Bromination of the N-Alkylpyridone Derivatives.—To a solution of the N-alkylpyridone derivative (1 mol.) in glacial acetic acid, bromine (2 mols.) in glacial acetic acid was added while stirring at room temperature. The solid pyridone dibromide that is formed was filtered, and then boiled with an alcoholic solution (50%) of sodium bicarbonate and the solution filtered while hot. On cooling, crystals of the pyridone dibromide separated and were recrystallized from ethanol in quantitative yield. Using one mol. only of bromine led to the formation of only half of the quantity of the dibromide derivative and half of the pyridone was recovered unchanged (*cf.* Table IV).

Treatment of N-methyl-3,5-dibromo-2,6-dimethyl-4-pyridone with sodium hydroxide gave only unchanged starting material.

N-Methyl-3,5-dibromolutidone did not react with activated magnesium on long boiling in ether or anisole even on activation with dimethylaniline.

Oxidation of the 4-Thiopyridone Derivatives.—To a hot solution of the thiopyridone derivative (0.5 g.) in glacial acetic acid (20 ml.) hydrogen peroxide (30% solution, 5 ml.) was added and heating was continued for half an hour on the water-bath. The solid residue that remained after the evaporation of the solvent crystallized from ethanol. Yields were quantitative and were identified as anhydro-pyridinesulfonic acids (*cf.* Table V).

2,6-Di-*p*-methoxyphenyl-4-pyrone[8] **(IVa)** did not react with hydroxylamine.

Treatment of 2,6-Diphenyl-4-pyrone Oxime with Methylamine.—Methylamine (7 ml.) of 40% solution and 2,6-diphenyl-4-pyrone oxime (0.2 g.) in ethanol (40 ml.) were refluxed for 7 hours. The crystals that separated on cooling were recrystallized from ethanol; m.p. and mixed m.p. with the starting oxime[9] 196°, yield *ca.* 0.18 g. With a saturated solution of picric acid, this oxime gave a picrate that recrystallized from ethanol in yellow crystals, m.p. 200°. *Anal.* Calcd. for $C_{23}H_{16}O_9N_4$: C, 56.3; H, 3.0; N, 11.4. Found: C, 56.1; H, 3.1; N, 11.6.

Treatment of 2,6-diphenyl-4-pyrone oxime (IIc) with phenylmagnesium bromide gave only starting material.

(8) A. Schönberg, M. Elkaschef, M. Nosseir and M. M. Sidky, THIS JOURNAL, **80**, 6312 (1958).

(9) F. Arndt, E. Scholz and P. Nachtwey, *ibid.*, **57**, 1903 (1924).

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

New Method of Removing Xanthate Groups from Carbohydrates. Chemical Structure of Methyl α-D-Glucopyranoside Monoxanthate[1]

BY JOHN J. WILLARD[2] AND EUGENE PACSU

RECEIVED JANUARY 22, 1960

A method of locating the xanthate groups in carbohydrates by classical means has been established. Methyl α-D-glucopyranoside xanthate in aqueous barium hydroxide solution forms carbon-6 xanthate in 20% yield, isolated as the crystalline S-benzyl ester I. The action of mercuric acetate on the crystalline tribenzoate III of I yields the crystalline tribenzoyl monothiolcarbonate IV which is quantitatively decomposed by oxidation with hydrogen peroxide in glacial acetic acid to give the known crystalline methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside (V) in high yield. That no benzoyl migration occurred during dexanthation is proved by synthesis of the identical monothiolcarbonate IV from the dexanthated tribenzoate V and benzyl chlorothiolformate.

The position of xanthate groups in viscose, or sodium cellulose xanthate, has posed a problem of considerable theoretical and commercial interest for many decades. When extensive investigations on this subject failed to result in a method by which the problem could be solved, we were led to study the reactions of a xanthate ester of methyl α-D-glucopyranoside as a model compound.

Methyl α-D-glucopyranoside was xanthated according to a procedure of Lieser[3] using aqueous barium hydroxide. Although Lieser converted the barium xanthate salt to the difficultly crystalline methyl xanthate ester *via* the silver salt, it was discovered in our laboratory that the action of benzyl bromide directly on the barium salt gives rapid conversion to the benzyl ester I. The benzyl xanthate ester, readily crystallized from benzene, was obtained in 20% yield, based on methyl α-D-glucopyranoside, and had m.p. 89–92° and $[\alpha]^{20}D$ 79.4° ($CHCl_3$). Analysis of the purified solution of xanthate barium salt for barium showed that under the optimum conditions as reported by Lieser, only 20% conversion of methyl α-D-glucopyranoside to a monoxanthate salt was obtained.

The crystalline triacetate II and tribenzoate III derivatives of the xanthate benzyl ester were prepared and had m.p. 105–107° and 123–124°, and $[\alpha]^{20}D$ 106.3° ($CHCl_3$) and $[\alpha]^{20}D$ 56.8° ($CHCl_3$), respectively.

Lieser speculated that the xanthate ester group was located at carbon-2, although his evidence was by no means conclusive.

Methyl α-D-glucopyranoside-(S-benzyl) xanthate (I) readily decomposed at 190° in high vacuum, giving nearly the theoretical yield of benzyl mercaptan, collected as a distillate. This observation was surprising in view of the fact that Freudenberg[4] reported that the diacetone derivative of glucose-3-(S-methyl) xanthate failed to undergo a Tschugaev reaction but rearranged at 300° to give the dithiol methyl carbonate derivative. A crystalline derivative could not be obtained from the residue of our reaction, and it was finally concluded that caramelization had probably occurred. The triacetate of the xanthate ester gave back only unchanged starting material after heating for one hour at 250°.

Methyl α-D-glucopyranoside-(S-benzyl) xanthate (I) failed to give a tosyl derivative or trityl derivative under conditions known to give those derivatives with compounds not substituted at the carbon-6-position.

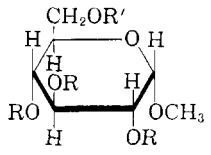
The tribenzoyl derivative III of methyl α-D-

(1) This paper was taken in part 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 and A. Hackl, *Ann.*, **511**, 121 (1934).

(4) K. Freudenberg and A. Wolf, *Ber.*, **60**, 232 (1927).



I, R = H–; R′ = $C_6H_5CH_2SC(=S)$–

II, R = $CH_3C(=O)$–; R′ = $C_6H_5CH_2SC(=S)$–

III, R = $C_6H_5C(=O)$–; R′ = $C_6H_5CH_2SC(=S)$–

IV, R = $C_6H_5C(=O)$–; R′ = $C_6H_5CH_2SC(=O)$–

V, R = $C_6H_5C(=O)$–; R′ = H–

VI, R = R′ = $C_6H_5C(=O)$–

VII, R = $C_6H_5C(=O)$–; R′ = CH_3–

VIII, R = $C_6H_5C(=O)$–; R′ = $CH_3C_6H_4SO_2$–

glucopyranoside-(S-benzyl) xanthate reacted readily with mercuric acetate in 90% aqueous dioxane. A white solid complex, apparently consisting of two moles of mercuric sulfide and one mole of mercuric acetate, formed after the addition of 1.5 moles of mercuric acetate. The complex was removed by filtration of the mercuric sulfide formed by treatment with hydrogen sulfide. From the filtrate a crystalline produce having m.p. 106–107° and $[\alpha]^{20}D$ 65.4° ($CHCl_3$) was obtained after two crystallizations from ethanol, and was recovered in 79% yield. In view of previous reports[5,6] that the action of heavy metal salts on xanthate esters exchanges the xanthate thion sulfur for oxygen, the product should be the S-benzyl monothiolcarbonate derivative IV, which was confirmed by elemental analysis. The presence of the S-benzyl group was also evidenced by the characteristic odor of benzyl mercaptan when the product was heated in dilute mineral acid.

Oxidation of this crystalline monothiolcarbonate derivative IV to the sulfone should result in an unstable grouping which would readily hydrolyze. Only unchanged starting material was recovered after prolonged oxidation with hydrogen peroxide in ethanol solution. When the oxidation was conducted in glacial acetic acid solution, however, four moles of hydrogen peroxide was consumed during two hours at 65°. Reactions were generally run for longer times at lower temperatures. The product of the reaction, crystallized first from moist acetic acid solvent and then recrystallized twice from moist ethanol, was recovered in 83% yield. It had m.p. 140–142° and $[\alpha]^{20}D$ 54.2° ($CHCl_3$). Helferich and Becker[7] and Bell[8] report $[\alpha]D$ 131.4° (pyridine),[7] m.p. 140–142°[8] and $[\alpha]^{17}D$ 54.8° ($CHCl_3$),[8] respectively, for methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside (V).

Methyl 2,3,4,6-O-tetrabenzoyl-α-D-glucopyranoside (VI) was prepared from the product V by benzoylating with one mole of benzoyl chloride in pyridine, showing that the hydroxyl group previously occupied by the monothiolcarbonate group had been liberated by the oxidation reaction. The tetrabenzoyl derivative VI, crystallized from ethanol, had m.p. 105°, consistent with the literature value.[7] The 6-O-methyl (VII) and 6-O-tosyl (VIII) derivatives also agreed in melting point (118° and 164°, respectively) with literature values.[7,8]

Application of the paper chromatographic procedures of Lenz and Holmberg[9] and Lemieux and Bauer[10] showed conclusively that the methyl ether substituent in the O-methyl-D-glucose obtained by hydrolysis from VII was located at the carbon-6 atom. Ohle and Tessmar[11] found that no migration of benzoyl group occurred when methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside (V) was refluxed in benzene solution with silver oxide. The tribenzoyl derivative is therefore confirmed as methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside.

It remained to be shown that benzoyl migration did not occur during dexanthation. Benzyl chlorothiolformate was synthesized according to a procedure recently described by Tilles[12] from one mole of phosgene and one mole of benzyl mercaptan in the presence of sodium hydroxide. The product was a light yellow oil with b.p. 125–126° (12 mm.). The same compound was reported by Arndt, Milde and Eckert[13] to have b.p. 133° (18 mm.). Benzyl chlorothiolformate reacted readily with the dexanthated tribenzoyl derivative V using pyridine catalyst to give a monothio carbonate derivative IV identical with that obtained originally from the xanthate ester. The absence of benzoyl group migration during dexanthation is therefore confirmed.

These reactions demonstrate a new method of removing xanthate ester groups from carbohydrates using mild conditions. They also show that in the monoxanthate ester of methyl α-D-glucopyranoside prepared with barium hydroxide as described by Lieser, the xanthate group is located at carbon-6 and not at carbon-2 as has been believed for many years.

Experimental[14]

Methyl α-D-Glucopyranoside-6-(S-benzyl) Xanthate (I).—The xanthation procedure of Lieser[1] was followed exactly up to the point of preparation of the xanthate ester. Twenty-five grams of methyl α-D-glucopyranoside was dissolved in 445 ml. of 0.43 *N* barium hydroxide and shaken vigorously for 13 to 15 hours at room temperature with 15 ml. of carbon disulfide. Carbon dioxide was introduced in a vigorous stream to precipitate excess barium hydroxide and to remove

(5) Th. Lieser and E. Leckzyck, *Ann.*, **519**, 279 (1935).

(6) Z. el Heweihi, "Mercaptale und Xanthogenate der Kohlenhydrate und Derivative der 6-thioglucose," Ph.D. dissertation, Zürich, 1950.

(7) B. Helferich and J. Becker, *Ann.*, **440**, 1 (1924).

(8) D. J. Bell, *J. Chem. Soc.*, 1177 (1934).

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

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

(11) H. Ohle and K. Tessmar, *Ber.*, **71**, 1843 (1938).

(12) H. Tilles, THIS JOURNAL, **81**, 714 (1959).

(13) F. Arndt, E. Milde and G. Eckert, *Ber.*, **56**, 1976 (1923).

(14) All melting points are uncorrected. All solvents were removed on a flash evaporator at 50° *in vacuo*.

inorganic, sulfur-containing by-products, which decomposed to evolve hydrogen sulfide. Barium carbonate was removed by filtration and the clear solution was shaken for 2 hours with 7 ml. of benzyl bromide. The product separated as a sirup on the sides of the flask and was recovered by decantation. It was taken up in ether, the solution dried with magnesium sulfate, and the ether removed *in vacuo*. The residue was soluble in boiling benzene, from which it crystallized as small needles, m.p. 83–87°. After two recrystallizations from benzene, the substance melted at 89–92° and had $[\alpha]^{20}D$ 79.8° ($CHCl_3$).

Anal. Calcd. for $C_{15}H_{20}O_6S_2$: C, 50.0; H, 5.56; S, 17.8. Found: C, 50.7; H, 5.60; S, 17.2.

Methyl 2,3,4-O-Triacetyl-α-D-glucopyranoside-6-(S-benzyl) Xanthate (II).—Two grams of methyl α-D-glucopyranoside-6-(S-benzyl) xanthate (I) was acetylated with 3 ml. of acetic anhydride by standing overnight in 15 ml. of pyridine. The product showed m.p. 105–107° and $[\alpha]^{20}D$ 106.3° ($CHCl_3$) after two crystallizations from ethanol, and crystallized as fine needles from that solvent.

Anal. Calcd. for $C_{21}H_{28}O_9S_2$: C, 51.9; H, 5.35; S, 13.2. Found: C, 52.3; H, 5.25; S, 12.8.

Methyl 2,3,4-O-Tribenzoyl-α-D-glucopyranoside-6-(S-benzyl) Xanthate (III).—A solution of 5.6 g. of methyl α-D-glucopyranoside-6-(S-benzyl) xanthate (I) in a mixture of 35 ml. of pyridine and 13 ml. of benzoyl chloride was kept overnight at room temperature. A sirup precipitated when the solution was poured into ice-water. The sirup was taken up in chloroform, the solution shaken with dilute hydrochloric acid, followed by sodium bicarbonate solution. The chloroform solution was then dried over magnesium sulfate, and the chloroform evaporated *in vacuo*. The product crystallized as prisms from ethanol solution; yield 9.2 g. (88%), m.p. 127–129° and $[\alpha]^{20}D$ 56.8° ($CHCl_3$) after two recrystallizations from ethanol.

Anal. Calcd. for $C_{36}H_{32}O_9S_2$: C, 64.3; H, 4.77; S, 9.53. Found: C, 64.6; H, 4.85; S, 9.40.

Methyl 2,3,4-O-Tribenzoyl-α-D-glucopyranoside-6-(S-benzyl) Monothiolcarbonate (IV).—Five grams (0.00744 mole) of methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside-6-(S-benzyl) xanthate (III) was dissolved in 50 ml. of 90% aqueous dioxane. Mercuric acetate solution was prepared by dissolving 3.6 g. (0.01132 mole) of mercuric acetate in 30 ml. of 90% aqueous dioxane followed by dropwise addition of glacial acetic acid to just dissolve the yellow mercuric oxide which always formed. A white solid probably consisting of 2 HgS·Hg$(OAc)_2$ precipitated when the two solutions were mixed. After the reaction mixture had stood for several hours at room temperature (or 2 hours at 60°), hydrogen sulfide was introduced for 15 minutes to remove the mercuric acetate from the complex as mercuric sulfide. The latter was filtered off through a carbon layer. A sirup was recovered by evaporating the solvents *in vacuo* and it was triturated with 50 ml. of water to remove residual acetic acid. The water was decanted, the sirup then taken up in chloroform and purified by the usual procedure. The product crystallized in clusters of prisms from ethanol; yield 3.9 g. (79%). After recrystallization from ethanol, the compound showed m.p. 106–107° and $[\alpha]^{20}D$ 56.4° ($CHCl_3$).

Anal. Calcd. for $C_{36}H_{32}O_{10}S$: C, 65.8; H, 4.88; S, 4.88. Found: C, 65.7; H, 4.97; S, 5.06, 5.22.

In a separate experiment, mercuric acetate solution of known concentration was slowly added to a solution of 2.0 g. of xanthate benzyl ester derivative I. The black precipitate of mercuric sulfide changed sharply to a white solid compound after the addition of 1.5 moles of mercuric acetate, indicating that one mole of mercuric acetate complexed with two moles of mercuric sulfide. The white complex was recovered by filtration, dried, and weighed; calcd. weight for 2HgS·Hg$(OAc)_2$, 2.18 g., found 1.92 g. No further precipitation occurred when additional mercuric acetate was added to the clear filtrate, indicating that conversion of xanthate ester to monothiolcarbonate ester was complete.

Methyl 2,3,4-O-Tribenzoyl-α-D-glucopyranoside (V).—Two grams of methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside-6-(S-benzyl) monothiolcarbonate (IV) was dissolved in 50 ml. of glacial acetic acid containing 2.2 ml. of 30% hydrogen peroxide. The temperature of the solution as well as that of a blank was maintained at 65°. One-ml. aliquots were removed periodically and the unused hydrogen peroxide in each aliquot was determined by addition of 25 ml. of water, 0.5 g. of solid potassium iodide and 5 ml. of sulfuric acid, followed by titration of the liberated iodine with standard 0.1 *N* sodium thiosulfate solution. Consumption of peroxide ceased after 100 minutes, 4 moles having been used up.

The product was first isolated as a white amorphous solid by pouring the solution into water containing sufficient sodium bicarbonate to neutralize the acetic acid. The product was recovered by filtration and washed thoroughly with water. Addition of barium chloride solution to the acidified (HNO_3) filtrate gave a heavy precipitate of barium sulfate, showing that the sulfur of the monothiolcarbonate derivative had indeed been oxidized to sulfate, as indicated by the consumption of peroxide. The sodium fusion test showed that the product was sulfur-free.

To neutralize the sulfuric acid formed during the oxidation reaction, a two-molar excess of potassium acetate was added to subsequent reaction mixtures.

In a second experiment, 10 g. of monothiolcarbonate derivative IV was treated as before for 3 days at room temperature. The reaction product crystallized as triangular plates from moist acetic acid solution. After two crystallizations from moist ethanol, 6.3 g. (83%) was obtained, which showed m.p. 140–142° and $[\alpha]^{20}D$ 54.2° ($CHCl_3$); literature values: m.p. 140–142°[8] and $[\alpha]^{17}D$ 54.8 ($CHCl_3$)[8]; m.p. 142–143°[11] and $[\alpha]^{20}D$ 54.1° ($CHCl_3$).[11]

Anal. Calcd. for $C_{28}H_{26}O_9$: C, 66.4; H, 5.13. Found: C, 66.4; H, 4.81.

Resynthesis of IV from V with Benzyl Chlorothiolformate.—To 29.3 ml. of benzyl mercaptan and 10 ml. of phosgene in 150 ml. of benzene there was rapidly added with stirring (cooling with a Dry Ice–acetone-bath) a solution of 13 g. of sodium hydroxide in 150 ml. of water in such a way that the temperature did not exceed 0°. Stirring was continued for an additional 0.5 hour, during which the aqueous layer was kept basic by the addition of sodium hydroxide as necessary. The benzene layer was dried over magnesium sulfate, and the product (10 ml.) recovered as a light-yellow oil, b.p. 125–126° at 12 mm.; reported[13] for benzyl chlorothiolformate, b.p. 133° (18 mm.).

Methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside (V), 0.64 g., was mixed with 0.29 g. of benzyl chlorothiolformate. The reaction mixture became warm during the addition of 10 drops of pyridine. The three components were mixed to a paste and heated on a steam-bath for 1 hour, after which the product was triturated with water, dissolved in chloroform, and purified in the usual manner. The resulting sirupy residue crystallized from ethanol giving 0.505 g., m.p. 106–107°; a mixed m.p. with the monothiolcarbonate derivative IV obtained previously from the xanthate ester was not depressed.

Methyl 2,3,4,6-O-Tetrabenzoyl-α-D-glucopyranoside (VI).—To 1.0 g. of methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside (V) dissolved in 15 ml. of pyridine was added 0.25 ml. of benzoyl chloride. The mixture was allowed to stand overnight and was then warmed on a steam-bath for 1 hour. After cooling, it was poured into ice-water and worked up in the usual manner. The product crystallized from ethanol as prisms, m.p. 103–105°, reported[7,11] for methyl 2,3,4,6-O-tetrabenzoyl-α-D-glucopyranoside, 105°.

Methyl 2,3,4-O-Tribenzoyl-6-O-methyl-α-D-glucopyranoside (VII).—A solution of 3.9 g. of methyl 2,3,4-O-tribenzoyl-α-D-glucopyranoside in 10 ml. of methyl iodide was shaken for 24 hours at room temperature with 10 g. of silver oxide (previously dried at 110° for 1 hour). After removal of silver salts by filtration, evaporation of methyl iodide left a sirup which crystallized from 6 ml. of methanol giving 2.52 g. (65%) of product in the form of triangular plates. Recrystallization from 20 ml. of methanol gave 2.0 g., m.p. 117–119°; literature values: m.p. 116–117°,[7,15] 119–120°[11]; $[\alpha]^{17}D$ 118.4° (pyridine),[15] $[\alpha]^{20}D$ 54.0 ($CHCl_3$).[15]

6-O-Methyl-D-glucose.—Two grams of methyl 2,3,4-O-tribenzoyl-6-O-methyl-α-D-glucopyranoside (VII) was treated with 12 ml. of *N* sodium hydroxide in 90% ethanol for 0.5 hour on a steam-bath. After careful neutralization with *N* hydrochloric acid, the solution was treated with Amberlite IR-120 cation exchange resin to remove sodium ion. The solution was made *N* in hydrochloric acid and refluxed for 2 hours. After neutralization with silver carbonate, the silver salts were removed by filtration. Hydrogen sulfide gas was introduced to precipitate the last traces of silver ion. The

(15) B. Helferich and E. Günther, *Ber.*, **64**, 1276 (1926).

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).