[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY, COLLEGE OF AGRICULTURE, KYOTO UNIVERSITY]

Synthesis of 2-Amino-2-deoxy-β-D-glucosides *via* 3,4,6-Tri-*O*-acetyl-2-benzylsulfonamido-2-deoxy-α-D-glucopyranosyl Bromide

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Received July 3, 1961

3,4,6-Tri-*O*-acetyl-2-benzylsulfonamido-2-deoxy-α-D-glucopyranosyl bromide has been prepared and used in the preparations of the methyl, ethyl, and *n*-propyl β-glycosides in good yields. Hydrogenolysis in the presence of hydrochloric acid removes the benzylsulfonyl group to give the corresponding 2-amino-2-deoxy-β-D-glucoside hydrochlorides. This procedure has been extended to disaccharide syntheses, and some substituted 2-amino-2-deoxy-β-D-glucosyl-disaccharides have been prepared.

It has been reported in the previous paper[1] that 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl bromide and chloride are very readily converted into 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-α-D-glucose hydrobromide and hydrochloride, respectively, in the presence of water through an acyl migration. A similar acyl migration has also been reported in 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyanosyl chloride.[2] Some *O*-glycosides of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranose[1] and β-D-galactopyranose[2] were prepared by prompt using of the freshly prepared chloroform solutions of the corresponding hexosyl halides, avoiding the acyl migration. However, more convenient methods free from the the danger of the acyl migration are desirable for the glycosidation particularly in regard to application for the synthesis of 2-amino-2-deoxy-hexosyl-disaccharides.

Investigations for this purpose have been reported[3,4] from other laboratories. The present paper describes use of 3,4,6-tri-*O*-acetyl-2-benzylsulfonamido-2-deoxy-α-D-glucopyranosyl bromide (V) for the glycosidation with methyl, ethyl, and *n*-propyl alcohols; hydrogenolysis in the presence of hydrochloric acid removes the sulfonyl group to give the corresponding alkyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glycopyranoside hydrochlorides. Some substituted 2-amino-2-deoxy-β-D-glucosyldisaccharides have also been prepared by this method. The benzylsulfonyl group has been employed successfully to protect the amino group in peptide synthesis.[5] In carbohydrate chemistry, some *O*-benzylsulfonyl esters are known and it is noted that the ester linkage is very readily cleaved on catalytic hydrogenation.[6]

2-Benzylsulfonamido-2-deoxy-D-glucose (II) was prepared in poor yield by the Schotten-Baumann reaction of 2-amino-2-deoxy-D-glucose hydrochloride (I) with benzylsulfonyl chloride in aqueous medium. This product was so crude that acetylation with acetic anhydride and pyridine did not give crystalline acetate. 1,3,4,6-Tetra-*O*-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranose (IV), however, was obtained in crystalline form and in high yield by the reaction of 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranose (III) with benzylsulfonyl chloride in pyridine. It was converted into 3,4,6-tri-*O*-acetyl-2-benzylsulfonamido-2-deoxy-α-D-glucopyranosyl bromide in good yield by the treatment with hydrogen bromide in acetic acid. This compound has a melting point of 65–75° and is stable in a vacuum desiccator for several days at room temperatures.

Methyl, ethyl, and *n*-propyl 3,4,6-tri-*O*-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranosides (VI) were prepared in good yields from V by the reactions with the corresponding alcohols in chloroform with silver oxide as the condensing agent and anhydrous sodium sulfate as the desiccant.

Hydrogenolysis of methyl 3,4,6-tri-*O*-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranoside (VIa) with Raney nickel in methanol solution in the presence of one equivalent of hydrogen chloride produced in 80% yield methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside hydrochloride (VIIa) from which was obtained methyl 2-amino-2-deoxy-β-D-glucoside hydrochloride (Xa) after removal of the acetyl groups with methanolic ammonia. This compound was also obtained in poor yield and less pure by hydrogenolyzing methyl 2-benzylsulfonamido-2-deoxy-β-D-glucoside (VIIIa) prepared by the deacetylation of methyl 3,4,6-tri-*O*-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranoside with methanolic ammonia. Treatment of methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucoside hydrochloride (VIIa) with sodium acetate in aqueous solution

(1) Y. Inouye, K. Onodera, S. Kitaoka, and H. Ochiai, *J. Am. Chem. Soc.*, 79, 4218 (1957). *Cf.* related work by F. Micheel and coworkers, as cited in: A. B. Foster and D. Horton, *Advances in Carbohydrate Chem.*, 14, 246 (1959).

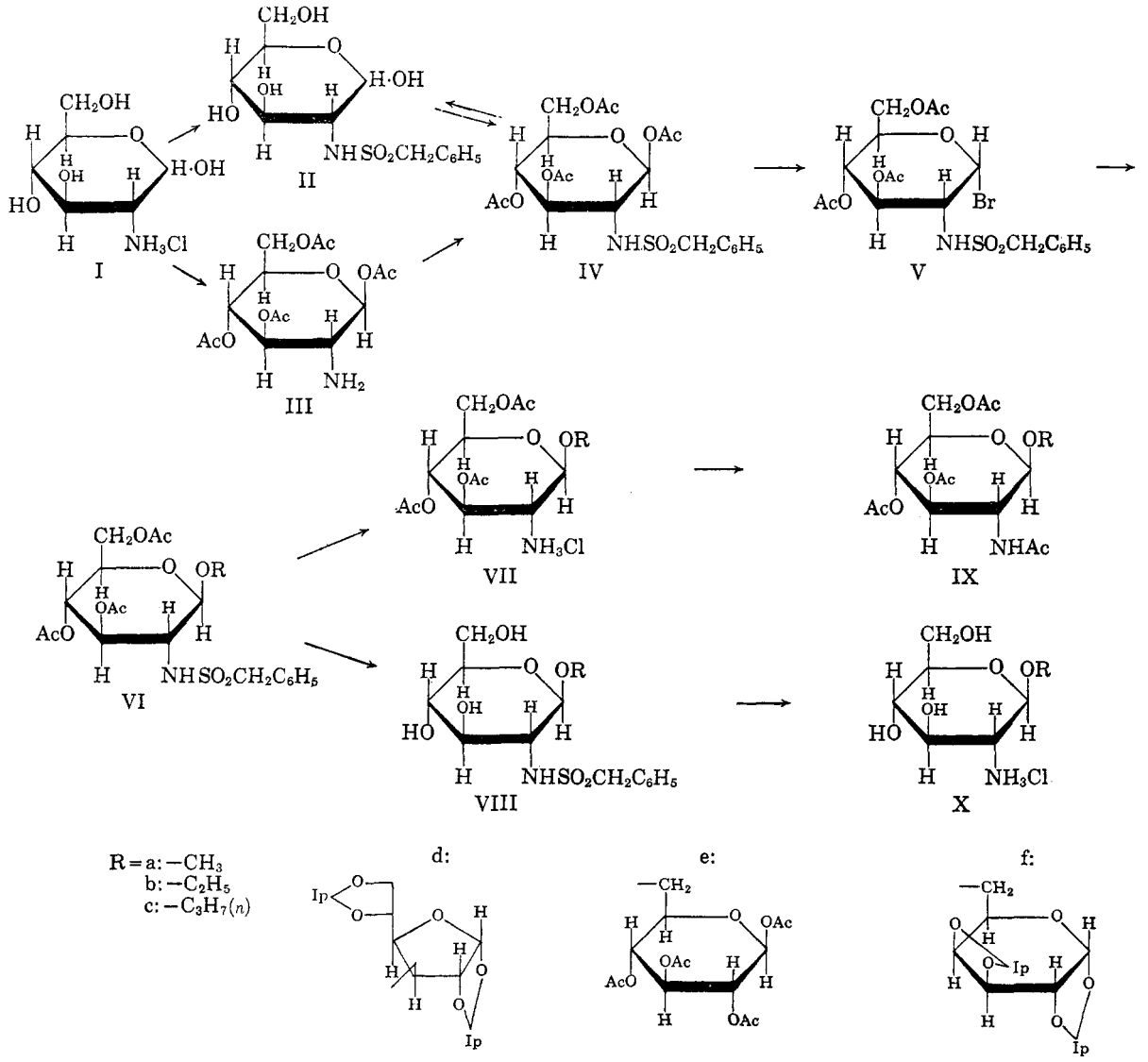
(2) Z. Tarasiejska and R. W. Jeanloz, *J. Am. Chem. Soc.*, 80, 6325 (1958).

(3) P. F. Lloyd and M. Stacey, *Chem. & Ind.*, 917 (1955); *Tetrahedron*, 9, 116 (1960).

(4) L. Zervas and S. Konstas, *Chem. Ber.*, 93, 435 (1960).

(5) H. B. Milne and C. H. Pong, *J. Am. Chem. Soc.*, 79, 639, 645 (1957).

(6) G. W. Kenner and M. A. Murray, *J. Chem. Soc.*, S. 178 (1949).



and then with acetic anhydride in chloroform extract gave methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (IXa), identical with the compound obtained from 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosyl bromide as reported previously.[1]

Ethyl and *n*-propyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside hydrochlorides (VIIb, VIIc) were similarly obtained by hydrogenolysis of the corresponding *N*-benzylsulfonyl derivatives (VIb, VIc) and acetylation gave the *N*-acetylated products (IXb, IXc).

The reaction with 3,4,6-tri-*O*-acetyl-2-benzylsulfonamido-2-deoxy-α-D-glucopyranosyl bromide was extended to the syntheses of some substituted 2-amino-2-deoxy-β-D-glucosyl disaccharides. The products thus obtained in crystalline form are 3-*O*-(3,4,6-tri-*O*-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (VId), 6-*O*-(3,4,6-tri-*O*-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranosyl)-1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose (VIe), and 6-*O*-(3,4,6-tri-*O*-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (VIf). Hydrogenolysis of the last compound gave 6-*O*-(3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose hydrochloride (VIIf).

EXPERIMENTAL[7]

2-Benzylsulfonamido-2-deoxy-D-glucose (II). A 2.15 g. sample (0.01 mole) of 2-amino-2-deoxy-D-glucose hydrochloride (I) was dissolved in 10 ml. of *N* sodium hydroxide (0.01 mole). To this was added with vigorous stirring half the volume of a solution of 1.9 g. (0.01 mole) of benzylsulfonyl chloride[8] in 20 ml. of acetone. When the reaction

(7) All melting points are uncorrected. The petroleum ether used throughout the experiments has b.p. 30–70°.

(8) J. M. Spra Gue and T. B. Johnson, *J. Am. Chem. Soc.*, 59, 1837 (1937).

solution turned acidic to litmus, 5 ml. of *N* sodium hydroxide and 5 ml. of the remaining acetone solution of benzylsulfonyl chloride were added with stirring. This procedure was repeated. The reaction solution was allowed to stand overnight and then concentrated under reduced pressure. The residual gel was brought on filter paper, washed with cold water, dried and crystallized from a large volume of hot ethanol-ether to yield 0.5 g. (13.7%) of II, m.p. 211° dec. This compound is sparingly soluble in water and in ordinary organic solvents, and therefore the rotatory power was not measured.

Anal. Calcd. for $C_{13}H_{19}NO_9S$: C, 46.80; H, 5.77; N, 4.50. Found: C, 46.82; H, 5.75; N, 4.21.

Acetylation in acetic anhydride and pyridine produced a brown amorphous powder which was not crystallized from any solvents.

II was also obtained by treating 1,3,4,6-tetra-*O*-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranose (IV) with methanolic ammonia at room temperature for 2.5 hr.; m.p. 213° dec.

Anal. Found: C, 46.67; H, 5.96; N, 4.41.

1,3,4,6-Tetra-O-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranose (IV). Nineteen grams of 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucose[9] was dissolved in 100 ml. of pyridine, and 19 g. of finely powdered benzylsulfonyl chloride was added in one portion. The mixture was shaken vigorously with ice cooling to give a yellow viscous solution, which was then shaken at room temperature for 3 hr. Dropping the solution into ice water with stirring precipitated a reddish yellow product which was collected by filtration, washed with ice water, and dried in a desiccator. It was dissolved in hot methanol, treated with charcoal, and filtered. Upon addition of ether and then petroleum ether to the cooled filtrate, prisms were obtained in a yield of 20 g. (77%); m.p. 135°, $[\alpha]_D^{29}$ −2.5° (*c* 4, chloroform).

Anal. Calcd. for $C_{21}H_{27}NO_{11}S$: C, 50.29; H, 5.23; N, 2.27. Found: C, 50.56; H, 5.23; N, 2.27.

3,4,6-Tri-O-acetyl-2-benzylsulfonamido-2-deoxy-α-D-glucopyranosyl bromide (V). An ice-cooled mixture of 50 ml. of acetic acid and 10 ml. of acetic anhydride was saturated with hydrogen bromide, and to this was added 10 g. of IV. After leaving overnight over phosphorus pentoxide, the pale yellow viscous solution was dropped into ice water with stirring. The resulting precipitate was collected by filtration and washed with ice water. It was dissolved in 50 ml. of ether, washed, and dried by usual procedures, and the ether solution evaporated under reduced pressure to give an amorphous substance. It was again taken up in ether, treated with charcoal and evaporated under reduced pressure. The yield of the product having m.p. 65–75° was 7.5 g. (72%). It was stable for several days in a vacuum desiccator but decomposed on standing in air overnight; it was soluble in ether, alcohol, chloroform, benzene, and acetone, $[\alpha]_D^{25}$ +89.4° (*c* 1.12, chloroform).

Anal. Calcd. for $C_{19}H_{24}NO_9SBr$: C, 43.68; H, 4.63; N, 2.68. Found: C, 43.78; H, 4.60; N, 2.72.

Methyl 3,4,6-tri-O-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranoside (VIa). To a mixture of 10 ml. of anhydrous chloroform, 2 ml. of methanol, 2 g. of freshly prepared silver oxide, and 5 g. of anhydrous sodium sulfate was added dropwise a chloroform solution of 0.9 g. of V with vigorous stirring. After stirring for 12 hr. at room temperature in the dark, the reaction mixture was filtered and the solid residue was washed with chloroform and the washings combined with the filtrate. The dark chloroform solution was treated with hydrogen sulfide to decompose the silver complex, and filtered to give a nearly colorless filtrate. It was washed with a saturated aqueous solution of sodium bicarbonate and then water, and dried with anhydrous sodium sulfate. Evaporation of the chloroform solution *in vacuo* gave a sirup which was dissolved in warm ether and cooled to separate colorless crystals. Recrystallization from methanol-ether afforded prisms weighing 0.6 g. (73%) and melting at 155–156° after drying *in vacuo;* $[\alpha]_D^{25}$ −53° (*c* 2, chloroform).

Anal. Calcd. for $C_{20}H_{27}NO_{10}S$: C, 50.74; H, 5.75; N, 2.96. Found: C, 50.84; H, 5.81; N, 3.22.

The synthesis with mercuric cyanide as the catalyst in place of silver oxide resulted in poor yield and less purity.

Methyl 3,4,6-tri-O-acetyl-2-amino-2-deoxy-β-D-glucopyranoside hydrochloride (VIIa). One gram of VIa was dissolved in 20 ml. of methanol containing exactly 1 molar equivalent of hydrogen chloride. A Raney nickel catalyst prepared from 15 g. of alloy according to the W-4 method[10] was added to this solution, and into the mixture was passed a stream of hydrogen with vigorous stirring for 2.5 hr. The catalyst was filtered and washed with methanol, and the washings were combined with the filtrate. After treatment with charcoal, the methanolic solution was concentrated under reduced pressure and ether was added to the residual thin sirup to effect crystallization; recrystallization was effected from methanol by adding ether. The yield was 0.6 g. (80%); m.p. 227–229°, $[\alpha]_D^{27}$ +13.6° (*c* 1.32, water). Fodor and Ötvös[11] reported m.p. 233° and $[\alpha]_D^{19}$ +17° (methanol).

Anal. Calcd. for $C_{13}H_{22}NO_8Cl$: C, 43.88; H, 6.21; N, 3.94. Found: C, 43.92; H, 6.14; N, 4.08.

Methyl 2-benzylsulfonamido-2-deoxy-β-D-glucoside (VIIIa). A solution of 1 g. of VIa in 15 ml. of methanol was saturated with ammonia at 0° and allowed to stand at room temperature for 3 hr. Concentration followed by chilling separated the crystalline product which was recrystallized from ethanol to give 0.68 g. (93%) needles with m.p. 202–203°, $[\alpha]_D^{27}$ −16.5° (*c* 0.67, methanol).

Anal. Calcd. for $C_{14}H_{21}NO_7S$: C, 48.41; H, 6.09; N, 4.03. Found: C, 48.64; H, 6.15; N, 4.28.

Acetylation of VIIIa in acetic anhydride and pyridine gave needles whose melting point and mixed melting point with VIa obtained above were 155–156°.

Methyl 2-amino-2-deoxy-β-D-glucoside hydrochloride (Xa). *A. By deacetylation of* VIIa. VIIa (0.5 g.) was deacetylated with methanolic ammonia, crystallized from methanol containing 1 equivalent (0.051 g.) of hydrogen chloride, and recrystallized from ethanol by adding ether to give 0.1 g. (31%) plates, m.p. 190°, $[\alpha]_D^{27}$ −23.4° (*c* 1, water).

Anal. Calcd. for $C_7H_{16}NO_5Cl$: C, 36.75; H, 7.02; N, 6.14. Found: C, 36.46; H, 7.03; N, 6.04.

This compound has been known.[12]

B. By hydrogenolysis of VIIIa. One gram of VIIIa was hydrogenolyzed in methanol in a manner similar to that for obtaining VIa to give 0.066 g. (10%) of Xa. The melting point and mixed melting point with the preparation obtained above were 187–189°.

Methyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranoside (IXa). VIIa (0.1 g.) was neutralized with aqueous sodium acetate solution and treated with chloroform and acetic anhydride. The organic layer yielded, after working up and recrystallization from methanol by adding ether and petroleum ether, 70 mg. of IXa in needles, m.p. 160°, $[\alpha]_D^{23}$ −29° (*c* 1, chloroform).

Anal. Calcd. for $C_{15}H_{23}NO_9$: C, 49.86; H, 6.42; N, 3.88. Found: C, 50.10; H, 6.46; N, 3.82.

This compound[13] was identical in all respects with the one prepared by the Koenigs-Knorr reaction from the fresh chloroform solution of 2-acetamido-3,4,5-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl bromide as reported previously.[1]

(9) M. Bergmann and L. Zervas, *Ber.*, **64**, 975 (1931); **65**, 1201 (1932).

(10) A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946).

(11) G. Fodor and L. Ötvös, *Acta Chim. Acad. Sci. Hung.*, **5**, 205 (1954).

(12) J. C. Irvine, *J. Chem. Soc.*, **103**, 48 (1913); A. B. Foster, D. Horton, and M. Stacey, *J. Am. Chem. Soc.*, 81 (1957).

(13) W. O. Cutler, W. N. Haworth, and S. Peat, *J. Chem. Soc.*, 1979 (1937).

Ethyl 3,4,6-tri-O-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranoside (VIb). This compound was obtained in 65.5% yield by quite a similar procedure described for the methyl glycoside; m.p. 138–139°, $[\alpha]_D^{25}$ −49° (*c* 2, chloroform).

Anal. Calcd. for $C_{21}H_{29}NO_{10}S$: C, 51.74; H, 6.00; N, 2.87. Found: C, 51.94; H, 5.80; N, 3.27.

Debenzylsulfonylation by hydrogenolysis gave ethyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside hydrochloride (VIIb) in 72% yield; m.p. 242°, $[\alpha]_D^{27}$ +16.3° (*c* 0.8, water).

Anal. Calcd. for $C_{14}H_{24}NO_8Cl$: C, 45.47; H, 6.54; N, 3.79. Found: C, 45.28; H, 6.69; N, 3.96.

Acetylation of VIIb produced in 80% yield ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside, m.p. 167°, $[\alpha]_D^{23}$ −23.3° (*c* 1, chloroform).

Anal. Calcd. for $C_{16}H_{25}NO_9$: C, 51.20; H, 6.71; N, 3.73. Found: C, 51.26; H, 6.78; N, 3.99.

Kuhn and Kirschenlohr[14] reported for this compound m.p. 167–169°, $[\alpha]_D^{20}$ −24.8° (methanol).

n-Propyl 3,4,6-tri-O-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranoside (VIc). This was obtained in 77% yield; m.p. 134°, $[\alpha]_D^{23}$ −40.7° (*c* 1.4, chloroform).

Anal. Calcd. for $C_{22}H_{31}NO_{10}S$: C, 52.70; H, 6.23; N, 2.79. Found: C, 52.98; H, 6.44; N, 2.74.

The debenzylsulfonylated hydrochloride (VIIc) was prepared in 72.5% yield; m.p. 230°, $[\alpha]_D^{27}$ +41.3° (*c* 0.8, water).

Anal. Calcd. for $C_{15}H_{26}NO_8Cl$: C, 46.93; H, 6.83; N, 3.65. Found: C, 46.72; H, 6.95; N, 3.66.

Acetylation of VIIc afforded in 60% yield the *N*-acetyated derivative (IXc), m.p. 164°, $[\alpha]_D^{23}$ −21.7° (*c* 1, chlorolform).

Anal. Calcd. for $C_{17}H_{27}NO_9$: C, 52.45; H, 6.99; N, 3.60. Found: C, 52.35; H, 7.03; N, 3.80.

This compound has been reported[14] to have m.p. 164–166°, $[\alpha]_D^{20}$ −22.7° (methanol).

3-O-(3,4,6-Tri-O-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranosyl) - 1,2:5,6 - di - O - isopropylidene - α - D-glucofuranose (VId). Four grams (0.015 mole) of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose was dissolved in 20 ml. of anhydrous chloroform. To this were added 5 g. of freshly prepared silver oxide and 5 g. of anhydrous sodium sulfate, and the mixture was stirred vigorously for 2 hr. A solution of 7.5 g. (0.015 mole) of V in 40 ml. of chloroform was added dropwise to the mixture in a period of 2 hr. After the addition was completed, 2.5 g. of silver oxide and 5 g. of sodium sulfate were added to the reaction mixture and stirring was continued for additional 48 hr. at room temperature in the dark. It was filtered with aid of charcoal and the solid residue washed with several portions of warm chloroform. The combined filtrate and washings were treated with hydrogen sulfide, and the clear filtrate was washed with an aqueous solution of sodium bicarbonate and then with water, dried over anhydrous sodium sulfate, and evaporated under reduced pressure to a pale yellow sirup. It was dissolved in ether, treated with charcoal, and allowed to stand in an ice box. There were separated colorless crystals which were washed with ether and recrystallized from ethanol-ether; yield 0.6 g. (6% based on V), m.p. 219°, $[\alpha]_D^{19}$ −35.5° (*c* 2, chloroform).

Anal. Calcd. for $C_{31}H_{43}NO_{15}S$: C, 53.06; H, 6.18; N, 2.00. Found: C, 53.11; H, 6.03; N, 2.05.

(14) R. Kuhn and W. Kirschenlohr, *Chem. Ber.*, **86**, 1331 (1953).

6-O-(3,4,6-Tri-O-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranosyl) - 1,2,3,4 - tetra - O - acetyl - β - D - glucopyranose (VIe). A similar procedure described in the synthesis of VId was used with 4 g. (0.012 mole) of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose dissolved in 20 ml. of anhydrous chloroform, 5 g. of silver oxide, 5 g. of anhydrous sodium sulfate, and 7.5 g. (0.015 mole) of V dissolved in 25 ml. of anhydrous chloroform. Recrystallization was effected from chloroform by adding methanol to give fine needles weighing 3.1 g. (34% based on V) and melting at 246° after being dried; $[\alpha]_D^{19}$ −18.5° (*c* 2, chloroform).

Anal. Calcd. for $C_{33}H_{42}NO_{19}S$: C, 50.24; H, 5.37; N, 1.78. Found: C, 50.10; H, 5.61; N, 1.78.

This substance is soluble in chloroform, dioxane and tetrahydrofuran and slightly soluble in methanol, ethanol, and acetone.

6-O-(3,4,6-Tri-O-acetyl-2-benzylsulfonamido-2-deoxy-β-D-glucopyranosyl) - 1,2:3,4 - di - O - isopropylidene - α - D - galactopyranose (VIf). A mixture of 17 g. (0.073 mole) of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, 10 g. of silver oxide, 10 g. of anhydrous sodium sulfate, and 40 ml. of anhydrous chloroform was stirred for 2 hr., and then 15 g. (0.028 mole) of V in 40 ml. of anhydrous chloroform was added dropwise during 3 hr. When the addition was half completed additional 5 g. each of silver oxide and anhydrous sodium sulfate was added. After being stirred for 48 hr. at room temperature in the dark, the mixture was worked up in a manner similar to the one described above. The finally obtained sirup was dissolved in methanol and dropped onto ice-water with vigorous stirring to produce a white precipitate which was collected by filtration and washed with cold water. This procedure was repeated once more in order to remove unchanged di-*O*-isopropylidene galactose. The white product was dried, dissolved in 50% hot ethanol and allowed to stand to separate a viscous matter. The supernatant was dropped into water with stirring to produce a white crystalline precipitate which, after leaving overnight, was filtered, washed with water, and dried *in vacuo* over phosphorus pentoxide. The yield of VIf with m.p. 91–100° and $[\alpha]_D^{19}$ −80° (*c* 2, chloroform) was 10 g. (49.6% based on V).

Anal. Calcd. for $C_{31}H_{43}NO_{15}S$: C, 53.06; H, 6.18; N, 2.00. Found: C, 52.89; H, 6.24; N, 2.13.

This compound is soluble in ethanol and ether and insoluble in water and petroleum ether.

6-O-(3,4,6-Tri-O-acetyl-2-amino-2-deoxy-β-D-glucopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose hydrochloride (VIIf). One gram of VIf was dissolved in 20 ml. of methanol. A Raney nickel catalyst prepared from 15 g. of alloy according to the W-4 method[10] was added and a stream of hydrogen was passed in. One equivalent of methanolic hydrogen chloride was added and the reaction mixture was vigorously stirred for 1 hr., when another equivalent of hydrochloric acid was added. Hydrogenolysis completed in 4 hr. The reaction mixture was filtered and the residue washed with methanol. The combined filtrate and washings were treated with charcoal and evaporated under reduced pressure to about 5 ml. to which was added an excess of ether to give a white precipitate. It was filtered, washed with ether, and recrystallized from hot methanol by addition of ether; yield 0.35 g. (42%), m.p. 245° (charring), $[\alpha]_D^{18}$ −21° (*c* 1, methanol).

Anal. Calcd. for $C_{24}H_{38}NO_{13}Cl$: C, 49.36; H, 6.56; N, 2.40. Found: C, 49.36; H, 6.54; N, 2.61.

This is soluble in water, and insoluble in ether.

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