field, integrated intensities (five), H-5 65 (16% enhancement), H-13 148 (4%).

Registry No.—**1**, 23753-56-2; **2**, 23758-04-5; **3**, 17940-97-5; **4a**, 23758-06-7; **4b**, 23758-07-8; **5a**, 23758-08-9; **5b**, 23758-09-0; **6**, 23758-10-3; **7**, 23758-11-4; **8**, 23758-12-5; **9a**, 23829-41-6; **9b**, 23829-42-7; **10**, 23758-13-6; **11**, 23758-14-7; **12**, 23758-16-9; **13**, 23758-17-0; **14a**, 23758-18-1; **14b**, 23758-19-2; **15**, 23753-57-3; **17**, 23758-20-5; **18**, 23758-21-6; tetrahydroscandenolide, 23758-15-8.

Studies in the Ganglioside Series. IV. Preparation of 2,3-Di-*O*-acetyl-1,6-anhydro-β-D-glucopyranose and Its Utilization in the Synthesis of Oligosaccharides[1]

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2,3-Di-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (V) has been prepared by cyclization of phenyl 2,3,6-tri-*O*-acetyl-4-*O*-*t*-butyl-β-D-glucopyranoside (III) and removal from IV of the protecting *t*-butyl group by trifluoroacetic acid. Compound III was obtained by acid-catalyzed addition of 2-methylpropene to phenyl 2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (II). The use of V as aglycon in the Koenigs–Knorr reaction will permit the synthesis of oligosaccharides containing a glycosidic linkage at C-4 of glucose. This is demonstrated by the synthesis of lactose and of the aminosaccharide 4-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-D-glucopyranose (XIII).

The carbohydrate chain of the gangliosides comprises a tetrasaccharide in which galactose is attached to glucose by a 1 → 4 linkage.[2,3] It is well known that the C-4 hydroxyl group in the *C1* conformation of glucopyranose, although equatorially oriented, exhibits rather low reactivity. Richardson[4,5] has shown that the differential reactivity of the secondary hydroxyls in glucopyranosides is not solely dependent on the conformation. The 4-OH is also sterically hindered by adjacent substituents, especially by the 5-acyloxymethyl group. Because of these features of the glucose molecule, the synthesis of disaccharides of the lactose type has posed a problem ever since. Curtis and Jones,[6] using the open chain form of glucose, condensed 2,3,5,6-di-*O*-isopropylidene-D-glucose diethyl acetal with acetobromogalactose and obtained a mixture of mono- and disaccharides from which lactose could be separated by charcoal and paper chromatography.

During the course of our studies[7-9] on the gangliosides it became imperative to devise a suitably substituted glucose derivative in which the free C-4 hydroxyl would have enhanced reactivity. Earlier investigators recognized the synthetic value of 1,6-anhydro-hexopyranoses. In 1933 Freudenberg[10] coupled unsubstituted 1,6-anhydro-β-D-glucopyranose with acetobromoglucose and obtained a mixture from which cellobiose could be isolated in a 2% yield. Hudson[11] first synthesized lactose *via* its epimer (4-*O*-galactopyranosyl-β-D-mannopyranose), employing 1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose as the aglycon. The presence in the mannose molecule of two neighboring *cis* hydroxyls offers a convenient means for selective substitution by the isopropylidene group. However, since the glucose molecule lacks this possibility, we explored a different route for the preparation of a 1,6-anhydro derivative in which the C-4 hydroxyl is free for reaction.

1,6-Anhydro-β-D-glucopyranose exists in the *1C* conformation. Although all of the hydroxyl groups are axially oriented, steric considerations indicate that those in positions 2 and 4 will react preferentially. The C-3 hydroxyl is the most hindered one, owing to the hemiacetal and anhydro rings, and to the C–C linkage at C-5.[12] Indeed, esterification with benzoyl chloride, tosyl chloride, or benzyl chloroformate was found to give high yields of the 2,4-diacyl derivatives,[12,13] and benzylation, even under drastic conditions, likewise produced the 2,4-dibenzyl derivative in appreciable amounts.[14]

We now report the synthesis of 2,3-di-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (V) (Scheme I). The route adapted involves blocking of the C-4 hydroxyl by the *t*-butyl group. This group has been used in peptide synthesis for the protection of hydroxyamino acids and is conveniently introduced by acid-catalyzed addition of 2-methylpropene.[15-17] Except for one case, in which a similar reaction was carried out by a different method and under drastic conditions,[18] no attempt has been made to employ this olefin in carbohydrate chemistry. The acid-catalyzed reaction of *t*-butyl alcohol with glucose was reported to give preferentially the 6-*O*-derivative,[19] whereas the use of *t*-butyl bromide met with little success.[20]

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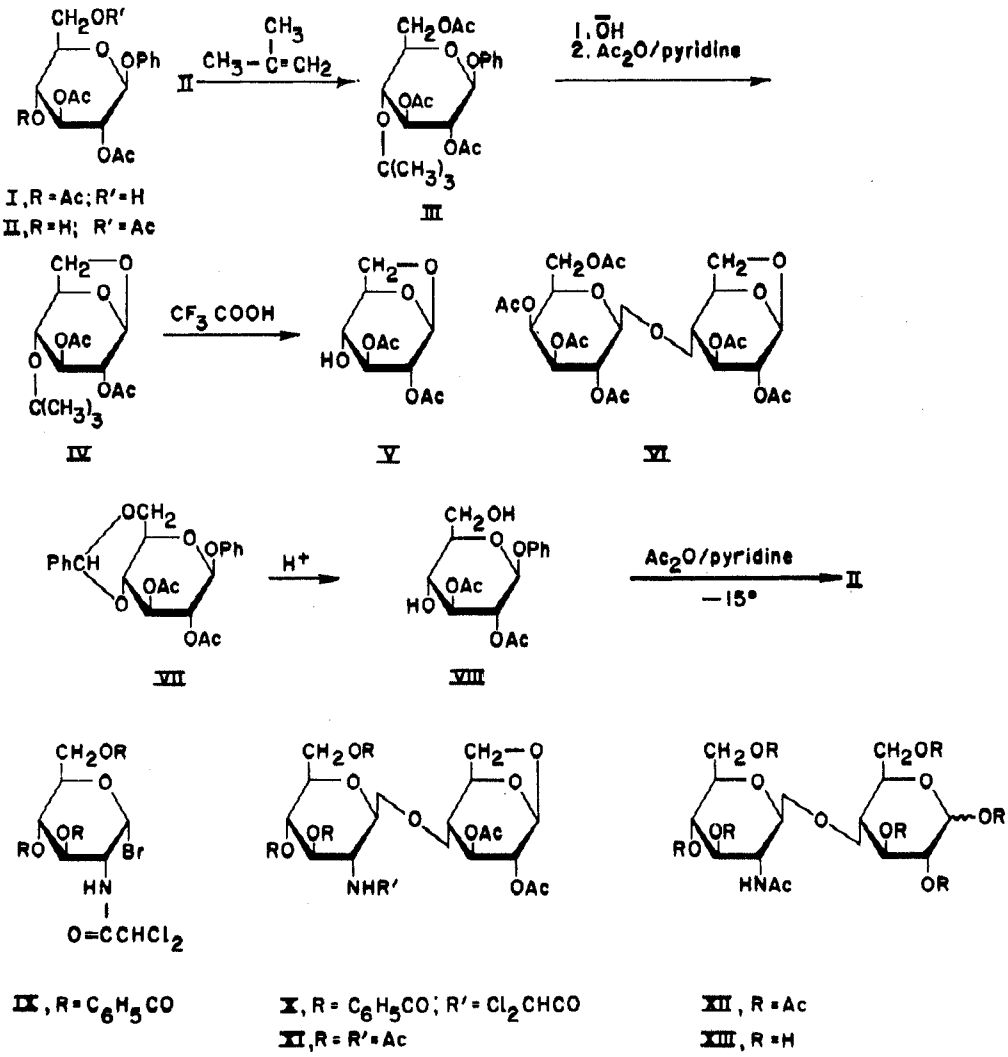
Scheme I



The reaction of II[21,22] with 2-methylpropene in the presence of a catalytic amount of concentrated sulfuric acid proceeded smoothly and afforded phenyl 2,3,6-tri-*O*-acetyl-4-*O*-*t*-butyl-β-D-glucopyranoside (III) in a 72% yield. Ring closure with potassium hydroxide followed by acetylation of the crude reaction product gave 64% 2,3-di-*O*-acetyl-1,6-anhydro-4-*O*-*t*-butyl-β-D-glucopyranose (IV). Removal of the *t*-butyl group with trifluoroacetic acid proceeded smoothly and gave an almost quantitative yield of 2,3-di-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (V).

While this investigation was in progress, another method for the preparation of V was reported which involves protection of the C-4 hydroxyl by the benzyl group. Seib,[22] investigating the acid-catalyzed polymerization of 1,6-anhydro-β-D-glucopyranose, prepared the 4-*O*-benzyl derivative of V *via* cyclization of phenyl-2,3,6-tri-*O*-acetyl-4-*O*-benzyl-β-D-glucopyranoside. The latter compound was prepared by benzylation of I with benzyl bromide in the presence of silver oxide, a reaction which took place with simultaneous 4 → 6 acetyl migration.[21] In our hands this reaction proceeded less satisfactorily. Considerably lower yields were obtained which probably resulted from partial deacetylation, as indicated by tlc.

The key intermediate II was initially prepared by alkaline rearrangement of I according to Helferich.[21] This method proved to be unsatisfactory, the yields being low and inconsistent. An alternative procedure was, therefore, considered. We found that II could be prepared more advantageously *via* the benzylidene derivative VII. Acetylation of VIII with 1 equiv of acetic anhydride under controlled conditions afforded 55% II, after chromatographic separation from the tetraacetate and a small amount of unchanged diacetate.

To simplify the preparation of V, an attempt was made to achieve the desired substitution by direct acetylation of 1,6-anhydro-β-D-glucopyranose. Treatment of the anhydro sugar with 2.5 equiv of acetic anhydride resulted in the formation of nearly equal amounts of the three diesters, in addition to the triacetate (25%). The desired diacetate V was obtained in 13% yield. The structures of the other two diacetates were determined by methylation with diazomethane-boron trifluoroetherate.[23] 2,4-Di-*O*-acetyl-1,6-anhydro-3-*O*-methyl-β-D-glucopyranose gave on deacetylation 1,6-anhydro-3-*O*-methyl-β-D-glucopyranose,[24] whereas 3,4-di-*O*-acetyl-1,6-anhydro-2-*O*-methyl-β-D-

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glucopyranose led, after ring opening by acetolysis, to 1,3,4,6-tetra-*O*-acetyl-2-*O*-methyl-α-D-glucopyranose.[23]

In a preliminary communication[25] we have shown that the Koenigs–Knorr reaction of V with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide gave a 49% yield of the hexaacetate VI.[26] Since VI has been earlier converted into lactose in high yield,[26] this route constitutes a new and convenient microscale synthesis of the disaccharide.

The significance of 2,3-di-*O*-acetyl-1,6-anhydro-β-D-glucopyranose as aglycon is further demonstrated by the synthesis of an amino sugar disaccharde as a model compound. 4-*O*-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-D-glucose (XIII) was synthesized by condensing V with 3,4,6-tri-*O*-benzoyl-2-deoxy-2-dichloroacetamido-α-D-glucopyranosyl bromide (IX), following the procedure described in previous papers of this series.[7-9] The resulting product X was converted into the N-acetyl derivative XI by alkaline hydrolysis and successive acetylation. Acetolysis of XI led, *via* XII, to the disaccharde XIII. This disaccharide has been obtained recently through enzymatic transfer of N-acetylglucosamine to glucose.[27] Its (N-unsubstituted) α isomer was found in hydrolysates of heparin.[28] It is noteworthy that the yield of the Koenigs–Knorr reaction product of V with IX was considerably lower than that of VI. This observation must be attributed to a steric hindrance due to the bulky molecule of the otherwise highly reactive bromide.

The present results provide a method for the attachment of the disaccharide 4-*O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-D-galactopyranose, recently synthesized in our laboratory,[9] to position 4 of glucose. Such a combination will lead to the trisaccharide inherent in the ganglioside of patients with Tay-Sachs disease[2,3] which presents one of the major objectives of our synthetic studies in this series.

Experimental Section[29]

Phenyl 2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside (VII).—A solution of phenyl 4,6-*O*-benzylidene-β-D-glucopyranoside[30] (8 g) in pyridine (30 ml) was treated in the cold with acetic anhydride (10 ml) and left overnight at room temperature. The solution was poured into ice–water; the precipitate was filtered, washed thoroughly with water, and dried, Crystallization from a mixture of chloroform–ethanol (1:10) gave the pure compound (8.6 g, 86%), mp 228–229°, $[\alpha]^{23}D$ −64.2° (*c* 1).

Anal. Calcd for $C_{23}H_{24}O_8$: C, 64.48; H, 5.65. Found: C, 64.56; H, 5.53.

Phenyl 2,3-Di-*O*-acetyl-β-D-glucopyranoside (VIII).—A solution of VII (20 g) in 60% aqueous acetic acid (350 ml) was kept at 80° for 45 min. The cooled solution was extracted several times with hexane and concentrated *in vacuo*. Tlc [benzene–ethyl acetate (1:2)] of the crystalline residue showed no starting material and only a faint spot of a compound moving more slowly than the major product. Crystallization from a mixture of acetone–ether–hexane gave 13.4 g (84%) of VIII, mp 142–143°, $[\alpha]^{23}D$ −45° (*c* 2).

Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.46; H, 5.92. Found: C, 56.69; H, 5.90.

Phenyl 2,3,6-Tri-*O*-acetyl-β-D-glucopyranoside (II).—A solution of the diacetyl derivative VIII (6.8 g, 20 mmol) in pyridine (50 ml) was cooled to −20°, and acetic anhydride (2.0 ml) was added in one portion. After 48 hr at −15°, the solution was concentrated *in vacuo*, and the reagents were coevaporated several times with toluene. Chromatography of the residue on silica gel with ethyl acetate–methylene chloride (8:92) gave 2.1 g (24%) of the fully acetylated glycoside. A mixture of the same solvents (15:85) eluted II (4.18 g, 55%) as a homogeneous product. Ethyl acetate–methylene chloride (3:1) removed unreacted material (0.60 g, 9%). The triacetate melted at 134–135° (lit. 130°[21] and 134.5–135.5°[22]); $[\alpha]^{23}D$ −54° (*c* 3.1).

Phenyl 2,3,6-Tri-*O*-acetyl-4-*O*-*t*-butyl-β-b-glucopyranoside (III).—To dry methylene chloride (76 ml) containing concentrated sulfuric acid (0.30 ml) was added at −5° isobutene (23 ml). After the mixture stirred for a few minutes at this temperature, phenyl 2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (3.82 g) was added in one portion. The solution was kept in a well stoppered flask at −2–0° for 1 hr and then overnight at room temperature. The cooled solution was shaken carefully with ice-cold 2.5% sodium hydrogen carbonate, washed with cold water to neutrality, and dried over sodium sulfate. Tlc [benzene–ethyl acetate (3:1)] showed a faint spot of unreacted material and a major faster moving spot. After evaporation of the solvent *in vacuo*, the residue was chromatographed on a silica gel column. The fraction eluted with methylene chloride–ethyl acetate (9:1) yielded 3.17 g (72%) of a homogeneous product. It was crystallized from ethyl acetate–hexane and had mp 139–140°, $[\alpha]^{22}D$ −44.7° (*c* 2). The nmr spectrum showed signals at τ 2.55–3.15 (five aromatic protons), 7.92, 7.95, and 7.96 (nine acetyl protons), and 8.80 (nine *t*-butyl protons).

Anal. Calcd for $C_{22}H_{30}O_9$: C, 60.26; H, 6.90. Found: C, 60.50; H, 6.63.

2,3-Di-*O*-acetyl-1,6-anhydro-4-*O*-*t*-butyl-β-D-glucopyranose (IV).—A solution of III (3.0 g) in 2-methoxyethanol (15 ml) and 15% aqueous potassium hydroxide (35 ml) was refluxed in an oil bath at 100–110° for 24 hr. The cooled solution was neutralized carefully with 2 *N* sulfuric acid and concentrated to dryness under reduced pressure. The remainder was extracted three–four times with boiling absolute alcohol, and the combined extracts were evaporated. The solid residue, dried over phosphorus pentoxide, was dissolved in hot pyridine (10 ml), and acetic anhydride (8 ml) was added to the filtrate. After standing at room temperature overnight, the reaction mixture was concentrated to dryness *in vacuo*, and the last traces of the acylating agent were removed by distilling with several portions of toluene. The residue was passed through a silical gel column. Methylene chloride–ethyl acetate (88:12) eluted a homogeneous product (1.32 g, 64%). After crystallization from ether–hexane, it melted at 140–141°, $[\alpha]^{22}D$ −48.8° (*c* 2.2), tlc [benzene–ethyl acetate (1:1)] R_f 0.72. The nmr spectrum showed signals at τ 7.85, 7.90 (six acetyl protons) and 8.75 (nine *t*-butyl protons).

Anal. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.34. Found: C, 55.60; H, 7.46.

2,3-Di-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (V).—To the *t*-butyl derivative IV (800 mg) dissolved in methylene chloride (10 ml) was added trifluoroacetic acid containing 1% water (1 ml). After standing for 15 min at room temperature, the solution was concentrated *in vacuo* and the remainder was treated with distilling toluene at room temperature. Tlc [benzene–ethyl acetate (1:1)] showed no starting material. The residual syrup (850 mg) refused to crystallize. It was chromatographed on silica gel (40 g) and eluted with ethyl acetate–methylene chloride (2:1). The oily product weighed 780 mg (92%), $[\alpha]^{22}D$ −44.6° (*c* 3.5) (lit.[22] $[\alpha]^{22}D$ −45°), tlc [benzene–ethyl acetate (1:1)] R_f 0.28.

Anal. Calcd for $C_{10}H_{14}O_7$: C, 48.78; H, 5.73. Found: C, 48.72; H, 5.70.

Partial Acetylation of 1,6-Anhydro-β-D-glucopyranose.—The anhydro sugar (laevoglucosan,[31] 6.48 g, 0.040 mol) dissolved in pyridine (60 ml) was treated overnight at room temperature with acetic anhydride (9.5 ml, 0.100 mol). After the solution was warmed at 50° for 1 hr, the excess of acylating reagent was removed *in vacuo* by coevaporating several times with toluene. Tlc [benzene–ethyl acetate (1:1)] showed, in addition to some

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unreacted material, the presence of triacetyllaevoglucosan (TAL) and of a monoacetyl derivative. Three further spots moving close to each other were assumed to be the three diacetates (R_f: a, 0.44; b, 0.38; c, 0.28). The product was chromatographed on a silica gel column from which the triacetate (2.9 g, 25%) was removed by methylene chloride–ethyl acetate (85:15). A 1:1 mixture of these solvents eluted pure a (140 mg), pure c (190 mg), and mixtures of the isomers totaling 5.25 g (53%). Rechromatography on silical gel with methylene chloride–ethyl acetate (1:1) and on silica gel G with ethyl acetate yielded the following homogeneous compounds.

2,4-Di-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (a).—Compound a (1.43 g, 15%) was crystallized from ether, mp 132–133°, $[\alpha]^{22}D$ −70.2° (*c* 3), R_{TAL} 0.65.

Anal. Calcd for $C_{10}H_{14}O_7$: C, 48.78; H, 5.73. Found: C, 49.02; H, 5.55.

3,4-Di-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (b).—Compound b (0.980 g, 10%) was crystallized from ethyl acetate–hexane, mp 96–97°, $[\alpha]^{22}D$ −79.5° (*c* 2.2), R_{TAL} 0.57.

Anal. Calcd for $C_{10}H_{14}O_7$: C, 48.78; H, 5.73. Found: C, 48.98; H, 5.61.

Compound c.—This oily product (1.25 g, 13%, R_{TAL} 0.41) was identical in every respect with V.

2,4-Di-*O*-acetyl-1,6-anhydro-3-*O*-methyl-β-D-glucopyranose.—Methylation of compound a with diazomethane–boron trifluoroetherate was effected by the procedure of Mastronardi, *et al.*[23] Methylene chloride–ethyl acetate (3:1) eluted 53% oil which could not be induced to crystallize, $[\alpha]^{22}D$ −57.7° (*c* 1.8), tlc [benzene–ethyl acetate (1:1)] R_f 0.67. The nmr spectrum showed signals at τ 6.52 (three methoxyl protons) and 7.86 and 7.88 (six acetyl protons).

Anal. Calcd for $C_{11}H_{16}O_7$: C, 50.77; H, 6.20. Found: C, 50.30; H, 6.09.

Deacetylation of the preceding compound in absolute methanol containing a catalytic amount of sodium methylate gave, after crystallization from acetone–pentane, 70% 1,6-anhydro-3-*O*-methyl-β-D-glucopyranose, mp 65–67°, $[\alpha]^{22}D$ −64° (*c* 2.1, acetone) (lit.[24] mp 65–66°, $[\alpha]^{20}D$ −64.8°).

3,4-Di-*O*-acetyl-1,6-anhydro-2-*O*-methyl-β-D-glucopyranose.—Methylation of compound b gave on chromatography (as described above) the pure diacetate (76%) as a waxy solid. After crystallization from ethyl acetate–hexane, the product melted at 45–46°, $[\alpha]^{22}D$ −86.8° (*c* 2.6), tlc [benzene–ethyl acetate (1:1)] R_f 0.58, nmr τ 6.48 (three methoxyl protons) and 7.85 and 7.90 (six acetyl protons).

Anal. Calcd for $C_{11}H_{16}O_7$: C, 50.77; H, 6.20. Found: C, 50.51; H, 6.15.

Ring opening in the preceding compound was effected by the method of Hudson.[11] The anhydro derivative (150 mg) was treated with a 7:3 mixture (8 ml) of acetic anhydride–acetic acid and concentrated sulfuric acid (0.1 ml) for 4 hr at 50°. Anhydrous sodium acetate (0.5 g) was added, and the mixture was concentrated *in vacuo*. The residue was extracted with chloroform; the extract was washed with water, dried, and evaporated. Crystallization from ethanol gave 155 mg (73%) of 1,3,4,6-tetra-*O*-acetyl-2-*O*-methyl-α-D-glucopyranose, mp 105–107°, $[\alpha]^{22}D$ +111° (*c* 1.6) (lit.[23] mp 106–108°, $[\alpha]^{20}D$ + 109°).

2,3-Di-*O*-acetyl-1,6-anhydro-4-*O*-(3,4,6-tri-*O*-benzoyl-2-deoxy-2-dichloroacetamido-β-D-glucopyranosyl)-β-D-glucopyranose (X).—To a solution of 2,3-di-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (V, 0.6 g) in dry benzene–nitromethane (2:1, 30 ml) were added mercuric cyanide (1 g) and the bromide IX[7] (3 g), and the reaction was allowed to proceed with stirring at 40° for 96 hr. The cooled solution was poured into a mixture of ice–water (100 ml) and methylene chloride (200 ml). The organic layer was washed four times with cold water, dried over sodium sulfate, and evaporated *in vacuo* to constant weight. The glycoside (200 mg, 10%) was eluted from a silica gel column with methylene chloride–ethyl acetate (92:8). After crystallization from isopropyl alcohol containing a few drops of ether, it melted at 112°, $[\alpha]^{23}D$ −38° (*c* 1), tlc (ethyl acetate) R_f 1.7. A strong band at 11.2 μ in the ir spectrum indicated the presence of a β-glycoside. The nmr spectrum showed signals at τ 2–2.9 (15 aromatic protons), 4.18 (dichloroacetyl proton), and 7.9 and 8.1 (six acetoxy protons).

Anal. Calcd for $C_{39}H_{37}Cl_2NO_{15}$: C, 56.39; H, 4.49; Cl, 8.54. Found: C, 56.12; H, 4.53; Cl, 8.65.

2,3-Di-*O*-acetyl-1,6-anhydro-4-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-β-D-glucopyranose (XI).—To a solution of X (160 mg) in absolute methanol (15 ml) was added at −15° 1 *N* barium methoxide (0.2 ml), and the mixture was allowed to stand in the refrigerator for 4 hr at 3–5°. The methanol was evaporated *in vacuo* at room temperature to about 5 ml, and 1 *N* barium methoxide (4 ml) and water (1 ml) were added. The hydrolysis of the dichloroacetyl group was accomplished after 24 hr at room temperature. The solution was neutralized with methanolic hydrogen chloride and evaporated *in vacuo* to dryness, whereupon the moisture was removed by coevaporation with isopropyl alcohol. The residue, dried thoroughly over phosphorus pentoxide, was shaken with pyridine (10 ml) and acetic anhydride (8 ml) overnight at room temperature. After removal of the acylating agents *in vacuo*, the residue was taken up with methylene chloride (100 ml) and water (50 ml), and the solution was washed with three portions of water (50 ml each). The residue resulting from the evaporation of the dried solution was crystallized from acetone–ether and yielded 110 mg (84%) of XI, mp 194–195°, $[\alpha]^{29}D$ −29.3° (*c* 1.1), tlc (ethyl acetate) R_V 0.31 or R_X 0.18.

1,2,3,6-Tetra-*O*-acetyl-4-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-α-D-glucopyranose (XII).—Opening of the 1,6-anhydro ring was effected as described previously. The disaccharide XI (80 mg) was stirred at 40° with a mixture of acetic anhydride (7 ml), acetic acid (3 ml), and concentrated sulfuric acid (0.05 ml). After 3 hr, anhydrous sodium acetate (0.3 g) was added, the solution was concentrated *in vacuo*, and the reagents were coevaporated with toluene to dryness. The residue was taken up with methylene chloride and passed through a silica gel G column (15 g). The product was obtained by elution with ethyl acetate, yield 77 mg (65%). After crystallization from acetone–ether, it melted at 148–151°, $[\alpha]^{29}D$ +24.0° (*c* 0.5), tlc (ethyl acetate) R_V 0.68 or R_{XI} 2.2.

Anal. Calcd for $C_{28}H_{39}NO_{18}$: C, 49.63; H, 5.80. Found: C, 49.97; H, 5.77.

4-*O*-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-D-glucopyranose (XIII).—To a solution of the octaacetyl derivative XII (55 mg) in absolute methanol (10 ml) was added at −15° 1 *N* barium methoxide (0.1 ml) and the mixture was allowed to stand for 4 hr in refrigerator (+5°). Neutralization with Dowex 50-X[8] (2 g) followed by evaporation of the filtrate afforded the crude disaccharide. It crystallized from alcohol on adding a few drops of ether to the warm solution. The disaccharide was homogeneous on tlc [benzene–methanol (1:1)], $R_{lactose}$ 0.95, mp 190–195° (with sintering at 175°), $[\alpha]^{27}D$ +30° (*c* 0.7, water). The infrared spectrum showed bands at 3.0 (OH), 6.05 and 6.45 (amide), and 11.2 μ (β-disaccharide).

Anal. Calcd for $C_{14}H_{25}O_{11}N \cdot H_2O$: C, 41.89; H, 6.78. Found: C, 41.83; H, 6.66.

Registry No.—II, 22348-26-1; III, 23740-46-7; IV, 23740-47-8; V, 22331-11-9; VII, 23740-55-8; VIII, 23740-56-9; X, 23740-57-0; XI, 23740-58-1; XII, 23740-59-2; XIII, 23740-60-5; 2,4-di-*O*-acetyl-1,6-anhydro-β-D-glucopyranose, 23740-49-0; 3,4-di-*O*-acetyl-1,6-anhydro-β-D-glucopyranose, 23740-50-3; 2,4-di-*O*-acetyl-1,6-anhydro-3-*O*-methyl-β-D-glucopyranose, 23740-51-4; 1,6-anhydro-3-*O*-methyl-β-D-glucopyranose, 23740-52-5; 3,4-di-*O*-acetyl-1,6-anhydro-2-*O*-methyl-β-D-glucopyranose, 23740-53-6; 1,3,4,6-tetra-*O*-acetyl-2-*O*-methyl-α-D-glucopyranose, 14199-55-4.