needles, m.p. 206–207°. Admixture with material obtained from V did not depress the melting point.

Acetylation of 53 mg. of VIII with 0.5 ml. of acetic anhydride and 1.0 ml. of pyridine was carried out in the usual way. The sirupy residue obtained after evaporation of the solvents by codistillation *in vacuo* with toluene crystallized in the presence of small amounts of ether and pentane on cooling with Dry Ice. Purification by chromatography on silicic acid gave 62 mg. (87%) of the **3,4-di-*O*-acetyl** derivative. By recrystallization from a mixture of ether and pentane, 49 mg. (69%) of long needles were obtained, m.p. 83.5–85°, $[\alpha]^{24}D$ +101 ± 2° (in chloroform, *c* 0.99). *Anal.* Calcd. for $C_{14}H_{23}O_8N$: C, 50.44; H, 6.95. Found: C, 50.45; H, 7.01.

One hundred and thirteen mg. of crude VIII, obtained from 130 mg. of VII by hydrolysis with 60% acetic acid, was refluxed overnight with 4 ml. of acetone and 10 ml. of methyl iodide in the presence of 0.5 g. of silver oxide. After a new addition of 0.5 g. of silver oxide, reflux was continued for 10 hours. The suspension was filtered through a layer of Celite and the silver residue washed with acetone. After evaporation, the combined filtrates gave 114 mg. of a crystalline residue, further chromatographed on silicic acid. Mixtures of ethyl acetate and acetone 1:1 eluted 60 mg. of crystalline fractions. Recrystallization from a mixture of acetone, ether and pentane gave methyl 2-acetamido-2-deoxy-3,4,6-tri-*O*-methyl-α-D-galactopyranoside (IX), m.p. 190–191.5°, showing no depression of melting point in admixture with authentic material[6]; $[\alpha]^{23}D$ +143 ± 2° (in chloroform, *c* 0.94).

6-*O*-Methyl-α-D-galactosamine Hydrochloride (2-Amino-2-deoxy-6-*O*-methyl-α-D-galactose Hydrochloride) (X).—A solution of 163 mg. of VIII in 5 ml. of 3 *N* hydrochloric acid was heated for three hours in a sealed tube at 100°. After cooling, the solution was evaporated *in vacuo* in the presence of absolute ethanol and gave 156 mg. of a crystalline residue. It was dissolved in methanol, the solution was filtered through a double layer of Darco G-60 and Celite, and concentrated under a stream of nitrogen to a volume of 2 ml. By addition of 4 ml. of acetone, 140 mg. (93%) of clusters of small prisms were obtained. The compound decomposed at 190–195° and showed mutarotation from $[\alpha]^{23}D$ +107.5° (after 5 minutes) to $[\alpha]^{23}D$ +92 ± 2° after 16 and 60 hours (in water, *c* 1.04). *Anal.* Calcd. for $C_7H_{16}O_5HCl$: C, 36.61; H, 7.02; Cl, 15.44; OCH_3, 13.51. Found: C, 36.42; H, 6.89; Cl, 15.47; OCH_3, 13.69.

2-Deoxy-2-(2′-hydroxynaphthylideneamino)-6-*O*-methyl-α-D-galactose (XI).—To a solution of 42 mg. of X in 1 ml. of water was added a solution of 90 mg. of 2-hydroxynaphthaldehyde and 60 mg. of $CH_3COONa \cdot 3H_2O$ in 6 ml. of methanol. The mixture was treated as previously described.[8] The residue was suspended in benzene and chromatographed on silicic acid. Elution with mixtures of ethyl acetate and acetone 1:1 and with pure acetone gave 59 mg. of crystalline fractions. Recrystallization of the main fractions from a mixture of methanol and acetone afforded 28 mg. (45%) of small yellow clusters of needles, m.p. 189–191°, with slight decomposition. The compound showed mutarotation from $[\alpha]^{23}_{5461}$ + 280° (after 20 minutes) to $[\alpha]^{27}_{5461}$ + 258 ± 3° after 17 and 45 hours (in methanol, *c* 0.98). *Anal.* Calcd. for $C_{18}H_{21}O_6N$: C, 62.24; H, 6.09. Found: C, 62.39; H, 6.15.

2-Acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-6-*O*-methyl-α-D-galactopyranose (XII).—Crude X, obtained by hydrolysis of 150 mg. of VII, was acetylated with 2 ml. of acetic anhydride and 3 ml. of pyridine for 20 hours at room temperature. The crystalline residue, obtained after removal of the solvents by codistillation with toluene and absolute ethanol, was chromatographed on silicic acid. Mixtures of ether and ethyl acetate, 2:1 and 1:1, eluted 171 mg. of crystalline fractions. Recrystallization from a mixture of ethanol, ether and pentane gave 103 mg. (55%) of needles, m.p. 219–220°, $[\alpha]^{23}D$ +101 ± 2° (in chloroform, *c* 1.03). *Anal.* Calcd. for $C_{15}H_{23}O_9N$: C, 49.86; H, 6.42. Found: C, 49.94; H, 6.44.

2-Acetamido-2-deoxy-6-*O*-methyl-D-galactose (XIII).—To a solution of 75 mg. of XII in 1.5 ml. of methanol was added 0.15 ml. of 1.6 *N* barium methoxide. After standing 15 hours at 0° and 2 hours at room temperature, the solution was diluted with 2 volumes of water and neutralized by a stream of carbon dioxide. After filtration, traces of barium ion were removed by passing through a column of Dowex 50, and the solution was evaporated to dryness *in vacuo*. The residue crystallized from a mixture of methanol and acetone to give 15 mg. (30%) of fine needles, m.p. 165–168°, $[\alpha]^{24}D$ + 92 ± 5° (in water, *c* 1.12), no mutarotation being observed. *Anal.* Calcd. for $C_9H_{17}O_6N \cdot H_2O$: C, 42.68; H, 7.56. Found: C, 42.68; H, 7.63.

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BOSTON, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF MEDICINE, HARVARD MEDICAL SCHOOL, AND THE MEDICAL SERVICES OF THE MASSACHUSETTS GENERAL HOSPITAL]

The Solvolysis of Sulfonyl Esters of Methyl α-D-Glucopyranoside and Methyl α-D-Altropyranoside[1]

BY ROGER W. JEANLOZ AND DOROTHY A. JEANLOZ

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The solvolysis in methyl Cellosolve solution in the presence of sodium acetate of sulfonyl (methylsulfonyl and *p*-tolylsulfonyl) esters in position 2 and 3 vicinal to a carboxyl (acetyl, benzoyl, α-ethyl-*n*-butyryl) ester of methyl α-D-glucopyranoside and methyl α-D-altropyranoside has been studied. Positions 4 and 6 were blocked by a benzylidene group or benzoyl groups. Walden inversion at the carbon linked to the sulfonyl group with retention of configuration at the carbon bearing the carboxyl ester was not observed. Hydrolysis of the carboxylic ester group took place, followed eventually by solvolysis of the sulfonyl group with epoxide formation and subsequent opening of the epoxide ring. The solvolysis in the presence of sodium methoxide of the methylsulfonyl and benzoyl esters at positions 2 and 3 of the 4,6-*O*-benzylidene derivatives was investigated.

In a series of papers started in 1942, Winstein and associates[2] have shown the influence of neighboring groups on the solvolysis of sulfonyl esters. By varying the solvolytic medium, they were able to effect solvolysis with or without retention of the configuration at the carbon linked to the sulfonyl group. These results were applied to the carbohydrate field by Baker and associates[3] and led to

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(2) See S. Winstein, *et al.*, THIS JOURNAL, **64**, 2796 (1942), to **74**, 5584 (1952).

(3) B. R. Baker and R. E. Schaub, *ibid.*, **75**, 3804 (1953); B. R. Baker, R. E. Schaub, J. P. Joseph and J. H. William, *ibid.*, **76**, 4044 (1954).

TABLE I

SOLVOLYSIS OF SULFONYL ESTERS OF METHYL α-D-GLUCOPYRANOSIDE AND METHYL α-D-ALTROPYRANOSIDE IN METHYL CELLOSOLVE SOLUTION IN THE PRESENCE OF SODIUM ACETATE

Compound, methyl sulfonyl-α-D-glucopyranoside	Products obtained after recrystallization, % 2-O- or 3-O-sulfonyl ester	2,3-Anhydro derivative	Methyl 4,6-O-Benzylidene-α-D-altropyranoside	Methyl 4,6-O-Benzylidene-α-D-glucopyranoside	Starting material
3-O-Acetyl-4,6-O-benzylidene-2-O-methyl-	48				18
3-O-Benzoyl-4,6-O-benzylidene-2-O-methyl-	67				16
3-O-Acetyl-4,6-O-benzylidene-2-O-*p*-tolyl-	68		7[a]		15
3-O-Benzoyl-4,6-O-benzylidene-2-O-*p*-tolyl-	27				55
2-O-Benzoyl-4,6-O-benzylidene-3-O-methyl-	28	19	22	2	12
2-O-Benzoyl-4,6-O-benzylidene-3-O-methyl-[b]	26	14	8	1	37
2-O-Benzoyl-4,6-O-benzylidene-3-O-*p*-tolyl-		10	17		32
4,6-O-Benzylidene-2-O-(α-ethyl-*n*-butyryl)-3-O-methyl-		2			89
4,6-O-Benzylidene-2-O-(α-ethyl-*n*-butyryl)-3-O-methyl-[c]		14	5		63
3,4,6-Tri-O-benzoyl-2-O-methyl-	5[d]				40[a]
2,4,6-Tri-O-benzoyl-3-O-methyl-		8			14
Methyl sulfonyl-α-D-altropyranoside					
3-O-Benzoyl-4,6-O-benzylidene-2-O-methyl-		21	21	1	21
2-O-Benzoyl-4,6-O-benzylidene-3-O-methyl-		23	11		17[e]

[a] Crude. [b] In butanol 95%. [c] In ethyl Cellosolve, 90%. [d] Methyl 6-O-benzoyl-2-O-methylsulfonyl-α-D-glucopyranoside. [e] Sirup; $[\alpha]^{25}D$ +104 ± 1° (in chloroform, *c* 1.23). *Anal.* C, 57.67; H, 6.60; S, 0.00.

the synthesis of D-allosamine[4] and D-gulosamine[5] in the hexose series.

Solvolysis of a sulfonyl ester *trans*-vicinal to a free or esterified hydroxyl group, with Walden inversion at the carbon bearing the sulfonyl group, and retention of configuration at the vicinal carbon to give a pair of *cis*-hydroxyl groups, has not been reported for carbons located in the cyclic part of a sugar molecule.[6] Generally, solvolysis takes place with formation of an epoxy ring and subsequent opening in *trans* configuration, with retention of the original configuration or Walden inversion at both carbons.

Because the failure to locate transformation products formed in a small yield could have been due to technical difficulties in separating complex mixtures of sugars, it was thought of interest to investigate the solvolysis of sulfonyl esters of carbohydrates using chromatographic procedures.

The study was at first carried out on derivatives of methyl 4,6-O-benzylidene-α-D-glucopyranoside, a compound possessing a conformation stabilized by the benzylidene ring. Attempts to measure the influence of the size of the ester groups were made by using methylsulfonyl and *p*-tolylsulfonyl groups, and acetyl and benzoyl groups at the remaining free hydroxyls at positions 2 and 3.[7] The reaction was carried out in aqueous methyl Cellosolve in the presence of sodium acetate as previously described,[2] and the results are reported in Table I.

Derivatives of D-allose or D-mannose, the sugars expected to be formed in the type of inversion described by Winstein, were not observed. The results are consistent with a sequence of reactions in which the carboxylic esters are hydrolyzed before any solvolysis of the sulfonyl group takes place and consequently neighboring group effects are not involved. When the sulfonyl group subsequently is split off, the known methyl 2,3-anhydro-4,6-O-benzylidene-α-D-allopyranoside is formed. The epoxy ring in turn reacts with water to give the compound possessing the hydroxyl groups at C_2 and C_3 in axial configuration, very little of the equatorial configuration being formed. The rates of hydrolysis of the carboxylic esters or of solvolysis of the sulfonyl esters agree with previously known reported data and replacement of aqueous methyl Cellosolve by aqueous butanol did not change significantly the results.

In order to increase the possibility of neighboring group effect, an attempt was made to decrease the rate of hydrolysis of the carboxylic ester by using the sterically hindered α-ethyl-*n*-butyryl ester.[8] The results (see Table I) were similar to the ones previously reported and elevation of the temperature resulted in unworkable mixtures.

In the D-galactose series, it has been found that solvolysis of the sulfonyl group in position 3 with neighboring group participation of the acetamido residue in position 2, takes place only after removal of the conformation stabilizing benzylidene group.[5] Therefore in the glucose series the influence of the benzylidene group was tested by attempting solvolysis on methyl 3,4,6-tri-O-benzoyl-2-O-methylsulfonyl-α-D-glucopyranoside and methyl 2,4,6-tri-O-benzoyl-3-O-methylsulfonyl-α-D-glucopyranoside. For identification purposes, methyl 2,3-anhydro-α-D-mannopyranoside was prepared according to Myers and Robertson,[9] but different physical constants were observed and no crystalline diacetate or dibenzoate could be obtained. For the same purposes, methyl 2,3-anhydro-α-D-allopyranoside was prepared,[10] as well as its crystalline 4,6-di-O-benzoyl derivative. From the reaction with sodium acetate in methyl Cellosolve, no derivatives of D-allose or D-mannose, respectively, could be obtained (see Table I). The only crystalline products isolated besides the starting material were methyl 6-O-benzoyl-2-O-methylsulfonyl-α-D-

(4) R. W. Jeanloz, THIS JOURNAL, **79**, 2591 (1957).
(5) Z. Tarasiejska and R. W. Jeanloz, *ibid.*, **79**, 2660, 4215 (1957).
(6) See R. S. Tipson, *Adv. Carbohydrate Chem.*, **8**, 171 (1953).
(7) R. W. Jeanloz and D. A. Jeanloz, THIS JOURNAL, **79**, 2579 (1957).
(8) M. S. Newman, *ibid.*, **72**, 4783 (1950).
(9) W. H. Myers and G. J. Robertson, *ibid.*, **65**, 8 (1943).
(10) G. J. Robertson and H. G. Dunlop, *J. Chem. Soc.*, 472 (1938).

glucopyranoside in the first case, its structure being ascertained by synthesis, and methyl 2,3-anhydro-4,6-di-*O*-benzoyl-α-D-allopyranoside in the second case.

It is evident that in the D-glucose series, no neighboring group effect plays a role in the solvolysis of a sulfonyl ester located in the ring, when the neighboring group is a carboxylic ester. This contrasts with the result obtained with a neighboring group consisting of a *N*-acetamido group. The inhibition of formation of the intermediate proposed by Winstein[2] cannot be related to the chair form of the pyranose ring, because this inhibition still exists when the molecule is free to change from the C1 to the 1C form. The fact that the carboxylic ester is easily hydrolyzed, in contrast to the *N*-acetamido group, seems not to be a dominant factor, as shown by the results obtained with the much more stable α-ethyl-*n*-butyryl group and by the recovery in all experiments of starting material still containing the carboxylic esters. Such difference in reactivity between carboxylic esters and acylamino groups certainly played no role in solvolysis of sulfonyl groups in the cyclohexane series. The results obtained with a neighboring acetoxy group[2] being easily applied to compounds with a neighboring benzamido group.[11]

In order to ascertain the influence of the conformation on the solvolysis of the sulfonyl esters, derivatives of methyl 4,6-*O*-benzylidene-α-D-altropyranoside[12,13] were allowed to react. Their hydroxyls at C_2 and C_3 are in axial conformation, whereas those of the glucose derivatives previously used had an equatorial conformation.

Monomethanesulfonylation of methyl 4,6-*O*-benzylidene-α-D-altropyranoside in pyridine solution did not afford crystalline derivatives, probably because of the great instability of the resulting axial monomethylsulfonyl derivatives. However, monobenzoylation proved to be successful and reaction with one mole of benzoyl chloride in pyridine solution gave a mixture, from which the sirupy 2,3-dibenzoate, a crystalline monobenzoate and a sirupy monobenzoate could be separated by chromatography in yields of 33, 19 and 20%, respectively, together with 18% of starting material.

The crystalline monobenzoate and the sirupy monobenzoate were shown to be, respectively, the 2-*O*-benzoyl and 3-*O*-benzoyl derivatives in the following way: They were converted into the monomethylsulfonyl derivatives, both of these derivatives being obtained in a sirupy state after chromatographic separation. These derivatives were quite unstable, as shown by slight deficiencies in the amount of sulfur. Reaction of the monomethylsulfonyl derivatives with sodium methoxide gave, respectively, methyl 2,3-anhydro-4,6-*O*-benzylidene α-D-mannopyranoside[14] and methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside[12] in excellent yields, conclusively establishing the positions of the benzoyl and methylsulfonyl groups in the starting materials.

In the benzoylation of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside in pyridine solution, it had been shown previously[7] that benzoyl chloride would favor the formation of the 2-*O*-benzoyl derivative, whereas benzoic anhydride would favor the 3-*O*-benzoyl derivative. Since in the above-described experiment in the altrose series with benzoyl chloride, the two isomers were formed in the same amount, it was of interest to use benzoic anhydride as esterifying agent. Under these conditions a large amount of the 2-benzoate was isolated besides traces of 2,3-dibenzoate and 3-benzoate. Conformation of the molecule seems to play a much larger role in the reactivities of the hydroxyl groups at C_2 and C_3 toward esterifying agents than neighboring group interaction of the methoxyl group at C_1.

Solvolysis of sulfonyl derivatives in *trans*-axial conformation is known to be faster than solvolysis of the corresponding derivatives in *trans*-equatorial conformation.[15] This observation affords an easy tool for experimental evidence of the respective conformation of the hydroxyl groups at position C_2 and C_3 in methyl 4,6-*O*-benzylidene-α-D-glucopyranoside and methyl 4,6-*O*-benzylidene-α-D-altropyranoside. Solvolysis was carried out on the four monobenzoate–monomethylsulfonates at room temperature with 2.5 moles of sodium methoxide. From reactions of both altrose derivatives, the 2,3-epoxides, methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside and methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside separated after a few minutes and when the reactions were stopped after one hour, yields of 82 and 90% had been obtained. From the reactions of both glucose derivatives no epoxide was isolated, but from the 2-*O*-benzoyl-3-*O*- methylsulfonyl derivative, methyl 4,6-*O*-benzylidene-3-*O*-methylsulfonyl-α-D-glucopyranoside[16] was obtained in excellent yield, whereas from the 3-*O*-benzoyl-2-*O*-methylsulfonyl derivative, some starting material was recovered, besides the debenzoylated 2-*O*-methylsulfonyl derivative, this result being consistent with the known greater instability of the carboxylic ester at position 2. These differences in solvolysis between glucose and altrose derivatives point to, respectively, *trans*-equatorial and *trans*-axial conformation for the diols at C_2–C_3. This conclusion is in agreement with the conformations previously proposed based on the optical rotation of the cuprammonium complexes.[17]

Attempts to solvolyze the sulfonyl esters of methyl 4,6-*O*-benzylidene-α-D-altropyranoside to a *cis*-diol by heating with sodium acetate in methyl Cellosolve were unsuccessful (see Table I). From the reaction of the 2-*O*-benzoyl-3-*O*-methylsulfonyl ester, a sirupy secondary compound was isolated with elementary analyses corresponding approximately to a diacetyl ester. Alkaline hydrolysis gave the starting material, but no further identification of this compound was attempted.

(11) G. E. McCasland, R. K. Clark, Jr., and H. E. Carter, THIS JOURNAL, **71**, 637 (1949).

(12) G. J. Robertson and C. F. Griffith, *J. Chem. Soc.*, 1193 (1935).

(13) N. K. Richtmyer and C. S. Hudson, THIS JOURNAL, **63**, 1727 (1941).

(14) G. J. Robertson and W. Whitehead, *J. Chem. Soc.*, 319 (1940).

(15) See W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 48.

(16) J. Honeyman and J. W. W. Morgan, *J. Chem. Soc.*, 3660 (1955).

(17) R. E. Reeves, *Adv. Carbohydrate Chem.*, **6**, 108 (1951).

In both reactions the results obtained were similar to the ones obtained in the glucose series, and no evidence of Walden inversion at C_2 with retention of configuration at C_3 or Walden inversion at C_3 with retention of configuration at C_2 was encountered.

Experimental[7,18]

Methyl 2-*O*-Methylsulfonyl-α-D-glucopyranoside.—To a solution of 500 mg. of methyl 4,6-*O*-benzylidene-2-*O*-methylsulfonyl-α-D-glucopyranoside[7] in 6 ml. of glacial acetic acid heated on the steam bath was added dropwise 4 ml. of water. After one hour of heating, 10 ml. of water was added and the solution was evaporated *in vacuo*, the last traces of solvent being removed by codistillation with dry toluene. After drying in the desiccator, the sirup was crystallized by addition of methanol. Recrystallization from a mixture of acetone and ether gave 326 mg. (87%) of elongated prisms, m.p. 117–118°, $[\alpha]^{26}D$ +120 ± 1° (in chloroform, *c* 3.22). *Anal.* Calcd. for $C_8H_{16}O_8S$: C, 35.29; H, 5.92; S, 11.78. Found: C, 35.36; H, 5.92; S, 11.63.

Application of the same procedure to methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside[12] gave **methyl 2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside** in a 94% yield after recrystallization from a mixture of acetone, ether and pentane; m.p. 139–140°, $[\alpha]^{23}D$ + 97 ± 2° (in chloroform, *c* 0.94).[19] *Anal.* Calcd. for $C_{14}H_{20}O_8S$: C, 48.26; H, 5.79; S, 9.20. Found: C, 48.45; H, 5.85; S, 9.09.

Methyl 6-*O*-Benzoyl-2-*O*-methylsulfonyl-α-D-glucopyranoside.—To a solution of 68 mg. of methyl 2-*O*-methylsulfonyl-α-D-glucopyranoside in 0.5 ml. of anhydrous pyridine, cooled at −20°, was added a cooled solution of 0.031 ml. (1.1 moles) of benzoyl chloride in 0.5 ml. of anhydrous pyridine. After standing one day at −20°, the solution was left at room temperature for a few hours. Ice was added and the mixture was extracted with chloroform. After washing with dilute sulfuric acid, saturated sodium bicarbonate and water, the solution was dried over sodium sulfate and evaporated *in vacuo*. The residue was dissolved in benzene and chromatographed on silicic acid. Elution with a mixture of ether and ethyl acetate 9:1 eluted crystalline fractions. Recrystallization from a mixture of acetone, ether and pentane gave 61 mg. (65%) of prismatic needles, m.p. 124–125°, $[\alpha]^{23}D$ +64 ± 2° (in chloroform, *c* 0.59). *Anal.* Calcd. for $C_{15}H_{20}O_9S$: C, 47.77; H, 5.34. Found: C, 47.79; H, 5.46.

Methyl 3,4,6-Tri-*O*-benzoyl-2-*O*-methylsulfonyl-α-D-glucopyranoside.—To a solution of 245 mg. of methyl 2-*O*-methylsulfonyl-α-D-glucopyranoside in 25 ml. of anhydrous pyridine, cooled at −20°, was added 0.5 ml. of benzoyl chloride. After 3 days at 0°, ice was added, and the solution was extracted as usual. The residual sirup, partially crystalline, was dissolved in benzene and chromatographed on silicic acid. Elution with a mixture of benzene and ether 9:1 gave crystalline fractions, which afforded, after recrystallization from a mixture of methanol and pentane or from aqueous methanol, 350 mg. (65%) of prismatic needles, m.p. 116–119°, $[\alpha]^{26}D$ +65 ± 2° (in chloroform, *c* 1.74). *Anal.* Calcd. for $C_{29}H_{28}O_{11}S$: C, 59.58; H, 4.83. Found: C, 59.61; H, 4.96.

Methyl 2-*O*-Benzoyl-3-*O*-methylsulfonyl-α-D-glucopyranoside.—A solution of 500 mg. of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-methylsulfonyl-α-D-glucopyranoside[7] was hydrolyzed as described above with 10 ml. of 60% acetic acid by heating for 0.5 hour. The residual sirup was purified by chromatography. Elution with a mixture of benzene and ether 4:1 gave crystalline fractions. After recrystallization from a mixture of acetone, ether and pentane 36 mg. (7%) of starting material was obtained. Elution with a mixture of ether and ethyl acetate 9:1 gave 360 mg. of sirup, $[\alpha]^{23}D$ +152 ± 2° (in chloroform, *c* 2.30). In the presence of pyridine, the product crystallized as an adduct with one mole of pyridine. Recrystallization from a mixture of acetone, ether, pentane and a trace of pyridine gave 413 mg. (85%) of rectangular platelets, m.p. 100–130°. *Anal.* Calcd. for $C_{15}H_{20}O_9S.C_5H_5N$: C, 52.74; H, 5.53; N, 3.08; S, 7.04. Found: C, 52.80; H, 5.62; N, 2.96; S, 6.92.

Methyl 2,4,6-Tri-*O*-benzoyl-3-*O*-methylsulfonyl-α-D-glucopyranoside.—A solution of 0.5 ml. of benzoyl chloride in 2 ml. of pyridine was added at −20° to a solution of 300 mg. of the pyridine adduct of methyl 2-*O*-benzoyl-3-*O*-methylsulfonyl-α-D-glucopyranoside dissolved in 10 ml. of ethylene dichloride. After standing at 0° for 3 days, the solution was treated with ice and extracted as usual. The residual sirup was purified by chromatography, the main fractions being eluted with a mixture of benzene and ether 9:1. Crystallization from a mixture of ether and pentane gave 235 mg. (61%) of prismatic needles, m.p. 156–157°, $[\alpha]^{24}D$ +124 ± 2° (in chloroform, *c* 1.36). *Anal.* Calcd. for $C_{28}H_{28}O_{11}S$: C, 59.58; H, 4.83. Found: C, 59.39; H, 4.92.

Methyl 4,6-*O*-Benzylidene-2-*O*-(α-ethyl-*n*-butyryl)-α-D-glucopyranoside.—To a solution of 10.0 g. of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside in 50 ml. of pyridine, cooled at −20°, was added 6.0 ml. (1.3 moles) of α-ethyl-*n*-butyryl chloride. After standing one hour at 0° and 0.5 hour at room temperature, the mixture was treated with ice and extracted as usual. Crystallization from a mixture of ether and pentane gave 10.25 g. of prismatic crystals; m.p. 110–111°, $[\alpha]^{25}D$ +92 ± 2° (in chloroform, *c* 2.14). *Anal.* Calcd. for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 63.11; H, 7.43.

Chromatography of the mother liquors gave 1.3 g. (13%) of a sirup, eluted by a mixture of benzene and ether 99:1, corresponding to **methyl 4,6-*O*-benzylidene-2,3-di-*O*-(α-ethyl-*n*-butyryl)-α-D-glucopyranoside**, $[\alpha]^{24}D$ +46 ± 1° (in chloroform, *c* 3.44). *Anal.* Calcd. for $C_{26}H_{38}O_8$: C, 65.25; H, 8.00. Found: C, 64.35; H, 8.30. Mixtures of benzene and ether 19:1 and 9:1 eluted an additional crop of the 2-monosubstituted ester which weighed 0.85 g. after crystallization (total yield, 11.10 g., 82%).

Mixtures of benzene and ether 9:1 and 4:1 eluted crystalline fractions. Recrystallization from a mixture of ether and pentane gave 165 mg. (1%) of fine needles, m.p. 145–146°, $[\alpha]^{26}D$ +83 ± 1° (in chloroform, *c* 1.55), to which the structure of **methyl 4,6-*O*-benzylidene-3-*O*-(α-ethyl-*n*-butyryl)-α-D-glucopyranoside** was attributed. *Anal.* Calcd. for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 63.12; H, 7.57.

Methyl 4,6-*O*-Benzylidene-2-*O*-(α-ethyl-*n*-butyryl)-3-*O*-methylsulfonyl-α-D-glucopyranoside.—To a solution of 5.0 g. of methyl 4,6-*O*-benzylidene-2-*O*-(α-ethyl-*n*-butyryl)-α-D-glucopyranoside in 20 ml. of pyridine, previously cooled at −20°, was added 2 ml. of methanesulfonyl chloride. After standing overnight at 0°, the solution was treated as usual. Crystallization from a mixture of ether and pentane gave 5.75 (96%) of prismatic needles, m.p. 110–111°, $[\alpha]^{25}D$ +68 ± 1° (in chloroform, *c* 4.09). *Anal.* Calcd. for $C_{24}H_{30}O_9S$: C, 55.00; H, 6.59; S, 6.99. Found: C, 54.24; H, 6.19; S, 6.42. In admixture with the starting material, the m.p. was depressed to 85–105°.

To a solution of 50 mg. of methyl 4,6-*O*-benzylidene-3-*O*-methylsulfonyl-α-D-glucopyranoside (for preparation, see below) in 0.5 ml. of pyridine, previously cooled at −20°, was added 0.1 ml. of α-ethyl-*n*-butyryl chloride. After standing overnight at 0°, the solution was treated as usual. Crystallization from a mixture of ether and pentane gave 56 mg. (88%) of prismatic needles, m.p. 109–111°, $[\alpha]^{25}D$ +68 ± 1° (in chloroform, *c* 0.87). In admixture with the product described above, the m.p. was not depressed.

Methyl 4,6-*O*-Benzylidene-3-*O*-(α-ethyl-*n*-butyryl)-2-*O*-methylsulfonyl-α-D-glucopyranoside.—To a solution of 100 mg. of methyl 4,6-*O*-benzylidene-2-*O*-methylsulfonyl-α-D-glucopyranoside[7] in 0.5 ml. of pyridine, previously cooled at 0°, was added 0.1 ml. of α-ethyl-*n*-butyryl chloride. After standing overnight at 0° the solution was treated as usual. Crystallization from a mixture of ether and pentane gave 117 mg. (92%) of prismatic needles, m.p. 130–131°, $[\alpha]^{26}D$ +43 ±1° (in chloroform, *c* 1.26). *Anal.* Calcd. for $C_{21}H_{30}O_9S$: C, 55.00; H, 6.59. Found: C, 55.12; H, 6.75.

Methyl 2,3-Anhydro-α-D-mannopyranoside.—The preparation of this compound was carried out on 1.0 g. of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannoside, as pre-

(18) R. W. Jeanloz, THIS JOURNAL, **76**, 555 (1954). Microanalyses by Dr. K. Ritter, Basel, Switzerland.

(19) Brown, Fasman, McGrath and Todd[20] reported m.p. 138–139°; Wood, Allerton, Diehl and Fletcher[21] reported m.p. 139–140°, $[\alpha]D$ +87.2° in chloroform.

(20) D. M. Brown, G. D. Fasman, D. I. Mcgrath and A. R. Todd, *J. Chem. Soc.*, 1448 (1954).

(21) H. B. Wood, Jr., R. Allerton, H. W. Diehl and H. G. Fletcher, Jr., *J. Org. Chem.*, **20**, 875 (1955).

viously described by Myers and Robertson.[9] After recrystallization from a mixture of acetone and ether, 495 mg. (75%) of stout prisms was obtained, with physical constants different from those previously reported; m.p. 82–83°, $[\alpha]^{25}D$ +108 ± 1° (in chloroform, *c* 1.18).[22] *Anal.* Calcd. for $C_7H_{12}O_5$: C, 47.72; H, 6.87. Found: C, 47.60; H, 6.81.

Methyl 2,3-Anhydro-4,6-di-*O*-benzoyl-α-D-allopyranoside.—To a solution of 235 mg. of methyl 2,3-anhydro-α-D-allopyranoside[10] in 1 ml. of pyridine, cooled at −20°, was added 1.5 ml. of benzoyl chloride. After standing one day at 0° the solution was extracted as usual. The residual product was dissolved in benzene and chromatographed on silicic acid, crystalline fractions being eluted with a mixture of benzene and ether 49:1. After recrystallization from a mixture of ether and pentane, 326 mg. (64%) of prismatic needles was isolated, m.p. 125–126°, $[\alpha]^{25}D$ +199 ± 1° (in chloroform, *c* 3.48). *Anal.* Calcd. for $C_{21}H_{20}O_7$: C, 65.61; H, 5.24. Found: C, 65.69; H, 5.23.

Benzoylation of Methyl 4,6-*O*-Benzylidene-α-D-altropyranoside with Benzoyl Chloride.—To a solution of 5.0 g. of methyl 4,6-*O*-benzylidene-α-D-altropyranoside[13] (m.p. 172–174°) in 35 ml. of anhydrous pyridine, cooled at −20°, was added a cooled solution of 2.1 ml. (1.0 mole) of benzoyl chloride in 21 ml. of anhydrous pyridine. After standing at 0° for 24 hours and at room temperature for 2 hours, ice was added and the solution was extracted as usual. The residue, weighing 7.0 g., was dissolved in benzene and chromatographed on silicic acid. Elution with a mixture of benzene and ether 49:1 gave 2.85 g. (33%) of **methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-altropyranoside**, as a colorless sirup, $[\alpha]^{19}D$ +9 ± 1° (in chloroform, *c* 1.52). *Anal.* Calcd. $C_{28}H_{26}O_8$: C, 68.56; H, 5.34. Found: C, 68.38; H, 5.48. Catalytic debenzoylation of this material gave the starting material in a yield over 85% after recrystallization. Elution with a mixture of benzene and ether 9:1 gave 1.44 g. (21%) of crude crystalline fractions. Recrystallization from a mixture of ether and pentane afforded 1.31 g. (19%) of **methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-altropyranoside**, as long needles, m.p. 138–139°, $[\alpha]^{19}D$ −5 ± 1° (in chloroform, *c* 1.25). *Anal.* Calcd. for $C_{21}H_{22}O_7$: C, 65.28; H, 5.74. Found: C, 65.12; H, 5.90. Further elution with a mixture of benzene and ether 9:1 gave 1.38 g. (20%) of **methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-altropyranoside**, as a colorless sirup, $[\alpha]^{20}D$ +131 ± 2° (in chloroform, *c* 1.39). *Anal.* Calcd. for $C_{21}H_{22}O_7$: C, 65.28; H, 5.74. Found: C, 65.32; H, 5.81. Elution with ether gave 0.96 g. of the crude starting material, or 0.93 g. (18%) after recrystallization, m.p. 171–172°.

Benzoylation of Methyl 4,6-*O*-Benzylidene-α-D-altropyranoside with Benzoic Anhydride.—A solution of 500 mg. of methyl 4,6-*O*-benzylidene-α-D-altropyranoside and 450 mg. (1.1 moles) of benzoic anhydride in 2 ml. of anhydrous pyridine was heated at 70° for 40 hours. After addition of ice, the reaction product was treated and chromatographed as described above. Elution with a mixture of benzene and ether 49:1 gave 38 mg. (4%) of 2,3-dibenzoate as a colorless sirup, $[\alpha]^{26}D$ +9 ± 1° (in chloroform, *c* 1.17). Elution with a mixture of benzene and ether 19:1 gave 270 mg. of crystalline fractions. After recrystallization from a mixture of ether and pentane, 240 mg. (35%) of methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-altropyranoside was obtained, m.p. 138–139°. Elution with a mixture of benzene and ether 4:1 gave 13 mg. (2%) of impure 3-*O*-benzoyl derivative, $[\alpha]^{26}D$ +110 ± 3° (in chloroform, *c* 0.46). Elution with a mixture of benzene and ether 2:1 gave 230 mg. of starting material which, after recrystallization, weighed 195 mg. (39%) and melted at 170–172°.

A similar experiment carried out at room temperature for 5 days gave nearly similar results, no 3-*O*-benzoyl derivative being isolated.

Methyl 2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-methylsulfonyl-α-D-altropyranoside.—To a solution of 1.0 g. of the 2-*O*-benzoyl ester in 6 ml. of anhydrous pyridine, cooled at −25°, was added 0.6 ml. of methanesulfonyl chloride. After standing at 0° for 2 days, the red colored solution was treated with ice and extracted as usual. The residue was dissolved in benzene and chromatographed on silicic acid. Elution with a mixture of benzene and ether 19:1 gave one peak of a colorless sirup, weighing 1.20 g. (100%), $[\alpha]^{26}D$ −12 ± 1° (in chloroform, *c* 1.72). *Anal.* Calcd. for $C_{22}H_{24}O_9S$: C, 56.89; H, 5.21; S, 6.90. Found: C, 57.44; H, 5.67; S, 6.09. These results are consistent with the presence of 10% of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside.

A solution of 119 mg. in 3 ml. of 1.0 *N* sodium methoxide was refluxed for 2 hours. After cooling, the solution was diluted with water, and extracted with chloroform. After washing with water and drying over sodium sulfate, the chloroform was evaporated *in vacuo*. The crystalline residue was recrystallized from a mixture of ether and pentane to give 65 mg. (97%) of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside, m.p. 148°, $[\alpha]^{24}D$ +103 ± 1° (in chloroform, *c* 1.30), and showing no depression of the m.p. in admixture with authentic material.[14]

Methyl 3-*O*-Benzoyl-4,6-*O*-benzylidene-2-*O*-methylsulfonyl-α-D-altropyranoside.—Treatment of 1.14 g. of methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-altropyranoside with 0.7 ml. of methanesulfonyl chloride, as described above, gave after chromatography a colorless sirup in quantitative yield; $[\alpha]^{25}D$ +75 ± 1° (in chloroform, *c* 2.15). *Anal.* Calcd. for $C_{22}H_{24}O_9S$: C, 56.89; H, 5.21; S, 6.90. Found: C, 57.56; H, 5.72; S, 5.97. These results are consistent with the presence of 10% of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside.

A solution of 121 mg. in 3 ml. of 0.22 *N* sodium methoxide was refluxed for one hour and subsequently treated as described above. Recrystallization from a mixture of acetone, ether and pentane gave 61 mg. (88%) of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside, m.p. 203–204°, $[\alpha]^{25}D$ +138 ± 1° (in chloroform, *c* 0.91), and showing no depression of the m.p. in admixture with authentic material.[12]

Reaction of the *O*-Benzoyl-*O*-methylsulfonyl Esters at Positions 2 and 3 of Methyl 4,6-*O*-Benzylidene-α-D-glucopyranoside and Methyl 4,6-*O*-Benzylidene-α-D-altropyranoside with Sodium Methoxide.—To 25 ml. of a 0.22 *N* solution of sodium methoxide (0.55 millimole) was added in each experiment 100 mg. (0.22 millimole) of the following derivatives: methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-methylsulfonyl-α-D-glucopyranoside,[7] methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-methylsulfonyl-α-D-glucopyranoside[7], methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-methylsulfonyl-α-D-altropyranoside and methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-methylsulfonyl-α-D-altropyranoside. After one hour at room temperature (20–30°) the solution was concentrated at room temperature under a stream of nitrogen and the residue was extracted with chloroform. After washing with water and drying over sodium sulfate, the chloroform solution was evaporated *in vacuo* and the residue recrystallized or purified by chromatography on silicic acid.

From the reaction of the first compound, 69 mg. (90%) of methyl 4,6-*O*-benzylidene-3-*O*-methylsulfonyl-α-D-glucopyranoside was isolated after recrystallization from a mixture of chloroform, ether and pentane; m.p. 145°, $[\alpha]^{25}D$ +92 ± 1° (in chloroform, *c* 1.74) and showing no depression of the m.p. in admixture with authentic material.[16]

From the reaction of the second compound, 13 mg. (13%) of starting material was recovered, in addition to 45 mg. (55%) of methyl 4,6-*O*-benzylidene-2-*O*-methylsulfonyl-α-D-glucopyranoside m.p. 135–136°, $[\alpha]^{25}D$ +75 ± 1° (in chloroform, *c* 1.76) and showing no depression of the m.p. in admixture with authentic material.[7,16]

From the reaction of the third compound 46 mg. (82%) of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside was isolated, m.p. 148°, showing no depression of the m.p. in admixture with authentic material.[14]

From the reaction of the fourth compound (90%) of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside was isolated, m.p. 203–204°, showing no depression of the m.p. in admixture with authentic material.[12] In the two last experiments, most of the material separated in less than five minutes, was filtered off, and the mother liquors were left to react for one hour and treated as described.

Reaction with Sodium Acetate in Methyl Cellosolve Solution.—Unless otherwise stated, 1 part of sugar was dissolved in 19 parts of methyl Cellosolve. One part of water and 1 part of $CH_3COONa \cdot 3H_2O$ was added and the solution was refluxed for 40 hours. After cooling, the solution was diluted with a large amount of chloroform, washed twice with water, and dried over sodium sulfate. After evaporation of the chloroform and most of the methyl Cellosolve *in vacuo*, at a temperature not exceeding 50°, the residue was dissolved in 100 parts of benzene and the solution was

(22) Myers and Robertson[9] reported m.p. 67°, $[\alpha]D$ +44.6° in chloroform.

chromatographed on silicic acid. The traces of methyl Cellosolve left in the residual material were eluted in the first benzene fraction. The results are reported in Table I.

In a general way, the starting materials were eluted by mixtures of benzene and ether 49:1, 19:1 or 9:1. Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside and methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside were eluted immediately afterward with the same mixtures of solvents. Methyl 4,6-*O*-benzylidene-2-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside was eluted by mixtures of benzene and ether 19:1 and 9:1, whereas the 2-*O*-methylsulfonyl derivative required the same solvents in proportions 4:1 and 2:1.

Methyl 4,6-*O*-benzylidene-3-*O*-methylsulfonyl-α-D-glucopyranoside was eluted with the same mixture of solvents in 1:1 proportion and was recrystallized from a mixture of acetone, ether and pentane as prismatic needles, m.p. 145–146°, $[\alpha]^{25}D$ +90 ± 1° (in chloroform, *c* 2.73).[23] *Anal.* Calcd. for $C_{15}H_{20}O_8S$: C, 49.89; H, 5.59; S, 8.90. Found: C, 49.91; H, 5.67; S, 8.87. In admixture with authentic material, the m.p. was not depressed. The compound was characterized by acetylating 50 mg. with acetic anhydride in pyridine solution in the usual manner. After crystallization from a mixture of ether and pentane, 55 mg. (98%) of methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-methylsulfonyl-α-D-glucopyranoside, m.p. 153–154°, was obtained, $[\alpha]^{25}D$ +72 ± 2° (in chloroform, *c* 1.08), showing no depression of the m.p. in admixture with authentic material.[7]

Methyl 4,6-*O*-benzylidene-α-D-altropyranoside was eluted with pure ether. Recrystallization from a mixture of acetone, ether and pentane gave shiny platelets, m.p. 173–174°, $[\alpha]^{24}D$ +114 ± 2° (in chloroform, *c* 1.02).[24] *Anal.* Calcd. for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.46; H, 6.54. In admixture with authentic material the m.p. was not depressed.

Methyl 6-*O*-benzoyl-2-*O*-methylsulfonyl-α-D-glucopyranoside was eluted with a mixture of ether and ethyl acetate 4:1, whereas methyl 4,6-*O*-benzylidene-α-D-glucopyranoside was eluted with a mixture of ether and methanol 9:1.

In view of the low yields in crystalline material resulting from the reaction of methyl 3,4,6-tri-*O*-benzoyl-3-*O*-methylsulfonyl-α-D-glucopyranoside and methyl 2,4,6-tri-*O*-benzoyl-2-*O*-methylsulfonyl-α-D-glucopyranoside due to probable loss of debenzoylated product during the extraction procedure, the mixture resulting from the reaction was evaporated to dryness. The residue was refluxed with an excess of 2 *N* HCl for two hours. The solution then was passed through a column of Dowex 50 in acid form and a column of Amberlite IRA 400 in carbonate form and evaporated *in vacuo*. The residue was chromatographed on Whatman No. 54 and No. 1 papers and developed with a mixture of butan-2-one, water and concentrated ammonia in proportions 55:4:1.5. The standards used were glucose, mannose, a mixture of altrose and altrosan, and allose. Identification of the spots was made with alkaline silver nitrate. No spot corresponding to mannose could be observed with the first compound.

For the second compound no very satisfactory solvent was found for the separation of D-allose from D-altrose. However, it was possible to ascertain that no significant amount of D-allose had been formed from D-glucose during the course of the reaction.

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(23) Honeyman and Morgan[16] reported m.p. 142–143°, $[\alpha]^{17}D$ +90° (in chloroform, *c* 1.0).

(24) Robertson and Griffith[12] reported m.p. 169–170° and $[\alpha]D$ +126.8° (in chloroform, *c* 0.567); Richtmyer and Hudson[13] reported m.p. 169–170°, $[\alpha]D$ +115.0° (in chloroform, *c* 2.0).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA]

The Constitution of the Hemicellulose of Sitka Spruce (*Picea sitchensis*). II. Structure of the Mannan Portion[1]

BY G. G. S. DUTTON AND K. HUNT[2]

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Extraction of sitka spruce chlorite holocellulose with aqueous sodium hydroxide yielded a hemicellulose fraction rich in D mannose and D-glucose. Methylation studies show that the sugar units are joined by β-1,4-links and that the chains, which are apparently unbranched, contain 40–60 sugar residues. One sample contained D-galactose in a terminal position. The structural features of these glucomannans are discussed.

It is commonly stated that one of the main chemical differences between the hemicelluloses of soft and hard woods is that the latter are predominantly xylans while the former are mixtures of xylans and appreciable amounts of mannans.[3] It is apparent that these two terms are oversimplifications in that there has been no evidence for the existence of a pure mannan in a wood hemicellulose and in the case of western hemlock hemicellulose the xylan fraction has been shown to be an arabomethoxyglucuronoxylan.[4] The observation[5] that the mannan-rich fraction of hemicelluloses is more soluble in sodium hydroxide than in potassium hydroxide has enabled a good separation of these components to be made. In the present work, sitka spruce chlorite holocellulose was extracted with 10% potassium hydroxide and the washed and air-dry residue re-extracted with 18% sodium hydroxide. The composition of the potassium hydroxide extract has been discussed and the structure of the aldobiouronic acid proved.[6] This paper is concerned with the nature of the sodium hydroxide extract and the approach to the problem has been in two ways. In one instance the crude extract was methylated with dimethyl sulfate and sodium hydroxide[7] and since the partially methylated material did not readily separate, the solution was dialyzed and evaporated between each of six successive treatments. Three further treatments with Purdie reagents[8] yielded the fully methylated polysaccharide which was fractionated from chloro-

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