the reactions can be expected to result predominantly in monosubstitution of *D*-glucopyranosyl units of the polysaccharides.

The course of development of 2-diethylaminoethyl substituents in amylose and the various forms of cotton cellulose is shown in Figures 1 and 2. The progression of nitrogen content with time of reaction for each type of composition is quite similar with 0.05*M*, *N,N*-diethylaziridinium chloride (Fig. 1) and 0.10*M* reagent (Fig. 2), although the extents of reaction are approximately 80% higher from the latter reactions.

The values of accessibilities of the hydroxyl groups of the various cotton celluloses calculated on the basis of the curves in Figure 1 are analogous to those from the corresponding curves in Figure 2. The averages of these values are summarized in Table I for reactions of $\frac{2}{3}$ -hr and 6-hr durations. It is interesting that the values of accessibilities at these two points (and the points in between) are alike.

The values of accessibilities described above were compared with those obtained on similar compositions by formylation with 90% formic acid. The results of formylation are unpublished data of Brannan, Mason, and Rowland¹¹; the method is that described by Rowland and Pittman¹²; white dextrin was the completely accessible standard. The values of accessibilities to 90% formic acid are summarized in Table I for a 24-hr duration of reaction at 30°C. These values are very similar to those

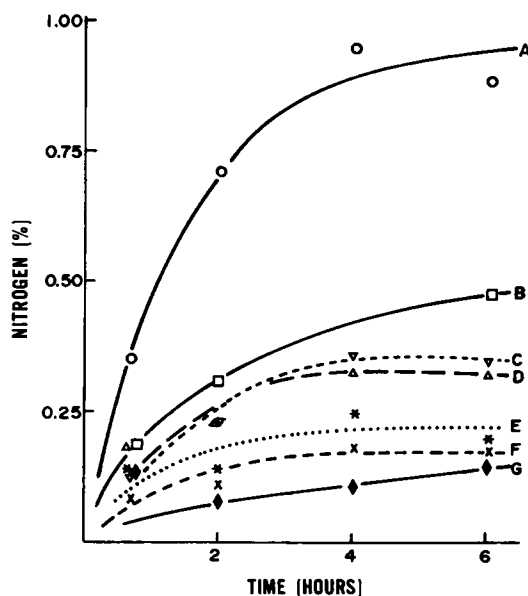


Fig. 1. Bound nitrogen as a function of duration of reaction of 0.05*M*, *N,N*-diethylaziridinium chloride with amylose (A) and celluloses: (B) decrystallized cotton; (C) grey yarn mercerized slack restretched; (D) grey yarn mercerized slack; (E) chopped fibers from printcloth passing 80 mesh screen; (F) 80 × 80 printcloth in small pieces; (G) hydrocellulose.

TABLE I
Fraction of Total Hydroxyl Groups Accessible in Cotton Cellulose^a

Cellulose	Reactions with <i>N,N</i> -diethylaziridinium chloride		Formylation 16-hr duration
	² / ₃ -hr duration	6-hr duration	
Decrystallized cotton ^b	0.51	0.48	0.84
Grey yarn, mercerized slack	0.32	0.33	—
Grey yarn, mercerized slack-restretched	0.30	0.34	0.35
80-mesh chopped printcloth ^c	0.25	0.20	—
Printcloth ^c	0.21	0.19	0.19
Hydrocellulose	0.12 ^d	0.15 ^d	ca. 0.14 ^e

^a Fraction of reaction in cellulose relative to amylose as a standard of complete accessibility.

^b Ball milled: vibratory ball mill for 120 min.

^c Desized, scoured, bleached printcloth in small pieces or put through a Wiley mill and 80-mesh screen.

^d This is the "exemplar hydrocellulose" described in a preceding report: printcloth chopped to 20-mesh and hydrolyzed in 2.5*N* hydrochloric acid at reflux for 40 min.

^e This value is estimated for hydrocelluloses on the basis of results reported by Nair and Mehta.¹⁵

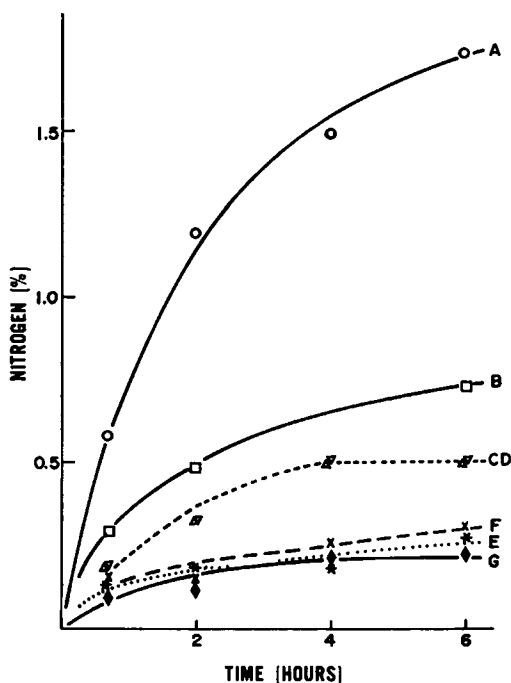


Fig. 2. Bound nitrogen as a function of duration of reaction of 0.10M N,N-diethylaziridinium chloride with amylose and celluloses. Same designations as for Fig. 1.

obtained with N,N-diethylaziridinium chloride; decrystallized cotton cellulose is the exception. The 84% accessibility of decrystallized cotton via formic acid is close to the values reported earlier (i.e., 89%, 90%).¹³ It may be concluded that the lower accessibility of the decrystallized cotton to N,N-diethylaziridinium chloride is due to a redevelopment of order in the presence of the 0.10N base.¹⁴ The value of accessibility of hydrocellulose to formic acid is estimated from the data of Nair and Mehta.¹⁵ This falls in line with the value determined via reaction with N,N-diethylaziridinium chloride.

Accessibilities of Hydroxyl Groups at C-6 and C-3 Relative to those at C-2

The determination of the selective accessibilities of the hydroxyl groups at C-2, C-3, and C-6 of the D-glucopyranosyl units of cellulose was described in detail earlier.⁴ Briefly, it involves measurement of the distribution of substituents formed under a specific set of reaction conditions, expression of the results as ratios of 6-O/2-O substituents and 3-O/2-O substituents, and division of these ratios by the corresponding ratios of substituents resulting from reaction under the same conditions with a cellulose in which all three types of hydroxyl groups are equally available for reaction.

The distribution of substituents resulting from the reactions of N,N-diethylaziridinium chloride with various crystalline celluloses in 0.5N

TABLE II
Distribution of Substituents in Cotton Celluloses

Cellulose	Normality of base for reaction	Nitrogen content, %	<i>O</i> -(2-Diethylamino)ethyl cellulose			
			2- <i>O</i> - ^a	3- <i>O</i> - ^a	6- <i>O</i> - ^b	3- <i>O</i> - ^b
Grey yarn	1.0	0.15	2.50	0.33	0.40	0.13
Grey yarn mercerized slack	0.5	0.14	2.25	0.57	0.44	0.25
	1.0	0.16	2.85	0.78	0.35	0.27
Grey yarn mercerized slack-restretched	0.5	0.13	2.10	0.55	0.48	0.26
	1.0	0.13	3.35	0.93	0.30	0.28
Printcloth ^c	0.5	0.03	2.55	0.25	0.39	0.10
	1.0	0.05	2.28	0.32	0.44	0.14
Hydrocellulose ^d	0.5	0.10	3.80	0.41	0.26	0.11
	1.0	0.10	3.11	0.32	0.32	0.10

^a Relative to 1.00 for the 6-*O*-position.

^b Relative to 1.00 for the 2-*O*-position.

^c From previous publications.^{4,5}

^d From previous publications.^{5,6}

TABLE III
Accessibilities of Hydroxyl Groups at C-6 and C-3 Relative to those at C-2 in Cotton Celluloses^a

Cellulose	$[\text{O}_6\text{H}]_a/[\text{O}_2\text{H}]_a$			$[\text{O}_3\text{H}]_a/[\text{O}_2\text{H}]_a$		
	in 0.5 <i>N</i> base	in 1.0 <i>N</i> base	Average	in 0.5 <i>N</i> base	in 1.0 <i>N</i> base	Average
	Grey yarn	—	0.70	—	—	0.35
Grey yarn, mercerized slack	0.73	0.77	0.75 ^b	0.71	0.68	0.70 ^b
Grey yarn mercerized slack-restretched	0.63	0.84	0.69	0.74	0.70	0.72
Printcloth	0.82	0.76	0.77 ^c	0.27	0.37	0.32 ^c
Hydrocellulose	0.55	0.55	0.55	0.28	0.29	0.29

^a These values are obtained by dividing the 6-*O*/2-*O* and 3-*O*/2-*O* ratios of distributions of substituents (Table II) by values of the corresponding ratios resulting from reactions involving cellulose in which all three of the hydroxyl groups are equally accessible. These values are 0.48 and 0.57 for the 6-*O*/2-*O* ratio in 0.5*N* and 1.0*N* base, respectively, and 0.38 and 0.37 for the 3-*O*/2-*O* ratio in 0.5*N* and 1.0*N* base, respectively.

^b Previously published values⁴ on slack mercerized printcloth were

$$[\text{O}_6\text{H}]_a/[\text{O}_2\text{H}]_a = 0.59, \quad [\text{O}_3\text{H}]_a/[\text{O}_2\text{H}]_a = 0.63.$$

^c Average based on data from reactions in 2*N* sodium hydroxide in addition to that listed.

and 1.0*N* sodium hydroxide is summarized in Table II. The values of selective accessibilities are shown in Table III. The selective accessibilities of the hydroxyl groups at C-6 and C-3 in fibers of grey yarns are little different from those of fibers of desized, scoured, bleached printcloth. The more selective accessibilities of the hydroxyl groups of hydrocellulose are quite evident from values in the table; these values have

been discussed relative to those of unmodified cotton fibers in an earlier publication.⁵

If there is a difference in the selective accessibilities of hydroxyl groups in slack mercerized and slack mercerized-restretched yarns, it is small and indistinguishable in these measurements. These results are quite comparable to those determined earlier for the fibers of slack mercerized printcloth (see footnote b of Table II). On the other hand, the selective accessibilities of the hydroxyl groups in these mercerized cotton celluloses are quite different, primarily in the values for the hydroxyl groups at C-3, from those for the original cotton celluloses (i.e., the grey yarn or the desized, scoured, bleached printcloth).

Estimates of Actual Accessibilities of Hydroxyl Groups at C-2, C-3, and C-6

Values of selective accessibilities of the hydroxyl groups at C-6 and C-3 relative to those at C-2 (as in Table III) may be converted to proportions of the three types of hydroxyl groups which are accessible in each of the celluloses. These values, which are listed in Table IV, provide the basis for an estimation of the actual accessibilities of each type of hydroxyl group, i.e., fraction of hydroxyl groups available at C-2 multiplied by fraction of total hydroxyl groups that is accessible. These specific accessibilities of the hydroxyl groups at C-2, C-3, and C-6 in the D-glucopyranosyl units of the various celluloses are also summarized in Table IV.

The representation in Figure 3 portrays what is less readily evident in the numbers, i.e., that the surfaces of crystalline cellulose, such as hydrocellulose, provide a predominance of hydroxyl groups at C-2 for reaction; that this predominance is similar but less pronounced in the case of the natural fibers, such as in grey yarn or desized, scoured, bleached printcloth; and that an equal availability of all three types of hydroxyl groups is approached most closely in the mercerized fibers, but even in these cases, the hydroxyl group at C-2 is approximately 30% more available than each of the other two for reaction.

TABLE IV
Accessibilities of Cotton Celluloses

Cellulose	Fraction of total hydroxyl group accessible ^a	Proportion of hydroxyl groups accessible at			Specific accessibilities of hydroxyl groups at		
		C-2	C-3	C-6 ^b	C-2	C-3	C-6 ^a
Grey yarn	0.20 ^c	0.49	0.17	0.34	0.10	0.03	0.07
Grey yarn mercerized slack	0.33	0.41	0.28	0.31	0.14	0.09	0.10
Grey yarn mercerized slack-restretched	0.34	0.41	0.30	0.29	0.14	0.10	0.10
Printcloth	0.19	0.48	0.15	0.37	0.09	0.03	0.07
Hydrocellulose	0.15	0.54	0.16	0.30	0.08	0.02	0.05

^a The fraction of the total of this kind of unit which is accessible.

^b Fraction of accessible hydroxyl groups that is calculated for specific hydroxyl groups.

^c Average of values for chopped fibers and printcloth.

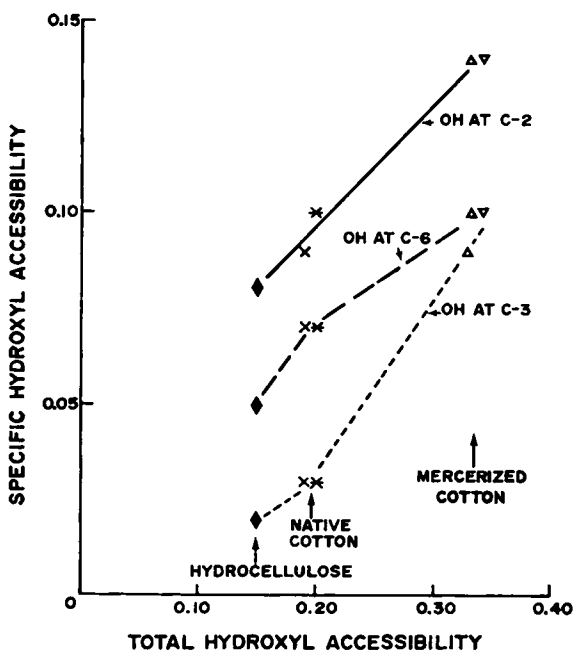


Fig. 3. Specific accessibilities of hydroxyl groups at C-2, C-3, and C-6 for various cotton celluloses as a function of total hydroxyl accessibilities.

Acknowledgment is made to Mr. A. L. Murphy for the samples of yarn, mercerized yarn, and mercerized-restretched yarn.

References

1. S. P. Rowland and E. R. Cousins, *J. Polym. Sci. A-1*, **4**, 793 (1966).
2. R. Jeffries, J. G. Roberts, and R. N. Robinson, *Text. Res. J.* **38**, 234 (1968).
3. S. Haworth, D. M. Jones, J. G. Roberts, and B. F. Sagar, *Carbohydrate Res.* **10**, 1 (1969).
4. S. P. Rowland, E. J. Roberts, and C. P. Wade, *Text. Res. J.*, **39**, 530 (1969).
5. S. P. Rowland, E. J. Roberts, and J. L. Bose, *J. Polym. Sci., A-1*, **9**, 1431 (1971).
6. S. P. Rowland, E. J. Roberts, J. L. Bose, and C. P. Wade, *J. Polym. Sci., A-1*, **9**, 1623 (1971).
7. S. P. Rowland, V. O. Cirino, and A. L. Bullock, *Can. J. Chem.*, **44**, 1051 (1966).
8. E. J. Roberts and S. P. Rowland, *Can. J. Chem.*, **47**, 1571 (1969).
9. C. C. Sweeley, R. Bentley, B. Makita, and W. W. Wells, *J. Amer. Chem. Soc.*, **85**, 2497 (1963).
10. E. J. Roberts and S. P. Rowland, *Can. J. Chem.*, **45**, 261 (1967).
11. M. A. F. Brannan, J. S. Mason, and S. P. Rowland, unpublished results.
12. S. P. Rowland and P. F. Pittman, *Text. Res. J.*, **35**, 421 (1965).
13. I. L. Wadehra, R. St. J. Manley, and D. A. I. Goring, *J. Appl. Polym. Sci.*, **9**, 2634 (1965).
14. I. L. Wadehra and R. St. J. Manley, *J. Appl. Polym. Sci.*, **9**, 2627 (1965).
15. G. P. Nair and P. C. Mehta, *Proceedings of the 7th Tech. Conf. ATIRA, Section B*, Ahmedabad Textile Industry's Research Assoc., India, 1965, pp. 61-71.

Received July 20, 1971