solution was filtered through a carbon layer and the water evaporated *in vacuo*.

The product was shown to be 6-O-methyl-D-glucose by paper chromatographic procedures. Oxidation with sodium paraperiodate according to the method of Lemieux and Bauer[10] gave only one spot with R_f 0.76; reported by those authors for 6-O-methyl-D-glucose, R_f 0.71. Authentic samples of 2- and 3-O-methyl-D-glucose gave R_f 0.23 and 0.40, respectively, which agree closely with the values 0.18 and 0.37 reported for those compounds by Lemieux and Bauer.

Lenz and Holmberg[9] separated 2-, 3- and 6-O-methyl-D-glucose directly using the top layer of a solvent system consisting of 2,4,6-collidine, ethyl acetate and water (2:5:5). Although inadequate resolution of the 2- and 3- isomers was obtained using their procedure, separation of the 6-methyl isomer was sufficient to identify the methylglucose prepared above as 6-O-methyl-D-glucose.

Methyl 2,3,4-O-Tribenzoyl-6-O-tosyl-α-D-glucopyranoside (VIII).—Methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside (V), 1.0 g., was treated with 0.4 g. of *p*-toluenesulfonyl chloride in 5 ml. of pyridine overnight at room temperature. The product was isolated by standard procedures and crystallized as long needles from ethanol, having m.p. 164–166° and $[\alpha]_D^{25}$ 64.8 ($CHCl_3$) (reported[8] 164° and $[\alpha]_D^{16}$ 64.8 ($CHCl_3$)).

Anal. Calcd. for $C_{34}H_{30}O_{11}S$: S, 4.85. Found: S, 4.61.

PRINCETON, N. J.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY, AND THE TEXTILE RESEARCH INSTITUTE AT PRINCETON, N. J.]

Location of Xanthate Groups in Viscose[1]

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The method of decomposing xanthate ester groups as described in the preceding communication was applied directly to the S-benzyl ester made from ripened viscose, in which the free hydroxyls had been protected with benzoyl blocking groups. The dexanthated derivative from ripened viscose gave benzoyl cellulose with D.S. 2.67 which being soluble in methyl iodide was readily methylated to the theoretical D.S. 0.33. Removal of the benzoyl blocking groups gave a methyl cellulose which was hydrolyzed to D-glucose and its O-methyl derivatives. Chromatographic procedures showed the predominant monomethyl glucose fraction to contain 37% 6-O-methyl, 20% 3-O-methyl and 43% 2-O-methyl isomers which indicate the actual location of xanthate groups in this commercial ripened viscose. The S-benzyl ester made from green viscose failed entirely to undergo the benzoylation reaction.

Numerous papers have appeared in the literature describing attempts to locate the xanthate substituents in sodium cellulose xanthate or viscose. The only authors who claimed a satisfactory solution to the problem used the method devised by Lieser[3] in 1929. The basic reaction of this method, involving quantitative displacement of the xanthate group by diazomethane, has recently been shown by several authors[4–7] to be highly questionable.

Cellulose xanthate esters have been known for a long time, having been introduced with the work of Lilienfeld[8] and Fink.[9] Purves and co-workers[5,7] used cellulose xanthate methyl ester and acetylated the free hydroxyl groups. Drastic oxidative and reductive reactions only partially removed xanthate ester groups while concurrently removing acetyl blocking groups. Lenz[6] blocked the free hydroxyls with carbanilate groups but was not able to selectively hydrolyze the xanthate ester groups.

A study in our laboratory of the benzyl xanthate ester derivative of methyl α-D-glucopyranoside resulted[10] in the discovery of a two-step reaction in which the xanthate ester group was readily removed under mild conditions. Mercuric acetate converted the xanthate ester to the monothiolcarbonate derivative. Hydrogen peroxide in glacial acetic acid then oxidized this monothiolcarbonate, which readily decomposed to regenerate the parent alcohol group. Furthermore, it was shown that migration of benzoyl ester blocking groups did not occur during dexanthation of methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside-6-(S-benzyl) xanthate.

Complete esterification of the free hydroxyl groups should be accomplished readily without loss of xanthate ester groups. It was anticipated that our dexanthation process could be applied to cellulose xanthate benzyl ester in which the free hydroxyls had been protected with benzoyl blocking groups. The liberated hydroxyls could then be methylated with Purdie reagent, and the methyl cellulose obtained after debenzoylation may be treated by known procedures to determine the location of the methyl ether substituents in the cellulose chain. Furthermore, application of this process to cellulose xanthate from both green and ripened viscose would provide an answer to the age-old question of change in xanthate group location during the ripening process.

Results and Discussion

The xanthate benzyl ester used in this work was prepared by the action of benzyl bromide on commercial viscose, as shown in equation 1. Ripened and green viscose gave xanthate benzyl esters with D.S. 0.31 and 0.41, respectively, where D.S. is defined as the average number of substituents per anhydroglucose unit.

(1) This paper was taken from the Ph.D. dissertation of John J. Willard, Princeton University, 1959, and was presented at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

(2) Textile Research Institute Fellow, 1956–1959.

(3) Th. Lieser, *Ann.*, **470**, 104 (1929).

(4) C. C. Woodrow, T. E. Mackey and D. D. Bachlott, A.C.S. Presentation, Cellulose Section, 131st Meeting, 1957.

(5) A. K. Sanyal, E. L. Falconer, D. L. Vincent and C. B. Purves, *Can. J. Chem.*, **35**, 1164 (1957).

(6) R. W. Lenz, Ph.D. dissertation, State University of New York, College of Forestry at Syracuse, 1955.

(7) D. L. Vincent and C. B. Purves, *Can. J. Chem.*, **34**, 1302 (1956).

(8) L. Lilienfeld, U. S. Patent 1,680,224 (1928).

(9) H. Fink, R. Stahn and A. Matthes, *Angew. Chem.*, **47**, 602 (1934).

(10) J. Willard and E. Pacsu, THIS JOURNAL, **82**, 4347 (1960).

$$R_{Cell}O\overset{\overset{S}{\|}}{C}S^- Na^+ + C_6H_5CH_2Br \longrightarrow R_{Cell}O\overset{\overset{S}{\|}}{C}SCH_2C_6H_5 + NaBr \quad (1)$$

Numerous attempts were made to methylate the free hydroxyls of the cellulose xanthate ester derivative. Several procedures available for methylating cellulose were tried, *i.e.*, dimethyl sulfate and alkali, sodium in liquid ammonia followed by methyl iodide, diazomethane and fluoroboric acid,[11] and sodium hydride and methyl iodide. By each procedure either complete methylation was not achieved or xanthate ester groups were decomposed during the methylation.

Cellulose xanthate benzyl ester from *ripened* viscose was readily benzoylated during two treatments with benzoyl chloride and pyridine to benzoyl D.S. 2.67. Infrared spectroscopy in chloroform solution was found to furnish a good initial criterion for complete substitution, no hydroxyl absorption then being observed.

Dexanthation was carried out in a solvent system consisting of four parts chloroform and one part acetic acid. Hydrogen sulfide was introduced after the mercuric acetate reaction was completed, precipitating all mercuric ion as mercuric sulfide.[10] The colloidal mercuric sulfide could not be removed. Hydrogen peroxide was therefore introduced in twenty-fold molar excess to oxidize and decompose the monothiolcarbonate and to convert mercuric sulfide during this process to mercuric sulfate, which was readily removed by centrifuging or filtration after completion of the oxidation reaction. A sulfur-free product was obtained, analyzing for benzoyl D.S. 2.67. Benzoyl analyses were carried out according to the procedure of Bernoulli.[12]

The resulting cellulose benzoate, readily soluble in methyl iodide, was methylated by Purdie procedure to methyl D.S. 0.33. The benzoyl groups were then removed with ethanolic alkali and the resulting methyl cellulose hydrolyzed to glucose and its methyl derivatives. Paper chromatographic procedures showed that no trimethylglucose and only a small amount of dimethylglucose were present.

The chromatographic procedure of Lemieux and Bauer[13] for qualitative identification of monomethylglucoses as well as the direct separation of the isomeric monomethylglucoses by Horio's[14] modification of the procedure of Lenz and Holmberg[15] showed that all of the three possible isomeric monomethylglucoses, namely 2-, 3- and 6-O-methylglucose were present in the hydrolyzate.

After separation of 10–20 mg. of hydrolyzate by the procedure of Horio, the respective isomers were eluted from the paper and estimated quantitatively by Rebenfeld and Pacsu's[16] extension of the hypoiodite procedure of Lippoid.[17] The location of xanthate groups in ripened viscose as thus found is shown in Table I. Somewhat inadequate separation of the 2- and 3-methylglucoses is responsible for the deviations in the results for those two isomers.

TABLE I

PERCENTAGE OF ISOMERS IN THE MONOMETHYL GLUCOSE FRACTION

Experiment	2-Methyl	3-Methyl	6-Methyl
1	43.2	20.0	36.8
2	49.1	14.5	36.4
3	35.2	27.2	37.6
Average	42.5%	20.6%	36.9%

Although a reliable estimation of the small dimethylglucose fraction could not be achieved by the method employed, the qualitative procedure of Lemieux and Bauer[13] indicated that only two of the three possible isomers were present. Moreover, the spot reported by those authors as representing 2,6-O-dimethyl-D-glucose was absent, indicating that the two isomers detected were 3,6-O-dimethyl-D-glucose and 2,3-O-dimethyl-D-glucose.

Numerous attempts to benzoylate the free hydroxyls in cellulose xanthate benzyl ester from *green* viscose were not successful. Acetylation with acetic anhydride in pyridine went readily to completion. The dexanthation reaction proceeded smoothly as described previously for the ripened viscose sample. However, the resulting cellulose acetate, D.S. 2.59, could not be fully methylated because it was not soluble in methyl iodide. All three of the monomethylglucose isomers were present in the hydrolyzate, although the low degree of methylation made the results of qualitative interest only.

The laboriousness of separating the monomethylglucoses chromatographically by existing procedures was the only general handicap experienced during application of the reaction sequence as outlined above. It is certain that future improvements in chromatographic techniques will facilitate that separation with regard to both effectiveness and time required, thereby expediting this new procedure for ascertaining the location of xanthate groups in various cellulose xanthate samples.

Experimental

Cellulose Xanthate Benzyl Ester.—Both green and ripened viscose, frozen in Dry Ice, were obtained from the du Pont Co. In the frozen state the viscose would keep for several weeks without loss of xanthate groups. The viscose was allowed to thaw in a refrigerator; 200 g. was diluted with 800 ml. of ice-cold water. Excess alkali was neutralized by addition of ice-cold 5% acetic acid with rapid stirring and cooling with an ice-bath until *p*H paper indicated *p*H 9. A threefold molar excess of benzyl bromide (6.6 ml.) was added slowly, and vigorous stirring was continued for 4 hours. The viscose went through a stage of gelation and then precipitation during the first half-hour. The cellulose xanthate ester derivative was recovered by filtration, washed thoroughly with water, alcohol, and ether. It was stored suspended in ether in a refrigerator.

Anal. Found (ripened viscose): S, 9.32, 9.32, 9.32, 9.06. Calcd. D. S. xanthate, 0.31. Found (green viscose): S, 11.63, 11.20, 11.37. Calcd. D. S. xanthate, 0.41.

(11) M. L. Caserio, J. D. Roberts, M. Neeman and W. S. Johnson, THIS JOURNAL, **80**, 2584 (1958).

(12) A. L. Bernoulli, M. Schenk and F. Rohner, *Helv. Chim. Acta*, **17**, 897 (1934).

(13) R. U. Lemieux and H. F. Bauer, *Can. J. Chem.*, **31**, 814 (1953).

(14) M. Horio, R. Imamura and H. Sakata, *J. Soc. Textile and Cellulose Ind., Japan*, **14**, 909 (1958).

(15) R. W. Lenz and C. V. Holmberg, *Anal. Chem.*, **28**, 7 (1956).

(16) L. Rebenfeld and E. Pacsu, *Textile Research J.*, **24**, 941 (1954).

(17) U. Lippoid, *Biochem. Z.*, **323**, 115 (1952).

Benzoylation of Cellulose Xanthate Ester of Ripened Viscose.—Approximately 45 g. of cellulose xanthate benzyl ester, still wet with ether, was suspended in 1 l. of pyridine in a 3-l. three-neck flask equipped with mechanical stirrer, thermometer and reflux condenser. Benzoyl chloride (106 ml.) was previously mixed with its own weight of pyridine and added slowly with rapid stirring. The cellulose derivative went readily into solution. Vigorous stirring was continued with heating at 94° for 2 hours. An additional 40 ml. of benzoyl chloride was introduced during the second hour. The product was precipitated by pouring the viscous solution, cooled to room temperature, into 2 l. of methanol. After drying overnight *in vacuo* at 50°, the product in a 2% absolute chloroform solution showed some hydroxyl absorption in the 2.8 μ region of the infrared.

Anal. Calcd. for D. S. xanthate 0.31, D. S. benzoyl 2.69: C, 66.44; H, 4.63; S, 3.9. Found: C, 65.78; H, 4.74; S, 4.15; benzoyl, D. S. 2.56.

The above product (90 g.) was rebenzoylated as above for 3 hours using 50 ml. of benzoyl chloride. The product then showed no absorption in the 2.8 μ region of the infrared.

Anal. Found: C, 65.74; H, 4.70; S, 3.60; D. S. benzoyl, 2.67.

For benzoyl estimation,[12] approximately 0.5 g. of accurately weighed sample was added to 20.0 ml. of 0.5 *N* sodium hydroxide solution (80% ethanol). After 24 hours at room temperature with occasional shaking, 20.0 ml. of 0.5 *N* sulfuric acid was added. The cellulose was removed by filtration and washed with 200 ml. of boiling water. The filtrate and combined washings were titrated with standard 0.1 *N* sodium hydroxide to phenolphthalein end-point. Blanks were run concurrently and the liberated benzoic acid determined from the difference in alkali consumption.

Removal of Xanthate Groups.—The benzoylated cellulose xanthate ester derivative (25 g.) was dissolved in 500 ml. of chloroform. Glacial acetic acid (150 ml.) containing 6.04 g. (20% molar excess) of mercuric acetate and 5 ml. of water was added. The solution was warmed at 40° for 2 hours. Hydrogen sulfide was then passed through the black solution for 5 minutes, followed by nitrogen or air until excess hydrogen sulfide had been removed.

Glacial acetic acid (50 ml.) containing 3.10 g. of potassium acetate and 17.9 ml. of 30% hydrogen peroxide was then added and the mixture warmed at 50° for 12 hours. Insoluble, white mercuric sulfate was removed by centrifugation. After extraction with water, the chloroform solution was dried over magnesium sulfate, and the product precipitated by pouring the chloroform solution into 1500 ml. of methanol. The snow-white product was recovered by filtration, washed with methanol, dried *in vacuo;* yield 20.5 g. A sodium fusion test showed the absence of sulfur. The sample in chloroform solution showed hydroxyl absorption in the 2.8 μ region of the infrared.

Anal. Calcd. for D. S. benzoyl 2.67: C, 67.45; H, 4.69. Found: C, 66.74; H, 4.81; D. S. benzoyl, 2.67.

Methylation of Cellulose Benzoate.—Cellulose benzoate D. S. 2.67 (10 g.) was dissolved in a mixture of 90 ml. of methyl iodide and 350 ml. of benzene. Silver oxide (30 g.) was added and the mixture was refluxed (62°) with stirring for 12 hours. An aliquot was removed and purified, after filtration, by precipitating into methanol, redissolving in chloroform, and precipitating into petroleum ether.

Methoxyl analyses were carried out by the Ziesel method as modified by Clark[18] and further modified by Steele and Pacsu.[19]

(18) E. P. Clark, "Semimicro Quantitative Organic Analysis," Academic Press, Inc., New York, N. Y., 1943, p. 73.

(19) R. Steele and E. Pacsu, *Textile Research J.*, **19**, 771 (1949).

Anal. Calcd. for D. S. 0.31: $-OCH_3$, 2.13. Found: $-OCH_3$, 1.13, 1.05.

The main reaction product was precipitated into petroleum ether, dried and redissolved in 150 ml. of methyl iodide. After 18 hours of stirring under reflux with 30 g. of silver oxide, an aliquot was removed and purified as before. After removal of benzoyl groups, the methyl cellulose was analyzed for methoxyl content.

Anal. Calcd. for D. S. 0.31: $-OCH_3$, 5.85. Found: $-OCH_3$, 6.16, 6.18, 6.31. Calcd. D. S. methyl ether, 0.33.

Debenzoylation and Hydrolysis.—Benzoyl groups were removed as described under benzoyl estimation. The resulting methyl cellulose was hydrolyzed by standing overnight in 1 ml. of 72% sulfuric acid per 0.1 g. of sample. The solution was then diluted tenfold and digested on a steam-bath for 4 hours. The sulfuric acid was neutralized to *p*H 7 with barium carbonate; barium sulfate was removed by filtration and thoroughly washed. The combined solutions were concentrated at 50° *in vacuo*, and the sirup recovered by drying in a vacuum oven at 50°. A 2% aqueous solution was prepared for use in paper chromatographic procedures.

Qualitative Paper Chromatography.—Approximately 20 mg. of the sirupy mixture was first separated into glucose, monomethylglucose and dimethylglucose fractions by standard procedures[16] using 10% undersaturated Partridge solvent and Whatman No. 1 filter paper. Guide spots were located on the paper with aniline hydrogen phthalate spray. The monomethyl- and dimethylglucose fractions were then treated according to the procedure for qualitative identification of Lemieux and Bauer.[13] This procedure involves oxidation of the methylglucoses with sodium paraperiodate for 1 hour at 0°, followed by chromatographic separation of the resulting oxidation products.

Monomethylglucoses.—R_f-Values reported[13]: 2-monomethyl, 0.18; 3-monomethyl, 0.37; 6-monomethyl, 0.71. Found, from monomethyl glucose fraction: R_f 0.23, 0.40, 0.76. Application of known 2-, 3- and 6-monomethylglucose gave R_f-values 0.23, 0.40 and 0.76, respectively. The spots were yellow, brown and yellow, respectively, in both cases.

Dimethylglucoses.—R_f-Values reported[15]: 2,6-dimethyl, 0.18 (yellow); 2,3-dimethyl, 0.55 (brown). Found: two weak spots, R_f 0.55 and 0.78, brown and yellow, respectively. By process of elimination the spot having R_f 0.78 probably represents 3,6-dimethylglucose.

Quantitative Separation of Monomethylglucoses.—Ten to twenty mg. of hydrolyzate was applied to Whatman No. 1 filter paper in a 4-inch line together with guide spots and developed with the top layer from a mixture of 2,4,6-collidine, ethyl acetate and water (2:5:5) nine times by the ascending technique.[14] Guide strips were cut off and the spots located with 3% anisidine hydrochloride in 1-butanol. The separated derivatives were eluted from the paper and estimated quantitatively according to the procedure of Rebenfeld and Pacsu.[16]

Found: (mmoles) in three determinations			
Glucose	2-Methyl	3-Methyl	6-Methyl
0.0249	0.0041	0.0019	0.0035
.0141	.0027	.0008	.0020
.0259	.0045	.0034	.0047

The above figures were used as the basis for the results shown in Table I.

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