

SYNTHESIS OF THE 6-ALDEHYDO DERIVATIVE OF CELLULOSE, AND A MASS-SPECTROMETRIC METHOD FOR DETERMINING POSITION AND DEGREE OF SUBSTITUTION BY CARBONYL GROUPS IN OXIDIZED POLYSACCHARIDES*†

DAVID M. CLODE AND D. HORTON‡

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 (U. S. A.)

(Received April 30th, 1971)

ABSTRACT

A position-specific method is described for the introduction of C-6 aldehyde functionality into cellulose (1) at two levels of degree of substitution (d.s.); the procedure involves photolysis of a 6-azido-6-deoxy derivative. A mass-spectrometric method for determining the d.s. of the 6-aldehydo derivative (7) of cellulose is also described.

INTRODUCTION

Previous reports from this laboratory have described the photolysis of primary azido derivatives of sugars as an excellent synthetic route for the preparation of a wide range of ω -aldehydo derivatives of protected and unprotected glycosides¹⁻⁴. The photolysis of analogous derivatives of such polysaccharides as amylose^{5,6} and starch⁶ has also been shown to provide a convenient route for the preparation of the respective 6-aldehydo derivative, and a preliminary report¹ of an application to the cellulose system has been given. The present paper describes in detail the photolysis of the 6-azido-6-deoxy derivative (8) of cellulose (1), at two levels of d.s., and characterization of the resultant 6-aldehydo derivative** (7) by formation of the (2,4-dinitrophenyl)hydrazone (10) and by a mass-spectrometric method.

DISCUSSION

6-Azido-6-deoxycellulose acetates of low d.s. by azide (8a), and of high d.s. by azide (8b), were prepared by two different routes.

Cellulose (1) was acetylated under conditions⁷ expected to lead to a product (4) having a d.s. of ~ 2.8 and having the remaining free hydroxyl groups situated

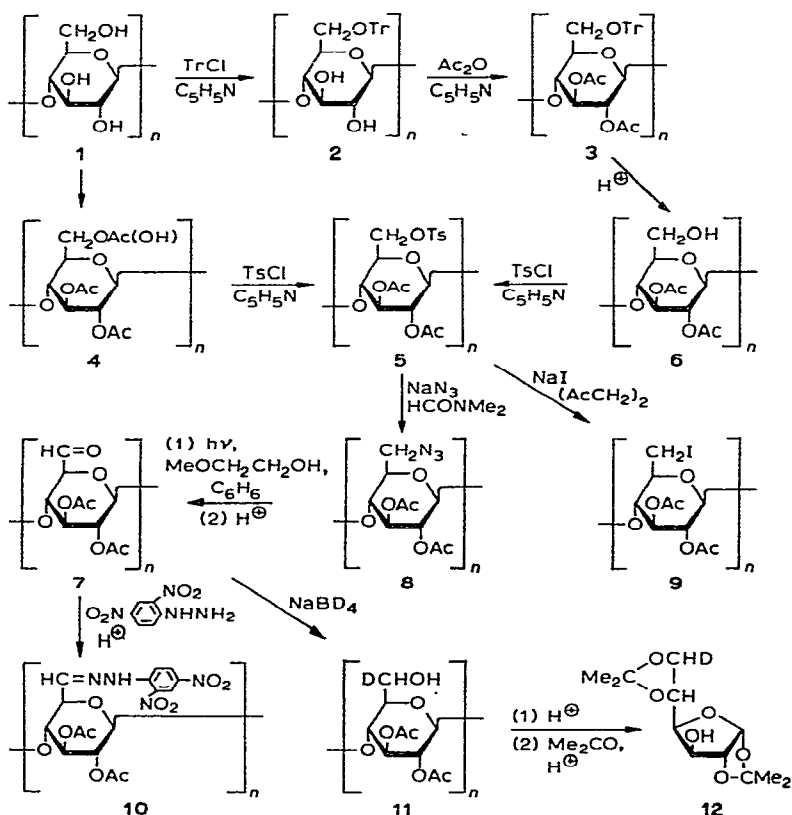
*Supported, in part, by the Agricultural Research Service, U. S. Department of Agriculture, Grant No. 12-14-100-9201(71) (The Ohio State University Research Foundation Project 2573) administered by the Northern Marketing and Nutrition Research Division, Peoria, Illinois, U. S. A.

†For a preliminary report, see Ref. 1.

‡To whom inquiries should be addressed.

**Strictly, a β -D-(1 \rightarrow 4)-linked copolymer of D-glucosylhexodialdo-1,5-pyranose and D-glucose residues.

mainly at C-6. *p*-Toluenesulfonylation of this acetate (**4**) gave an acetylated *O*-*p*-tolylsulfonfylcellulose (**5a**) having a d.s. by the sulfonate group of ~ 0.25 . The sulfonate groups were shown to be located almost exclusively at C-6, because they were almost completely replaced by iodine when **5a** was treated with sodium iodide in 2,4-pentanedione⁸, and an acetylated 6-deoxy-6-iodocellulose (**9a**) having a d.s. by the iodo group of ~ 0.25 was obtained. Treatment of the acetylated 6-*O*-*p*-tolylsulfonfylcellulose (**5a**) with sodium azide in *N,N*-dimethylformamide led to displacement of the sulfonyloxy groups and formation of acetylated 6-azido-6-deoxycellulose (**8a**) of d.s. ~ 0.25 by the azide group.



The degrees of substitution (d.s.) of the cellulose derivatives were determined from the data of elementary analyses by use of the FORTRAN computer program of Horton and Pardoe⁹. This program computes analytical data for a range of d.s. values for polysaccharide derivatives containing two substituents, and matches the percentages calculated to those obtained experimentally.

In another route, which gave 6-azido-6-deoxycellulose acetate (**8b**) of high d.s. by the azido group, cellulose (**1**) was treated with chlorotriphenylmethane¹⁰ and the resulting 6-*O*-tritylcellulose (**2**), of d.s. ~ 1.0 , was acetylated. Complete acetylation

was found difficult to accomplish, and the resulting 2,3-di-*O*-acetyl-6-*O*-tritylcellulose (**3**) had a d.s. by the acetyl group of only 1.7. Complete hydrolysis of the trityl groups was effected by using a mixture of acetic and hydrochloric acids⁸, and analysis for the acetyl group confirmed that no hydrolysis of acetyl groups had occurred. The 2,3-di-*O*-acetylcellulose (**6**) was then *p*-toluenesulfonylated under conventional conditions to give an acetylated 6-*O*-*p*-tolylsulfonylcellulose (**5b**) of d.s. 0.62 by the sulfonate group. A second *p*-toluenesulfonylation of a small amount of this material did not substantially increase the sulfur content of the product, indicating that all the available primary hydroxyl groups in **6** had been substituted. More-vigorous conditions would probably be necessary to sulfonylate the secondary hydroxyl groups. Evidently, some migration of acetyl groups from secondary to primary hydroxyl groups occurred during the detritylation step. The use of acetic acid-hydrogen bromide for the hydrolysis of the trityl group would probably minimize the acetyl migration. The extent of *p*-toluenesulfonylation on primary and secondary hydroxyl groups was again determined by the iodination method⁸. It was found that sulfonylation of **5b** had occurred almost exclusively at O-6, because a 6-deoxy-6-iodocellulose acetate (**9b**) of d.s. 0.6 by the iodo group was obtained. Treatment of the acetylated 6-*O*-*p*-tolylsulfonylcellulose (**5b**) with sodium azide in *N,N*-dimethylformamide gave acetylated 6-azido-6-deoxycellulose (**8b**) of d.s. 0.68 by the azido group.

Photolysis of the 6-azido-6-deoxy derivatives (**8a**, **8b**), followed by mild hydrolysis, gave the 6-aldehyde derivatives (**7a**, **7b**) as Fehling-positive solids. The low-d.s. product **7a** contained no nitrogen, and the high-d.s. product **7b** contained a small proportion (0.92%). By analogy with previous work¹¹⁻¹³, the photolysis of the azide is presumed to proceed *via* an intermediate nitrene ($R-CH_2N:$) that rearranges, by a 1,2-hydrogen migration, to give an imine intermediate converted by very mild hydrolysis with acid into the expected aldehyde.

Two methods were then employed to determine the extent (degree of substitution) to which aldehyde groups were incorporated into the two polymers. For the acetylated 6-aldehydocellulose (**7a**) having low d.s. by the aldehyde group, the (2,4-dinitrophenyl)hydrazone (**10a**) was prepared, and found to have a d.s. of 0.2 in the hydrazone group, as calculated from the nitrogen analysis. However, a convenient and more reliable alternative method for determining d.s. by the carbonyl group was by reduction of the 6-aldehyde derivative (**7a**) with sodium borodeuteride, hydrolysis of the resulting 6-deuterioglucose acetate (**11a**), and preparation of a derivative suitable for determining, by mass spectrometry, the position and extent of incorporation of deuterium. The derivative selected in this instance was 1,2:5,6-di-*O*-isopropylidene- α -D-glucopyranose. The ratio of peak intensities for the deuterated and non-deuterated derivatives (after correction for the natural abundance of ¹³C, ²H, and ¹⁷O) was then expected to give the percentage of deuterated material in the mixture, and, thus, in the parent polymer. Examination by mass spectrometry of the crystalline 1,2:5,6-di-*O*-isopropylidene- α -D-glucopyranose-6-*d* (**12a**), obtained by acetonation of the acid-hydrolyzed 6-deuterioglucose acetate (**11a**) of low d.s., showed ions having *m/e* 245, 187, and 101 (known¹⁴ to contain the C-6 moiety in the

non-deuterated material), accompanied by less-intense peaks one mass unit higher (m/e 246, 188, and 102). From the ratio of the peak intensities for the deuterated and non-deuterated fragments, as already described, the d.s. by isotopic replacement in the polymer **11a** was calculated to be 0.19 (see Table I-A).

The d.s. by aldehyde in the 6-aldehydocellulose acetate (**7b**) of high d.s. was likewise calculated by formation of a (2,4-dinitrophenyl)hydrazone (**10b**) (giving a d.s. value of 0.45), and also by the mass-spectrometric method (giving a d.s. value of 0.43, see Table I-B).

CONCLUSIONS

The foregoing reactions provide a convenient route for the preparation of acetylated 6-aldehydocellulose of various degrees of substitution by the aldehyde group. These products, and such labeled derivatives as those obtainable by reduction of the aldehyde with sodium borotritide, may be useful in studies on cellulolytic enzymes. They also open up the possibility of novel applications of cellulosic materials in forming modified polymers by use of various crosslinking procedures with the aldehyde groups on the chain. The borodeuteride reduction-mass spectrometry procedure, with the use of 1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose and other derivatives whose mass-spectral fragmentations are known, provides a general method for determining on a microscale the position and extent of carbonyl-group incorporation into specifically or non-specifically oxidized polysaccharides.

EXPERIMENTAL

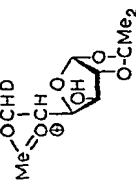
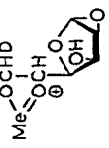
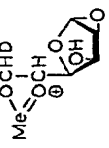
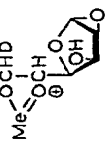
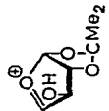
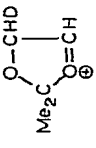
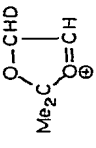
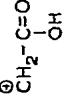

General methods. — Infrared spectra were recorded with a Perkin-Elmer Model 137 i.r. spectrometer. Mass spectra were measured with an A.E.I. MS-9 double-focusing, high-resolution spectrometer with an accelerating potential of 8 kV, an ionizing potential of 70 eV, and a source temperature of 250°. Elemental analyses were made by W. N. Rond. T.l.c. was conducted on Silica Gel G (E. Merck, Darmstadt, Germany) activated at 110°, and indication was effected with sulfuric acid. Column chromatography was performed with Silica Gel 7734 (70–325 mesh ASTM, E. Merck).

Irradiations were conducted with unfiltered light from a 450-W Hanovia Type L mercury-arc lamp (Hanovia Lamp Division, Engelhard Inc., Newark, N. J.), Model 679A, having a 4.5-inch arc. The lamp was placed in a water-cooled, quartz immersion-well (Hanovia Model 19431), and the whole assembly was mounted in a Pyrex reaction-vessel. The most suitable irradiation time was ascertained by periodic sampling and examination by i.r. spectroscopy.

Acetylated 6-O-p-tolylsulfonylcellulose of low d.s. at O-6 (5a). — *p*-Toluene-sulfonyl chloride (20 g) was added to a solution of cellulose acetate (4, 10 g) {prepared by a standard procedure⁷ from Whatman No. 1 cellulose powder (**1**); *Anal.*¹⁵ Calc. for $[C_6H_{7.2}O_5(CH_3CO)_{2.8}]_n$: (CH_3CO) , 43.1. Found: (CH_3CO) , 43.0} in anhydrous

TABLE I

MASS-SPECTRAL DATA FOR 1,2:5,6-DI-O-ISOPROPYLIDENE- α -D-GLUCOFURANOSE-6-d

m/e	Fragment	Relative abundances ^a		Abundance of natural isotopes (² H + ¹³ C + ¹⁷ O), %	Corrected relative abundances ^a		Percentage of deuterated compound in mixture ^a		Calc. d.s. by aldehyde in parent polymer (7) ^a	
		A	B		A	B	A	B	A	B
246		0.65	0.65		0.42	0.555				
245		1.8	0.75	12.69	1.8	0.75	19	42.5	0.19	0.43
188		0.25	0.3		0.176	0.268				
187		0.8	0.35	9.23	0.8	0.35	18	43	0.18	0.43
159		0.3	0.2							
102		1.2	1.75		0.964	1.62				
101		4.1	2.3	5.76	4.1	2.3	19	41	0.19	0.41
59			5.5							
43		10	10							

^aSeries A, low d.s. at C-6; series B, high d.s. at C-6.

pyridine (100 ml), and the mixture was stirred for 4 h at 25°. The mixture was then diluted with acetone (50 ml), and poured into ethanol (600 ml). The precipitate was filtered off, washed with ethanol, and dried in a vacuum oven at 50°, to give a white, fluffy product; yield 9.8 g (87%). A sample was dissolved in acetone and dialyzed against running water for 36 h, and the non-dialyzable portion was freeze-dried to give an ash-free product.

Anal. Calc. for $[C_6H_7O_2(OCOCH_3)_{2.7}(OSO_2C_7H_7)_{0.25}(Cl)_{0.05}]_n$: C, 50.10; H, 5.35; Cl, 0.56; S, 2.54. Found: C, 49.96; H, 5.31; Cl, 1.17; S, 2.68.

6-O-Tritylcellulose¹⁰ (2). — This derivative was prepared from cellulose (1) by the method of Green¹⁰. It contained 59.2% of trityl groups, as determined by the procedure of Green¹⁰, corresponding to a d.s. of 0.96.

2,3-Di-O-acetyl-6-O-tritylcellulose (3). — Acetic anhydride (100 ml) was added to a solution of 6-O-tritylcellulose (2, 70 g) in anhydrous pyridine (1 liter), and the mixture was stirred for 20 h at 80°. The solution was diluted with methanol (100 ml), and poured into ethanol (3 liters), and the light-brown precipitate formed was filtered off. The solid was dispersed in more ethanol, and the suspension filtered; after repeating this procedure twice more, the product was dried in a vacuum oven at 50°, to give a light-brown solid; yield 77 g (93%).

Anal. Calc. for $[C_6H_7.3O_{2.3}(OCOOH_3)_{1.7}(OC(C_6H_5)_3)_{1.0}]_n$: C, 71.69; H, 5.76. Found: C, 71.97; H, 5.72.

2,3-Di-O-acetylcellulose (6). — A mixture of acetic acid (84 ml) and concentrated hydrochloric acid (42 ml) was added with stirring to a suspension of 2,3-di-O-acetyl-6-O-tritylcellulose (3, 60 g) in acetic acid (420 ml), and the mixture was kept for 1 h at room temperature⁸. The mixture was then diluted with acetone (150 ml), and the product was precipitated by adding methanol (3 liters), which was also used to wash the product. The dried product was redissolved in aqueous acetone, and precipitated by methanol, to give a light-brown product, yield 19 g (63%), which showed no content of trityl groups.

Anal. Found: acetyl. 31.63, corresponding to a d.s. of 1.72.

Acetylated 6-O-p-tolylsulfonylcellulose of high d.s. at O-6 (5b). — *p*-Toluenesulfonyl chloride (30 g, ~2 equivs.) was added to a solution of 2,3-di-O-acetylcellulose (6, 15 g) in anhydrous pyridine (250 ml). The mixture was stirred for 19 h at room temperature, and then diluted with acetone (100 ml). The product was precipitated by ethanol (2.5 liters), filtered off, washed with ethanol, and dried in a vacuum oven at 50°, to give 5b as a light-brown solid; yield 20.7 g (97%).

Anal. Calc. for $[C_6H_7.56O_{2.56}(OCOCH_3)_{1.7}(OSO_2C_7H_7)_{0.62}(Cl)_{0.12}]_n$: C, 49.79; H, 5.17; Cl, 1.29; S, 6.00. Found: C, 50.15; H, 5.32; Cl, 1.50; S, 5.95.

A second *p*-toluenesulfonylation of a small amount of this material did not substantially increase the sulfur content of the product.

Iodide exchange-reactions with the sulfonylated derivatives⁸ 5a and 5b. — Sodium iodide (1 g) was added to a solution of the *p*-tolylsulfonyl derivative (5a or 5b, 1 g) in either 2,4-pentanedione or 2,5-hexanedione (30 ml), and the mixture was stirred for 2 h at 120°. The product was precipitated by water, and washed with more water,

filtered off, and dissolved in acetone. The solution was then dialyzed against running water for 24 h. The non-dialyzable portion was freeze-dried, and then further dried in a vacuum oven at 50°, to give the iodinated derivative (**9a** or **9b**) as a fluffy product.

From **5a**, there was obtained 6-deoxy-6-iodocellulose acetate of low d.s. at C-6 (**9a**), yield 0.72 g (73%).

Anal. Calc. for $[C_6H_7O_2(OCOCH_3)_{2.7}(OSO_2C_7H_7)_{0.06}(I)_{0.24}]_n$: C, 45.60; H, 5.03; I, 9.79; S, 0.62. Found: C, 45.50; H, 5.70; I, 10.58; S, 0.70.

From **5b**, there was obtained acetylated 6-deoxy-6-iodocellulose of high d.s. at C-6 (**9b**); yield 0.88 g (92%).

Anal. Calc. for $[C_6H_{7.58}O_{2.58}(OCOCH_3)_{1.7}(OSO_2C_7H_7)_{0.12}(I)_{0.6}]_n$: C, 38.66; H, 4.28; I, 24.0; S, 1.21. Found: C, 39.15; H, 4.35; I, 24.48; S, 1.39.

Azide exchange-reactions with 5a and 5b. — Sodium azide (20 g) was added to a solution of the *p*-tolylsulfonyl derivative (**5a** or **5b**, 5 g) in anhydrous *N,N*-dimethylformamide (300 ml). The mixture was stirred for 72 h at 110°, and then poured into water. The precipitate formed was filtered off, washed well with water, and dissolved in acetone. The solution was dialyzed against running water for 48 h. In an alternative procedure, the reaction mixture was allowed to cool, diluted with water, and then dialyzed against running water for 48 h. The non-dialyzable portion was freeze-dried, and further dried in a vacuum oven at 50° to give the product.

Starting from **5a**, acetylated 6-azido-6-deoxycellulose of low d.s. at C-6 (**8a**) was obtained as a light-brown solid; yield 2.13 g (47%); λ_{\max}^{KBr} 4.73 (N_3) and 5.72 μm ($C=O$).

Anal. Calc. for $[C_6H_7O_2(OCOCH_3)_{2.7}(N_3)_{0.25}(OSO_2C_7H_7)_{0.05}]_n$: C, 48.70; H, 5.35; N, 3.63; S, 0.55. Found: C, 48.20; H, 5.65; N, 3.35; S, 0.67.

Starting from **5b**, acetylated 6-azido-6-deoxycellulose of high d.s. at C-6 (**8b**) was obtained as a brown solid; yield 3.4 g (89%); λ_{\max}^{KBr} 4.73 (N_3) and 5.72 μm ($C=O$).

Anal. Calc. for $[C_6H_{7.6}O_{2.6}(OCOCH_3)_{1.7}(N_3)_{0.68}(OSO_2C_7H_7)_{0.02}]_n$: C, 45.16; H, 5.10; N, 11.27; S, 0.25. Found: C, 44.85; H, 5.02; N, 11.03; S, 0.34.

Photolysis of the 6-azido-derivatives (8a and 8b). — The acetylated 6-azido derivative (**8a** or **8b**, 0.5 g) was dissolved in 5:1 2-methoxyethanol–benzene (180 ml), and photolyzed under nitrogen for 6 h at 20°, with unfiltered light from a mercury arc¹⁶. The resulting suspension was concentrated under diminished pressure to ~50 ml, *m* hydrochloric acid (50 ml) was added, and the mixture was stirred for 75 min at room temperature, and then dialyzed against running water for 16 h. The nondialyzable portion was freeze-dried, to give the 6-aldehydo derivative (**7**) as an ash-free, Fehling-positive solid. Acetylated 6-aldehydocellulose of low d.s. in the C-6 group (**7a**) was obtained from **8a**, as a white solid, free from nitrogen. Acetylated 6-aldehydocellulose of high d.s. in the C-6 group (**7b**), prepared from **8b**, was a light-brown solid, and contained a small proportion of nitrogen (Found: N, 0.92).

A solution of (2,4-dinitrophenyl)hydrazine (50 mg for **7a**, and 100 mg for **7b**) in 2-methoxyethanol (20 ml) was added to a solution of the aldehydo derivative (100 mg) in 2-methoxyethanol (20 ml), and *m* hydrochloric acid (3 ml) was added. The mixture was stirred for 16 h at room temperature, and the dark-red solution was then

dialyzed against running water for 72 h. The non-dialyzable portion was freeze-dried, and further dried in a vacuum oven at 50°, to give the (2,4-dinitrophenyl)hydrazone (**10**) as an orange solid. T.l.c. (4:1 dichloromethane–ethyl acetate) did not show a spot corresponding to that shown by a sample of (2,4-dinitrophenyl)hydrazine.

Anal. (for **10a**, prepared from **7a**). Calc. for $[C_{3.1}H_{4.2}O_{2.1}(CHOCOCH_3)_{2.7}(C=NNHC_6H_3(NO_2)_2)_{0.2}]_n$: N, 3.62. Found: N, 3.71.

Anal. (for **10b**, prepared from **7b**). Calc. for $[C_{3.85}H_{5.7}O_{2.85}(CHOCOCH_3)_{1.7}(C=NNHC_6H_3(NO_2)_{20.45})_n$: N, 8.04. Found: N, 8.46.

Reduction of the 6-aldehydo derivatives (7a and 7b). — A solution of sodium borodeuteride (200 mg) in water (50 ml) was added to a suspension of the acetylated 6-aldehydocellulose (**7a** or **7b**, 0.4 g) in water (50 ml), and the mixture was stirred for 16 h at room temperature. More sodium borodeuteride (200 mg) was then added, and the mixture was stirred for a further 8 h, and then dialyzed for 72 h against running water. The non-dialyzable portion was freeze-dried, to give the acetylated 6-deuterio derivative (**11**) of cellulose as a fluffy solid that gave a negative Fehling test.

*1,2:5,6-Di-O-isopropylidene- α -D-glucofuranose-6-d (**12**).* — The 6-deuterio derivative (**11a** or **11b**, ~250 mg) was stirred for 20 h at 110° with 0.5 M sulfuric acid (30 ml), and the resulting suspension was made neutral with barium carbonate. The mixture was then filtered through Celite, and the filtrate evaporated under diminished pressure to a solid. T.l.c. (1:1 ethyl acetate–ethanol) showed one main component, corresponding to a reference sample of D-glucose. To this material were added acetone (20 ml), concentrated sulfuric acid (0.05 ml), and anhydrous copper(II) sulfate (0.5 g), and the mixture was shaken for 20 h at room temperature, made neutral by the addition of lead carbonate and water, and filtered. The filtrate was evaporated under diminished pressure, and the resulting syrup was partitioned between dichloromethane and water. The organic layer was dried (magnesium sulfate) and evaporated under diminished pressure to a syrup that crystallized on standing. T.l.c. (1:1 dichloromethane–ethyl acetate) showed a single component, which had the same mobility as 1,2:5,6-di-O-isopropylidene- α -D-glucofuranose. The product was purified on a column of silica gel (5 g) by elution with 9:1 dichloromethane–ethyl acetate. Fractions (10 ml) were collected, and examined by t.l.c. (1:1 dichloromethane–ethyl acetate); fractions 6–13, containing the desired product, were combined, and evaporated under diminished pressure to a syrup that crystallized spontaneously. The mass spectra of the crystalline products from **11a** (low d.s. at C-6) and **11b** (high d.s. at C-6) are shown in Table I.

Calculation of degrees of substitution. — The computer program of Horton and Pardoe⁹ was employed. For the disubstituted cellulose derivatives, the molecular formula $C_6H_7O_2(OH)[3-(x+y)](A)_x(B)_y$ was used, where x and y are the d.s. by the two substituents A and B. For the acetylated derivatives, the molecular formula $C_6H_7O_2(OH)[3-(z+x+y)](A)_x(B)_y(OAc)_z$ was used, where the value of z (degree of acetyl substitution) was “read in” on a data card, and the values of x and y were computed, as before, to fit the remaining analytical data.

ACKNOWLEDGMENT

The authors thank C. R. Weisenberger for recording the mass spectra.

REFERENCES

- 1 D. M. CLODE AND D. HORTON, *Carbohydr. Res.*, 12 (1970) 477.
- 2 D. M. CLODE, R. HEMS, D. HORTON, A. E. LUETZOW, AND H. SHOJI, *Abstr. Papers Amer. Chem. Soc. Meeting*, CARB 005 (1969) 157.
- 3 D. M. CLODE, D. HORTON, E. K. JUST, A. E. LUETZOW, AND KERSTIN D. PHILIPS, *Abstr. Papers ACS-CIC Meeting, Toronto, Canada, May 24-29*, CARBO 21 (1970).
- 4 D. HORTON, A. E. LUETZOW, AND J. C. WEASE, *Carbohydr. Res.*, 8 (1968) 366.
- 5 D. M. CLODE, D. HORTON, M. H. MESHREKI, AND H. SHOJI, *Chem. Commun.*, (1969) 694.
- 6 D. M. CLODE AND D. HORTON, *Carbohydr. Res.*, 17 (1971) 365.
- 7 L. J. TANGHE, L. B. GENUNG, AND J. W. MENCH, *Methods Carbohydr. Chem.*, 3 (1963) 193.
- 8 C. J. MALM, L. J. TANGHE, AND B. C. LAIRD, *J. Amer. Chem. Soc.*, 70 (1948) 2740.
- 9 D. HORTON AND W. D. PARDOE, *Carbohydr. Res.*, 12 (1970) 269.
- 10 J. W. GREEN, *Methods Carbohydr. Chem.*, 3 (1963) 327.
- 11 D. H. R. BARTON AND L. R. MORGAN, JR., *J. Chem. Soc.*, (1962) 622.
- 12 R. A. ABRAMOVITCH AND B. A. DAVIS, *Chem. Rev.*, 64 (1964) 149.
- 13 R. M. MORIARTY AND M. RAHMAN, *Tetrahedron*, 21 (1965) 2877.
- 14 D. C. DEJONGH AND K. BIEMANN, *J. Amer. Chem. Soc.*, 86 (1964) 67.
- 15 L. J. TANGHE, L. B. GENUNG, AND J. W. MENCH, *J. Amer. Chem. Soc.*, 3 (1963) 201.
- 16 D. HORTON AND J. S. JEWELL, *J. Org. Chem.*, 31 (1966) 509.

Carbohydr. Res., 19 (1971) 329-337