bromide in acetic acid according to the conditions of Lloyd and Stacey[3] for a compound described as I, gave V in almost quantitative yield, with physical constants in agreement with those reported[3]; n.m.r. data[28]: $\tau$ 8.15 (6-OAc), 7.93 (4-OAc), 7.89 (3-OAc), 3.40 (doublet, H-1, $J_{1,2}$ = 3.5 c.p.s.).

**2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-$\alpha$-D-glucopyranose (III).**—This compound[12,13] was prepared in 56% yield by direct acetylation of 2-amino-2-deoxy-D-glucose hydrochloride by the acetic anhydride–sodium acetate procedure.[12] It could also be obtained by acetylation of II with acetic anhydride in an excess of pyridine.[11] The pure material had m.p. 139.5–140.5°, $[\alpha]_D$ +93° (*c* 1.0, chloroform); $\lambda_{max}^{KBr}$ 2.92 (NH), 5.74 (OAc), 6.00, 6.57 (NHAc), and 11.82 $\mu$ (equatorial H at C-1); n.m.r. data[28]: $\tau$ 8.09 (6-OAc), 7.98 (3,4-OAc), 7.93 (2-NAc), 7.81 (1-OAc), 3.82 (doublet, H-1, $J_{1,2}$ = 3.5 c.p.s.); X-ray powder diffraction data[28]: 12.28 m, 9.31 vs (1), 7.03 w, 6.28 w, 5.99 vw, 5.44 s, 5.13 m, 4.80 m, 4.58 vw, 4.37 m, 4.17 s (2), 4.00 m, 3.63 s (3), 3.52 m, 3.35 m, 3.13 m.

**2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-$\beta$-D-glucopyranose (IX).**—The following procedure provided a facile route to this compound. 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-$\alpha$-D-glucopyranosyl chloride (VI)[8] (3.47 g.) was dissolved in acetic acid (30 ml.), mercuric acetate (3.18 g.) was added, and the mixture was stirred for 2 hr. at room temperature. Chloroform (150 ml.) was added to the clear solution followed by water (10 ml.), the mixture was shaken, and the organic layer was separated and dried over magnesium sulfate. After evaporation of the chloroform, the product was crystallized from methanol–ether yielding 3.20 g. (86%), m.p. 186–186.5°. A second recrystallization gave small prisms, m.p. 186.0–186.5°, $[\alpha]_D$ +1.5 ± 0.5° (*c* 1, chloroform); $\lambda_{max}^{KBr}$ 3.10 (NH), 5.73 (OAc), 6.02, and 6.50 $\mu$ (NHAc); n.m.r. data[28]: $\tau$ 8.09 (6-OAc), 7.97 (3,4-OAc), 7.93 (2-NAc), 7.89 (1-OAc), 4.27 (doublet, H-1, $J_{1,2}$ 8.5 c.p.s.); X-ray powder diffraction data[28]: 9.31 m, 7.08 s, (2,2), 6.66 w, 6.24 m, 5.19 w, 4.85 vs (1), 4.60 w, 4.21 m, 3.79 s (2,2), 3.55 s (3), 3.25 w. The product was only moderately soluble in chloroform, almost insoluble in water, and readily soluble in methanol. The above route provides a synthesis of IX from 2-amino-2-deoxy-D-glucose hydrochloride, in 67% over-all yield, by way of 2-acetamido-2-deoxy-D-glucose and VI.[7,8]

A sample of VIII (347 mg.), as used in the conversion to VII, was acetylated with acetic anhydride in excess pyridine solution, and after conventional processing crystalline IX was obtained in 290-mg. (75%) yield, m.p. 185–186°. A repeat preparation with the hydrochloride salt of VIII (383 mg.) also gave IX in 310-mg. (80%) yield. Similar results were obtained when VIII·HCl was acetylated by the acetic anhydride–sodium acetate procedure.[15] In all cases the product was identical with that prepared by the first procedure.

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# Aryl Thioglycopyranosides, Aryl Glycopyranosyl Sulfones, and the Novel Oxidation–Acetylation of Aryl 1-Thio-$\beta$-D-glucopyranosides to 6-*O*-Acetyl-$\beta$-D-glucopyranosyl Aryl Sulfones[1]

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When *p*-tolyl 1-thio-$\beta$-D-glucopyranoside in a mixture of glacial acetic acid and 30% hydrogen peroxide is allowed to stand for several days at room temperature, the product, obtained in nearly quantitative yield, is not the expected $\beta$-D-glucopyranosyl *p*-tolyl sulfone but the 6-*O*-acetyl derivative of the sulfone. Experiments indicate that this novel acetylation reaction may occur at the intermediate sulfoxide stage. A number of other aryl thioglycosides and aryl glycosyl sulfones are described, and some of their reactions and their infrared and nuclear magnetic resonance spectra are discussed.

In an attempt to find new antimalarials, Montgomery, Richtmyer, and Hudson[3] prepared a series of substituted phenyl 1-thio-$\beta$-D-glucopyranosides. In 1947, one of these compounds, the *p*-tolyl 1-thio-$\beta$-D-glucopyranoside (IV), was dissolved in glacial acetic acid and oxidized with an excess of 30% hydrogen peroxide for several days at room temperature. The product, obtained in nearly quantitative yield, was expected to be the $\beta$-D-glucopyranosyl *p*-tolyl sulfone (III),[4] but carbon and hydrogen analyses corresponded almost exactly to the values required for a 1:1 double compound between the sulfone and the sulfoxide.[5] This seemed quite plausible in view of a paper entitled "Mixed Crystals of Sulfoxides and Sulfones" that had been published shortly before.[6] Ten years later, however, when an infrared spectrum of our compound revealed what appeared to be strong carbonyl absorption at 1695 cm.$^{-1}$, the problem seemed to warrant further study.

A survey of the literature showed that the oxidation products of thioglycosides included both sulfones and sulfoxides. Wrede and Zimmermann[7] prepared the first sulfones; these were mainly of the bis($\beta$-D-glycopyranosyl) sulfone type and were made by oxidation of the acetylated bis($\beta$-D-glycopyranosyl) sulfides with potassium permanganate in acetic acid and then deacetylating the crystalline products. Micheel and Schmitz[8] described the first sulfoxide, ethyl $\alpha$-D-glucopyranosyl sulfoxide; this was obtained by the oxidation of ethyl 1-thio-$\alpha$-D-glucopyranoside with dilute aqueous hydrogen peroxide. Bonner and Drisko[9] oxidized five acetylated thioglycosides to their respective sulfones by heating either with aqueous potassium

(1) Presented in part before the Division of Carbohydrate Chemistry at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) Associate in the Visiting Program of the National Institutes of Health, Oct., 1961, to Sept., 1963.

(3) E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson, *J. Org. Chem.*, **11**, 301 (1946).

(4) It was thus listed, under Survey No. 15418* and N.I.H. No. 2873 by G. R. Coatney, W. C. Cooper, N. B. Eddy, and J. Greenberg in "Survey of Antimalarial Agents," Public Health Monograph No. 9, U. S. Government Printing Office, 1953, p. 214.

(5) *Anal.* Calcd. for $C_{26}H_{36}O_{13}S_2$: C, 50.31; H, 5.85. Found: C, 50.30; H, 5.80.

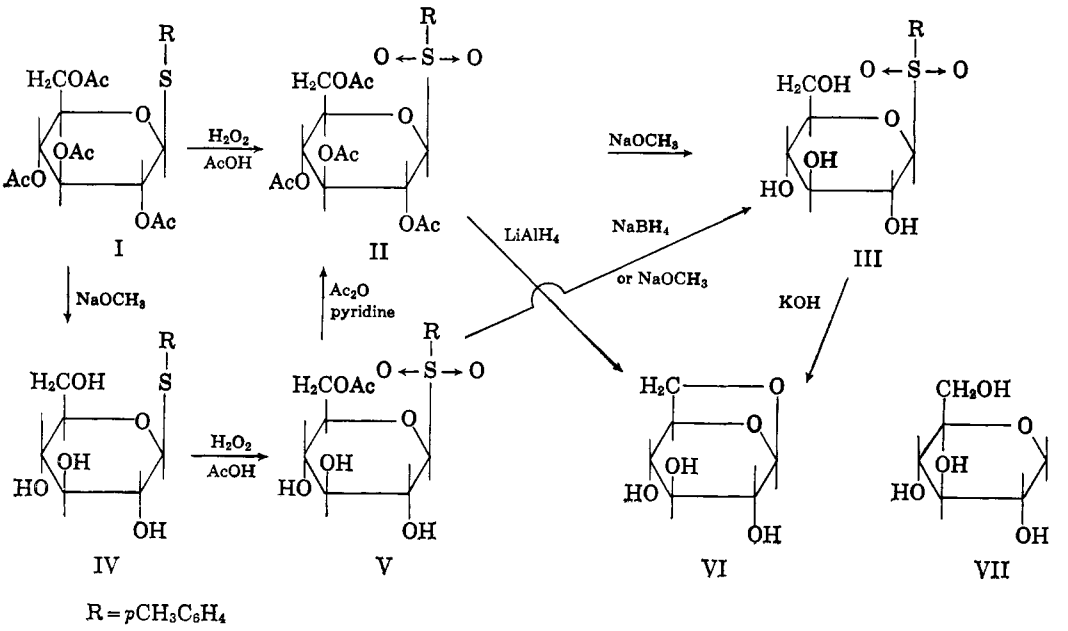
(6) H. Rheinboldt and E. Giesbrecht, *J. Am. Chem. Soc.*, **68**, 973 (1946).

(7) F. Wrede and W. Zimmermann, *Z. physiol. Chem.*, **148**, 65 (1925).

(8) F. Micheel and H. Schmitz, *Ber.*, **72**, 992 (1939).

(9) W. A. Bonner and R. W. Drisko, *J. Am. Chem. Soc.*, **70**, 2435 (1948).

SCHEME I




permanganate in acetic acid or with 30% hydrogen peroxide in acetic acid. They attempted to oxidize phenyl tetra-*O*-acetyl-1-thio-β-D-glucopyranoside with one molecular equivalent of permanganate and thus obtain the sulfoxide, but isolated instead only a mixture of sulfone and starting thioglucoside. Wagner and Kühmstedt,[10] however, were able to prepare sulfoxides by the action of one and sulfones by the action of two or more molecular equivalents of 30% hydrogen peroxide in glacial acetic acid upon the completely acetylated derivatives of *p*-hydroxyphenyl 1-thio-β-D-glucopyranoside and *p*-β-D-glucopyranosyloxyphenyl 1-thio-β-D-glucopyranoside.

In this investigation we have prepared three new aryl 1-thio-β-D-gluco- and galactopyranosides (X, XVII, and XX) and their tetraacetates (VIII, XIV, and XVIII) by well-known procedures; five new aryl β-D-gluco- and β-D-galactopyranosyl sulfone tetraacetates (II, IX, XI, XV, and XIX) by the action of 30% hydrogen peroxide in glacial acetic acid upon the corresponding thioglycoside tetraacetates[11]; and, by deacetylation, three new aryl β-D-gluco- and β-D-galactopyranosyl sulfones (III, XII, and XVI). Although sulfoxides have been isolated in the sugar series,[8,10] we, like Bonner and Drisko,[9] were unsuccessful with *p*-tolyl 1-thio-β-D-glucopyranoside tetraacetate (I) and limited amounts of hydrogen peroxide or sodium metaperiodate,[12] and with iodosobenzene.[13] When one molecular equivalent of potassium permanganate in glacial acetic acid was used and the product deacetylated, a paper chromatogram dipped in silver nitrate reagents revealed mainly the thioglucoside with some sulfone; a paper chromatogram sprayed with a new specific reagent sensitive to sulfoxides[14] indicated the probable presence of only a very small amount of sulfoxide. In an example outside the sugar series an interesting possibility of disproportionation reactions between two sulfoxide molecules has been suggested[15] to explain the failure of repeated efforts to isolate the desired sulfoxide.

The degradation of β-D-glucopyranosyl *p*-tolyl sulfone (III) with hot aqueous potassium hydroxide, like that of the unoxidized phenyl and *p*-dimethylaminophenyl 1-thio-β-D-glucopyranosides reported earlier,[16] yielded 1,6-anhydro-β-D-glucopyranose (levoglucosan, VI). The reductive desulfurization with Raney nickel of tetra-*O*-acetyl-β-D-glucopyranosyl sulfone (II), followed by deacetylation, yielded 1,5-anhydro-D-glucitol (polygalitol, VII) just as the desulfurization of the unoxidized *p*-phenyl and *p*-tolyl 1-thio-β-D-glucopyranosides had.[17] These degradation and desulfurization reactions confirm the pyranoside ring structures of the sulfones as determined by periodate oxidation methods. The attempted reduction of the sulfone tetraacetate (II) with lithium aluminum hydride also yielded levoglucosan (VI), and the sulfone thus appears to be sensitive to the basicity of that solution even at room temperature. Acetolysis and bromine in chloroform[18] seemed to cause no reaction with the sulfone tetraacetate (II). (See Scheme I.)

As noted earlier in this paper, the action of 30% hydrogen peroxide in glacial acetic acid upon the free *p*-tolyl 1-thio-β-D-glucopyranoside (IV) led not to the expected sulfone (III) but to a compound that showed carbonyl absorption in its infrared spectrum. Subse-

(10) G. Wagner and H. Kühmstedt, *Naturwissenschaften*, **46**, 425 (1959); *Arch. Pharm.*, **294**, 147 (1961).

(11) Bonner and Drisko (ref. 9) reported that partial deacetylation occurred when their reaction mixture was refluxed for 2 hr.; we have observed no deacetylation when the reaction is carried out at room temperature.

(12) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

(13) A. H. Ford-Moore, *J. Chem. Soc.*, 2126 (1949).

(14) J. F. Thompson, W. N. Arnold, and C. J. Morris, *Nature*, **197**, 380 (1963).

(15) H. H. Szmant and L. Alfonso, unpublished work cited by H. H. Szmant, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, p. 161.

(16) E. M. Montgomery, N. K. Richtmyer, and C. S. Hudson, *J. Org. Chem.*, **10**, 194 (1945).

(17) H. G. Fletcher, Jr., and N. K. Richtmyer, *Advan. Carbohydrate Chem.*, **5**, 1 (1950); N. K. Richtmyer, *Methods Carbohydrate Chem.*, **2**, 193 (1963).

(18) W. A. Bonner [*J. Am. Chem. Soc.*, **70**, 770 (1948)] found that bromine in glacial acetic acid effects acetolysis with the unoxidized compounds; *e.g.* phenyl tetra-*O*-acetyl-1-thio-β-D-glucopyranoside is converted into α-D-glucose pentaacetate in good yield. The corresponding tetra-*O*-acetyl-β-D-glucopyranosyl phenyl sulfone was unaffected by bromine in glacial acetic acid [W. A. Bonner, *ibid.*, **70**, 3491 (1948)].

quent experiments and analyses showed that it contained an acetyl group at C-6 and accordingly must be the 6-*O*-acetyl-β-D-glucopyranosyl *p*-tolyl sulfone (V). Since acetylation of this compound produced the sulfone tetraacetate (II) and deacetylation produced the free sulfone (III), the presence of an *O*-acetyl group was established. When oxidized with periodate, the compound consumed 2 moles of oxidant and liberated 1 mole of formic acid per mole of compound; thus, the hydroxyls at C-2, C-3, and C-4 were free and the acetyl group could be only at C-6. This allocation was verified by the nuclear magnetic resonance spectra (see Experimental) of this compound and of 6-*O*-acetyl-β-D-glucopyranosyl *p*-bromophenyl sulfone, the only other similar compound that could be obtained crystalline following the action of hydrogen peroxide and glacial acetic acid upon nine other thioglycosides. Compound V could be prepared also, but in low yield, by the unimolecular acetylation of III with acetic anhydride and pyridine.

The acetylating action of acetic acid upon carbohydrates has been reported by Duff,[19] who obtained modest yields of the 6-*O*-acetyl derivatives of D-glucose and D-galactose by heating the sugars in 50% aqueous acetic acid for about 24 hr. at 100°. Appreciable amounts of esters were detected even with lower concentrations of acetic acid and at lower temperatures. On the basis of rotational and paper chromatographic evidence only, de Grandchamp-Chaudun[20a] has reported that, when D-glucose, D-fructose, D-galactose, and maltose are dissolved in glacial acetic acid at room temperature and left for several months, each is converted completely into two acetates. The identification of these products has not yet been revealed.

In an effort to learn something of the mechanism of formation of the 6-*O*-acetyl compounds, we dissolved small amounts of the *p*-tolyl 1-thio-β-D-glucopyranoside (IV) and the corresponding β-D-glucopyranosyl *p*-tolyl sulfone (III) each separately in (a) glacial acetic acid, (b) glacial acetic acid plus 30% hydrogen peroxide, and (c) glacial acetic acid plus water equal in volume to that of the hydrogen peroxide solution in (b). The six solutions were kept for 7 days at 25° and then concentrated in a vacuum desiccator. Only the thioglucoside (IV) in solution (b) yielded the 6-*O*-acetylsulfone (V), while the other solutions gave unchanged starting materials.[20b] The practically quantitative unimolecular acetylation that accompanies the oxidation of *p*-tolyl 1-thio-β-D-glucopyranoside to the corresponding sulfone by hydrogen peroxide in glacial acetic acid thus appears to be a novel type of acetylation. Since the thioglucoside (IV) was not attacked by glacial acetic acid and the sulfone (III) was not acetylated by the glacial acetic acid–hydrogen peroxide mixture, we can only postulate that acetylation takes place at the intermediate sulfoxide stage. Since we have been unable to isolate the intermediate sulfoxide, the problem remains a puzzle and warrants still further investigation.

Data on infrared and n.m.r. spectra are reported in the Experimental section.

(19) R. B. Duff, *J. Chem. Soc.*, 4730 (1957).

(20) (a) A. de Grandchamp-Chaudun, *Compt. rend.*, **252**, 1397 (1961). (b) NOTE ADDED FEBRUARY 24, 1964.—Phenyl β-D-glucopyranoside also was unaffected by a mixture of glacial acetic acid and 30% hydrogen peroxide under these conditions.

## Experimental

Paper chromatography was carried out on Whatman No. 1 filter paper by the descending method at room temperature in 1-butanol–pyridine–water (6:4:3). The locations of the spots were revealed by dipping the papers in silver nitrate in acetone followed by sodium hydroxide in aqueous ethanol.[21a] The values for $R_{gal}$ and $R_{glu}$ refer to the rate of migration of the compounds on paper chromatograms relative to that of galactose and glucose, respectively. Melting points were determined in capillary tubes.

**Tetra-*O*-acetyl-β-D-glucopyranosyl *p*-Tolyl Sulfone (II).**[21b]—To a solution containing 3.7 g. of *p*-tolyl tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (I)[3] in 40 ml. of glacial acetic acid was added 7.4 ml. of 30% hydrogen peroxide. After 9 days at 25° the solution was diluted with water until crystallization appeared to be complete. The product weighed 3.6 g. (91%) and melted at 151–153°. After three recrystallizations from six parts of 95% ethanol the prismatic needles of the sulfone tetraacetate showed m.p. 152–153° and $[\alpha]^{20}D$ −35.1° (*c* 1, chloroform).

*Anal.* Calcd. for $C_{21}H_{26}O_{11}S$: C, 51.85; H, 5.39; S, 6.6; OAc, 35.4. Found: C, 51.95; H, 5.17; S, 6.7; OAc, 35.3.

**β-D-Glucopyranosyl *p*-Tolyl Sulfone (III).**—Deacetylation of 4.0 g. of the sulfone tetraacetate (II) in 150 ml. of methanol was accomplished catalytically by the addition of 2 ml. of 0.4 *N* methanolic barium methoxide. After 36 hr. at 25° the solution was neutralized with carbon dioxide and concentrated *in vacuo* to a sirup that crystallized as needles (2.0 g.) upon the addition of a small amount of water. Recrystallization from ethyl acetate afforded glistening needles of the sulfone, m.p. 153–154° (followed by slow charring), $[\alpha]^{20}D$ −28.4° (*c* 1, pyridine), $\lambda_{max}^{MeOH}$ 225 mμ (ε 15,400), $R_{gal}$ 2.55.

*Anal.* Calcd. for $C_{13}H_{18}O_7S$: C, 49.05; H, 5.70; S, 10.1. Found: C, 49.32; H, 5.81; S, 10.5.

**6-*O*-Acetyl-β-D-glucopyranosyl *p*-Tolyl Sulfone (V) from *p*-Tolyl 1-Thio-β-D-glucopyranoside (IV).**—Ten grams of anhydrous[22] IV was dissolved in 47 ml. of glacial acetic acid, 18 ml. of 30% hydrogen peroxide was added, and the mixture was left at 25° for 7 days. It was then concentrated to a crystalline residue (11.7 g.) in a vacuum desiccator over potassium hydroxide pellets. The product was recrystallized from 200 ml. of boiling water to give 9.8 g., m.p. 187–188°, and then several times from ethyl acetate. The fine, silky, plate-like needles of the sulfone monoacetate melted sharply at 191° with the evolution of gas and blackening, $[\alpha]^{20}D$ −4.4° (*c* 3, pyridine), $\lambda_{max}^{MeOH}$ 225 mμ (ε 15,000), $R_{gal}$ 2.73.

*Anal.* Calcd. for $C_{15}H_{20}O_8S$: C, 49.99; H, 5.59; S, 8.9; OAc, 11.9; mol. wt., 360. Found: C, 50.05; H, 5.60; S, 8.8; OAc, 12.4; mol. wt. (Mechrolab vapor pressure osmometer), 347.

**6-*O*-Acetyl-β-D-glucopyranosyl *p*-Tolyl Sulfone (V) from β-D-Glucopyranosyl *p*-Tolyl Sulfone (III).**—The unimolecular acetylation of 1.6 g. of III was attempted by dissolving it in 3 ml. of dry pyridine and 0.47 ml. of acetic anhydride and leaving the mixture overnight at 25°. The mixture was concentrated *in vacuo* to a sirup; paper chromatograms showed this sirup to consist of starting sulfone predominantly, together with the sulfone monoacetate and higher acetates. The sirup, when dissolved in ethanol and left overnight, deposited a small amount of crystalline material whose $R_{gal}$ value corresponded to that of the monoacetate. Recrystallization from ethanol afforded fine needles that were identified by melting point and mixture melting point as the sulfone monoacetate (V).

**Some Reactions of Tetra-*O*-acetyl-β-D-glucopyranosyl *p*-Tolyl Sulfone (II). With Lithium Aluminum Hydride.**—To 2.3 g. of powdered lithium aluminum hydride suspended in 40 ml. of

(21) (a) W. E. Trevelyan, D. P. Procter, and J. S. Harrison, *Nature*, **166**, 444 (1950). (b) NOTE ADDED FEBRUARY 24, 1964.—Since submitting this paper for publication we found that we had overlooked a remarkable reaction observed by B. Helferich and H. Schirp [*Chem. Ber.*, **86**, 547 (1953)]. They treated the *p*-tolylsulfonylhydrazone derived from 2,3,4,6-tetra-*O*-acetyl-β-D-glucose with dinitrogen trioxide and obtained a 13% yield of the tetra-*O*-acetyl-β-D-glucopyranosyl *p*-tolyl sulfone (II), m.p. 148° and $[\alpha]^{21}D$ −33.8° in chloroform. They suggested that the hydrazone might first have been oxidized to an azo compound that then, by analogy with the Sandmeyer reaction, decomposed into nitrogen and the acetylated sulfone. Deacetylation gave the β-D-glucopyranosyl *p*-tolyl sulfone (III), m.p. 145–148°, and rotation was not reported.

(22) Originally described as the monohydrate with $[\alpha]^{20}D$ −57.0° when recrystallized from water, the compound crystallizes in the anhydrous form as elongated prisms from ethyl acetate, m.p. 146–147°, $[\alpha]^{20}D$ −60.3° (*c* 2.1, pyridine). *Anal.* Calcd. for $C_{13}H_{18}O_8S$: C, 54.53; H, 6.34; S, 11.2. Found: C, 54.78; H, 6.37; S, 11.3.

tetrahydrofuran was added dropwise, with stirring, a solution of 4.7 g. of the sulfone tetraacetate (II) in 40 ml. of tetrahydrofuran. An additional 0.6 g. of lithium aluminum hydride was added, stirring was continued for another 3 hr., and the reaction mixture was left overnight. The excess reagent then was decomposed by the addition of 50 ml. of water, the precipitate was filtered and washed with hot water, and the solution was deionized by passage through columns of Amberlite IR-120 and Amberlite IR-45 ion-exchange resins. Concentration *in vacuo* left a yellowish sirup that crystallized slowly to yield 1,6-anhydro-β-D-glucopyranose (levoglucosan, VI); the product, after one recrystallization from ethanol, had m.p. 175–176°, undepressed on admixture with authentic material of m.p. 177–178°.

**Reductive desulfurization** of 1 g. of the sulfone tetraacetate (II) with 10 g. of Raney nickel in boiling ethanol for 5 hr. yielded a sirup that crystallized only very slowly. It was, therefore, deacetylated catalytically with methanolic barium methoxide and the product was identified as 1,5-anhydro-D-glucitol (polygalitol, VII) by paper chromatography and, after one recrystallization from methanol, by melting point and mixture melting point of 141–142°.

When the sulfone tetraacetate (II) was refluxed 8.5 hr. with an **excess of methanolic sodium methoxide**, the product appeared to consist, from paper chromatographic evidence alone, principally of 1,6-anhydro-β-D-glucopyranose with a small proportion of a methyl D-glucopyranoside. Under the same conditions *p*-tolyl 1-thio-β-D-glucopyranoside tetraacetate (I) appeared only to be deacetylated, for paper chromatography showed only a spot with the same $R_f$ value as *p*-tolyl 1-thio-β-D-glucopyranoside (IV).

The attempted **acetolysis** of the sulfone acetate (II) by letting it stand a month at 25° with a 70:30 mixture of acetic anhydride and glacial acetic acid containing 2% of concentrated sulfuric acid resulted in no reaction and the starting material was recovered. Similarly, **bromine** seemed neither to substitute nor cleave the molecule when a mixture of 1.14 g. of the sulfone acetate (II), 0.4 g. of bromine, 1 g. of sodium bicarbonate, and 25 ml. of chloroform was stirred vigorously while being irradiated with an ultraviolet lamp. After the color of the bromine had been discharged (*ca.* 30 min.), the solution was filtered and concentrated, and the crystalline residue recrystallized from benzene–petroleum ether (b.p. 20–40°) to give unchanged sulfone acetate.

**Some Reactions of β-D-Glucopyranosyl *p*-Tolyl Sulfone (III). With Periodate.**—The sulfone was oxidized overnight with sodium metaperiodate and the excess of reagent was determined by the ion-exchange method described by Smith and Willeford.[23] The reaction consumed 2.2 moles of oxidant and liberated 0.9 mole of formic acid per mole of sulfone. Formaldehyde was not detectable with the dimedon reagent.

**Alkaline degradation** of 0.26 g. of the sulfone (III) in 10 ml. of 1 *N* potassium hydroxide and 2 ml. of water did not occur to any appreciable extent in 48 hr. at 25° because there was no observable change in rotation. However, when the solution was heated on a steam bath, the observed rotation in a 1-dm. tube changed overnight from $\alpha^{20}D$ −0.29° to −1.05° (constant). Paper chromatographic examination showed a spot of $R_{gal}$ 3.2 identical with that of 1,6-anhydro-β-D-glucopyranose (VI). The solution was deionized and concentrated to a sirup that crystallized slowly; recrystallized from ethanol, the product melted at 178°, a value not depressed when the compound was mixed with 1,6-anhydro-β-D-glucopyranose.

**Some Reactions of 6-*O*-Acetyl-β-D-glucopyranosyl *p*-Tolyl Sulfone (V). With Periodate.**—The monoacetate (V), when oxidized with sodium metaperiodate overnight at 25°, consumed 2.02 moles of oxidant (determined by the Smith–Willeford ion-exchange technique[23]) and liberated 0.9 mole of formic acid per mole of compound. No formaldehyde could be detected by the chromotropic acid method.

**Acetylation of V** (0.9 g.) in 10 ml. of acetic anhydride and 15 ml. of pyridine for 2 days at 25°, followed by pouring the mixture into ice–water, yielded a white, crystalline precipitate. The product was recrystallized from ethanol to give 0.83 g. of prismatic needles, m.p. 150–151°, with no depression when mixed with authentic tetra-*O*-acetyl-β-D-glucopyranosyl *p*-tolyl sulfone (II).

**Deacetylation of V with methanolic barium methoxide** yielded β-D-glucopyranosyl *p*-tolyl sulfone (III), identified by melting point, mixture melting point, and $R_{gal}$ 2.55. **Deacetylation with sodium borohydride** occurred when the monoacetate (V) was left with an excess of methanolic sodium borohydride overnight; the product, isolated in the usual manner and recrystallized from ethyl acetate, was identified as the free sulfone (III) by melting point and mixture melting point 151–152° and $R_{gal}$ 2.55.

**Reductive desulfurization** of 1 g. of the sulfone monoacetate (V) with 12 g. of Raney nickel by refluxing in 40 ml. of ethanol for 12 hr. yielded a sirup. Paper chromatographic examination showed the presence of two substances, the one of $R_{gal}$ 2.2 believed to be polygalitol and the other, in larger proportion, of $R_{gal}$ 3.8 believed to be polygalitol 6-acetate because it gave a positive test when sprayed with alkaline hydroxylamine followed by ferric chloride.[24] The sirupy mixture, upon deacetylation with methanolic barium methoxide, yielded the expected 1,5-anhydro-D-glucitol (polygalitol, VII).

***o*-Tolyl Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (VIII).**—This substance was prepared in 47% yield by the condensation of tetra-*O*-acetyl-α-D-glucopyranosyl bromide and *o*-toluenethiol according to the procedure described by Purves.[25] The broad needles obtained by recrystallization from ethanol melted at 104–105° and showed $[\alpha]^{20}D$ −17.2° (*c* 1, chloroform) in good agreement with the m.p. 104–106° and $[\alpha]D$ −16.4° reported by Černý, Zachystalová, and Pacák[26]; those authors had prepared it by the arylation of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose with diazotized *o*-toluidine.

**Tetra-*O*-acetyl-β-D-glucopyranosyl *o*-Tolyl Sulfone (IX).**—Oxidation of 4.0 g. of VIII with 8 ml. of 30% hydrogen peroxide in 40 ml. of glacial acetic acid for 10 days at 25°, followed by dilution of the mixture with water and recrystallization from ethanol, afforded 2.85 g. of the sulfone acetate (IX) as white needles, m.p. 170–171°, $[\alpha]^{20}D$ −27.2° (*c* 1, chloroform). Deacetylation with barium methoxide failed to give a crystalline sulfone.

*Anal.* Calcd. for $C_{21}H_{26}O_{11}S$: C, 51.85; H, 5.39; S, 6.6; OAc, 35.4. Found: C, 51.90; H, 5.28; S, 6.7; OAc, 35.8.

***o*-Tolyl 1-Thio-β-D-glucopyranoside (X).**—The catalytic deacetylation of 25 g. of VIII furnished, after recrystallization from ethyl acetate, 13.3 g. of the thioglucoside (X) as fine needles, m.p. 149–150°, $[\alpha]^{20}D$ −57.8° (*c* 1, pyridine).

*Anal.* Calcd. for $C_{13}H_{18}O_5S$: C, 54.53; H, 6.34; S, 11.2. Found: C, 55.00; H, 6.62; S, 11.0.

**Tetra-*O*-acetyl-β-D-glucopyranosyl *p*-Bromophenyl Sulfone (XI).**—Oxidation of *p*-bromophenyl tetra-*O*-acetyl-β-D-glucopyranoside[3] with hydrogen peroxide in glacial acetic acid gave a 97% yield of the sulfone tetraacetate. Recrystallization from ethanol afforded long needles with m.p. 169–170° and $[\alpha]^{20}D$ −31.8° (*c* 2.5, chloroform).

*Anal.* Calcd. for $C_{28}H_{23}BrO_{11}S$: C, 43.57; H, 4.20; Br, 14.49; S, 5.8; OAc, 31.2. Found: C, 43.80; H, 4.32; Br, 14.21; S, 5.8; OAc, 30.8.

***p*-Bromophenyl β-D-Glucopyranosyl Sulfone (XII).**—Deacetylation of XI gave the free sulfone (XII); recrystallized from ethyl acetate in long fine needles, it melted at 166–167° dec. and showed $[\alpha]^{20}D$ −28.0° (*c* 0.8, pyridine), $R_{glu}$ 2.9, $\lambda_{max}^{MeOH}$ 234 mμ (ε 17,400).

*Anal.* Calcd. for $C_{12}H_{15}BrO_7S$: C, 37.61; H, 3.95; Br, 20.85; S, 8.4. Found: C, 37.83; H, 4.07; Br, 20.86; S, 8.1.

**6-*O*-Acetyl-β-D-glucopyranosyl *p*-Bromophenyl Sulfone (XIII).**—Oxidation of 1.6 g. of *p*-bromophenyl 1-thio-β-D-glucopyranoside[3] with 30% hydrogen peroxide in glacial acetic acid for 10 days resulted in a nearly quantitative yield of the sulfone 6-acetate (XIII). Recrystallized from ethanol, the fine, white needles showed m.p. 180–181° (followed by charring), $[\alpha]^{20}D$ −3.0° (*c* 0.7, pyridine), $R_{glu}$ 3.1, $\lambda_{max}^{MeOH}$ 234 mμ (ε 19,500).

(23) M. A. Smith and B. R. Willeford, Jr., *Anal. Chem.*, **26**, 751 (1954). Earlier, W. A. Bonner and R. W. Drisko [*J. Am. Chem. Soc.*, **70**, 2435 (1948); **73**, 3699 (1951)] had attempted to determine the ring structure of their sulfones by standard periodate procedures, but ran into difficulty because the end point in the final titration, with a starch indicator, faded rapidly. They were able to circumvent that difficulty by extracting the oxidation mixture with ethyl acetate to remove the dialdehyde before adding arsenite and making the final titration with iodine. The spectrophotometric method for the determination of periodate consumed [G. O. Aspinall and R. J. Ferrier, *Chem. Ind.* (London), 1216 (1957)] was unsatisfactory because the maximum of light absorption due to the periodate ion (223 mμ) is very close to that found for the *p*-tolyl sulfone moiety (228 mμ).

(24) M. Abdel-Akher and F. Smith, *J. Am. Chem. Soc.*, **73**, 5859 (1951).

(25) C. B. Purves, *ibid.*, **51**, 3619 (1929).

(26) M. Černý, D. Zachystalová, and J. Pacák, *Collection Czech. Chem. Commun.*, **26**, 2206 (1961).

Periodate oxidation of this sulfone monoacetate liberated 0.8 mole of formic acid and the consumption of oxidant (determined by the direct method, with a fading end point) amounted to 1.7 moles per mole of compound. No formaldehyde was detected with the dimedon reagent.

*Anal.* Calcd. for $C_{14}H_{17}BrO_8S$: C, 39.54; H, 4.03; Br, 18.79; S, 7.5; OAc, 10.1. Found: C, 39.49; H, 4.15; Br, 18.70; S, 7.5; OAc, 10.2.

**p-Tolyl Tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (XIV).**—Condensation of tetra-*O*-acetyl-α-D-galactopyranosyl bromide with *p*-toluenethiol in the usual manner gave about a 90% yield of crude product. Upon recrystallization from ethanol, the needles of XIV showed m.p. 116–117° and $[\alpha]^{20}D$ +6.0° (*c* 1, chloroform).

*Anal.* Calcd. for $C_{21}H_{26}O_9S$: C, 55.50; H, 5.77; S, 7.1. Found: C, 55.65; H, 5.87; S, 7.0.

**Tetra-*O*-acetyl-β-D-galactopyranosyl *p*-Tolyl Sulfone (XV).**—Oxidation of 3.7 g. of the thiogalactoside acetate (XIV) with hydrogen peroxide in glacial acetic acid led to the sulfone tetraacetate (XV). The product was recrystallized from aqueous ethanol as fine needles (2.8 g.), m.p. 133–134°, $[\alpha]^{20}D$ −20.3° (*c* 0.8, chloroform).

*Anal.* Calcd. for $C_{21}H_{26}O_{11}S$: C, 51.85; H, 5.39; S, 6.6; OAc, 35.4. Found: C, 51.63; H, 5.51; S, 6.7; OAc, 35.1.

**β-D-Galactopyranosyl *p*-Tolyl Sulfone (XVI).**—Deacetylation of the acetylated sulfone (XV) gave the free sulfone (XVI); recrystallized from isopropyl alcohol as acicular prisms, it melted at 166–167° (followed by charring) and showed $[\alpha]^{20}D$ −16.7° (*c* 1, pyridine), $\lambda_{max}^{MeOH}$ 225 mμ (ε 14,200).

*Anal.* Calcd. for $C_{13}H_{18}O_7S$: C, 49.05; H, 5.70; S, 10.1. Found: C, 48.89; H, 5.85; S, 10.1.

**p-Tolyl 1-Thio-β-D-galactopyranoside (XVII).**—Deacetylation of the thiogalactoside tetraacetate (XIV) gave the free thiogalactoside (XVII): the long needles obtained by crystallization from water showed m.p. 142–143° and $[\alpha]^{20}D$ −55.8° (*c* 1.2, pyridine).

*Anal.* Calcd. for $C_{13}H_{18}O_5S$: C, 54.53; H, 6.34; S, 11.2. Found: C, 54.33; H, 6.25; S, 11.3.

***o*-Tolyl Tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (XVIII).**—Condensation of tetra-*O*-acetyl-α-D-galactopyranosyl bromide with *o*-toluenethiol gave a 51% yield of XVIII after one recrystallization from ethanol as prismatic needles, m.p. 98–99°, and $[\alpha]^{20}D$ ±0.0° (*c* 1, chloroform).

*Anal.* Calcd. for $C_{21}H_{26}O_9S$: C, 55.50; H, 5.77; S, 7.1; OAc, 37.9. Found: C, 55.63; H, 5.82; S, 7.0; OAc, 37.5.

**Tetra-*O*-acetyl-β-D-galactopyranosyl *o*-Tolyl Sulfone (XIX).**—Oxidation of the thiogalactoside tetraacetate (XVIII) with hydrogen peroxide in glacial acetic acid gave the sulfone tetraacetate (XIX) as small, prismatic needles from aqueous ethanol, with m.p. 90–91° and $[\alpha]^{20}D$ −19.2° (*c* 1.1, chloroform). Deacetylation of XIX failed to give a crystalline product.

*Anal.* Calcd. for $C_{21}H_{26}O_{11}S$: C, 51.85; H, 5.39; S, 6.6; OAc, 35.4. Found: C, 51.63; H, 5.53; S, 6.8; OAc, 35.6.

***o*-Tolyl 1-Thio-β-D-galactopyranoside (XX).**—Deacetylation of XVIII gave crystalline XX; the compound crystallized from ethyl acetate as feathery needles that melted at 148–149° and showed $[\alpha]^{20}D$ −49.7° (*c* 0.1, pyridine).

*Anal.* Calcd. for $C_{13}H_{18}O_5S$: C, 54.53; H, 6.34; S, 11.2. Found: C, 54.61; H, 6.40; S, 11.3.

**Thioglycosides That Did Not Give Crystalline 6-*O*-Acetylglycosyl Aryl Sulfones.**—The three new thioglycosides reported in this paper (X, XVII, and XX) and the following five old ones[3] failed to yield crystalline 6-acetates when oxidized with 30% hydrogen peroxide in glacial acetic acid: phenyl, *p*-acetylphenyl, *p*-chlorophenyl, 2,5-dichlorophenyl, and *N*-benzyl-*N*-methyl-*p*-aminophenyl β-D-glucopyranosides.

**Oxidation of Thioglycosides with Peroxypropionic Acid.**—One gram of *p*-tolyl 1-thio-β-D-glucopyranoside (IV) was dissolved in 20 ml. of boiling isopropyl alcohol and to the hot solution was added 7 ml. of carefully redistilled 3.5 *N* peroxypropionic acid.[27] The reaction mixture was left at 25° overnight and then another 7 ml. of oxidant was added. After 1 hr. the solution was concentrated *in vacuo* to a thick sirup; dilution with ethyl acetate yielded crystalline material that was identified by its $R_f$ value and by melting point and mixture melting point as β-D-glucopyranosyl *p*-tolyl sulfone (III).

In a variation of this procedure, 1 g. of *p*-tolyl 1-thio-β-D-galactopyranoside (XVII) was dissolved in 7 ml. of dimethylformamide and 13 ml. of dioxane and then 6.5 ml. of 6 *N* peroxypropionic acid was added. After 1 hr. at 25° the mixture was heated on the steam bath, an additional 5 ml. of oxidant was added, and heating was continued for 0.5 hr. Concentration *in vacuo* left a semicrystalline residue from which some sirupy material was removed by extraction with ethyl ether. The residue, on recrystallization from hot isopropyl alcohol, afforded 0.5 g. of acicular prisms with m.p. and m.m.p. 166–167° (followed by charring) and $[\alpha]^{20}D$ −16.7° (*c* 1, pyridine); the product was thus identified as β-D-galactopyranosyl *p*-tolyl sulfone (XVI), and the C, H, and S analyses were in accord.

**Infrared Data.**—The infrared spectra were obtained with a Perkin-Elmer recording infrared spectrophotometer Model 21. Since no infrared data on glycosyl sulfones and their acetates seem to have been reported previously, we have listed the principal absorption bands of some representative compounds below. Nujol mulls were used unless otherwise noted. When chloroform, carbon disulfide, or pyridine was used as a solvent, the absorption bands listed were so strong that they could not be attributed, except perhaps in very small part, to the solvent used. It will be observed that all sulfones have one or more absorption bands near 1325 (the mean absorption frequency attributed to asymmetric $SO_2$ stretching vibrations in C–$SO_2$–C compounds[28]) and 1140 cm.$^{-1}$ (the mean absorption frequency attributed to symmetric $SO_2$ stretching vibrations in C–$SO_2$–C compounds[28]). The principal ester carbonyl absorption band appears, as expected, between 1745 and 1760 cm.$^{-1}$ for all sulfide and sulfone tetraacetates. In the two sulfone 6-acetates (V and XIII), however, this band appeared at 1690 and 1695 cm.$^{-1}$, respectively, when measured in Nujol mulls but shifted to 1740 and 1750 cm.$^{-1}$, respectively, when measured in pyridine.

*p*-Tolyl 1-thio-β-D-glucopyranoside (IV): 3280, 1106, 1084, 1044, 1033, 1020, 990, 810, and 800 cm.$^{-1}$.

*p*-Bromophenyl 1-thio-β-D-glucopyranoside[3]: 3570, 3250, 1107, 1087, 1078, 1064, 1045, 1033, 1010, 990, 817, and 797 cm.$^{-1}$.

β-D-Glucopyranosyl *p*-tolyl sulfone (III): 3500, 3350, 1640, 1602, 1355, 1335, 1305, 1295 (sh), 1288, 1257, 1193, 1144 (sh), 1133, 1117, 1098, 1083, 1055, 1041, 1015, 1002, 878, 841, 811, 705, and 653 cm.$^{-1}$.

*p*-Bromophenyl β-D-glucopyranosyl sulfone (XII): 3520, 3370, 1580, 1360, 1307, 1290, 1278, 1147, 1137, 1118, 1102, 1083, 1067, 1060, 1044, 1008, 880, 841, 820, 732, and 703 cm.$^{-1}$.

β-D-Galactopyranosyl *p*-tolyl sulfone (XVI): 3450, 3240, 1318, 1306, 1276, 1260, 1145, 1123, 1093, 1081, 1062, and 1037 cm.$^{-1}$.

*p*-Tolyl tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (I): 1750, 1298, 1250 (sh), 1228, 1104, 1083, 1042, 983, 918, 820, and 809 cm.$^{-1}$.

Tetra-*O*-acetyl-β-D-glucopyranosyl *p*-tolyl sulfone (II): 1745, 1323, 1263 (sh), 1243, 1224, 1211, 1154, 1107, 1085, 1063, and 1036 cm.$^{-1}$.

Compound II in potassium bromide pellet: 3400 ($H_2O$?),[29] 1760, 1630 ($H_2O$?),[29] 1600, 1432, 1368, 1323, 1228, 1152, 1083, 1058, and 1034 cm.$^{-1}$.

Compound II in chloroform: 1755, 1600, 1365, 1325, 1305, 1143, 1124, 1084, 1058, 1032, and 834 cm.$^{-1}$.

Compound II in carbon disulfide: 1760, 1363, 1334, 1235, 1215, 1147, 1085, 1061, 1033, and 810 cm.$^{-1}$.

Compound II in pyridine: 3370 ($H_2O$?),[29] 1755, 1660, 1363, 1323, 1220 (?), and 1083 cm.$^{-1}$.

Tetra-*O*-acetyl-β-D-glucopyranosyl *p*-bromophenyl sulfone (XI): 1755, 1342, 1330, 1243, 1226, 1153, 1115, 1063, 1036, 1008, 807, and 745 cm.$^{-1}$.

Compound XI in chloroform: 1760, 1580, 1388 (sh), 1368, 1343, 1152, 1130, 1084, 1068, 1035, and 1012 cm.$^{-1}$.

6-*O*-Acetyl-β-D-glucopyranosyl *p*-tolyl sulfone (V): 3390, 1690, 1600, 1344, 1328, 1285, 1255, 1150, 1110, 1088, 1050, 1022, 987, 922, 808, 704, and 673 cm.$^{-1}$.

Compound V in pyridine: 3140, 1740, 1320, 1235, 1112, 1082, and 1045 cm.$^{-1}$.

6-*O*-Acetyl-β-D-glucopyranosyl *p*-bromophenyl sulfone (XIII): 3400, 1695, 1350, 1333, 1315, 1295, 1287, 1273, 1255, 1155, 1143, 1112, 1092, 1082, 1069, 1049, 1013, 817, and 743 cm.$^{-1}$.

(27) D. L. MacDonald, *Methods Carbohydrate Chem.*, **1**, 73 (1962).

(28) L. J. Bellamy, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, p. 49.

(29) Spectra obtained in potassium bromide pellets and in pyridine solution may show absorption bands near 3400 and 1630 cm.$^{-1}$; these are attributable to the presence of water and occur frequently unless special precautions are taken for the rigorous exclusion of moisture.

Compound XIII in pyridine: 3150, 1750, 1385, 1365, 1335, 1275, 1235, 1083, and 1050 cm.$^{-1}$.

**Nuclear Magnetic Resonance Data.**—The n.m.r. spectra were recorded on a Varian Model A-60 spectrometer; pyridine was used as the solvent and tetramethylsilane as the internal reference. We are indebted to Dr. John D. Stevens of this laboratory for the following interpretation.

Nuclear magnetic resonance spectra confirmed that the hydroxyl group on C-6 was acetylated in the two sulfone monoacetates (V and XIII). The spectrum for β-D-glucopyranosyl *p*-tolyl sulfone (III) showed signals at $\tau$ 7.83 (aromatic methyl group), at 5.3 to 6.1 (broad band due to protons on C-2 to C-6), and at 4.83 (doublet, spacing 9.0 c.p.s.). The doublet at $\tau$ 4.83 arises from the anomeric hydrogen atom. Since the spacing for this doublet is typical of 1,2 diaxially oriented hydrogen atoms on a six-membered ring,[30] this observation verifies the β-D-glucopyranosidic linkage in the sulfone. A similar spectrum was obtained for the *p*-bromophenyl β-D-glucopyranosyl sulfone (XII, doublet at $\tau$ 4.77, spacing 8.6 c.p.s.). 6-*O*-Acetyl-β-D-glucopyranosyl *p*-tolyl sulfone (V) showed signals at $\tau$ 8.13 (acetyl group), 7.75 (aromatic methyl group), a series of broad peaks between 5.25 and 6.13, and a doublet (spacing 9.2 c.p.s.) at 4.89. The low-field doublet in the spectrum of this compound is attributed to the anomeric hydrogen atom and the absence of any signals downfield from this proton is strong evidence for the absence of an acetoxy group on C-2, C-3, or C-4. [For comparison, the spectrum of methyl tetra-*O*-acetyl-β-D-glucopyranoside in pyridine solution showed protons on C-2, C-3, and C-4 at $\tau$ 4.3 to 4.6 and the anomeric hydrogen at 5.2 (spacing 7.5 c.p.s.)[31]]. For tetra-*O*-acetyl-β-D-glucopyranosyl *p*-tolyl sulfone (II), signals with intensity corresponding to two protons occurred at $\tau$ 4.0 to 4.47 and another group of signals with two-proton intensity occurred at 4.5 to 4.97; thus, the signals due to protons on C-1 to C-4 all occur at $\tau$-values less than 5. Similarly, no peaks occurred downfield from the doublet at $\tau$ 4.83 (spacing 9.0 c.p.s.) due to the anomeric hydrogen atom in the n.m.r. spectrum of 6-*O*-acetyl-β-D-glucopyranosyl *p*-bromophenyl sulfone (XIII).

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(30) R. U. Lemieux, R. K. Kullnig, H. F. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

(31) N. Mori, S. Omura, O. Yamamoto, T. Suzuki, and Y. Tsuzuki [*Bull. Chem. Soc. Japan*, **36**, 1047 (1963)] have shown that for methyl tetra-*O*-acetyl-β-D-glycopyranosides in chloroform solution the signals due to the anomeric hydrogen appear at higher field than those due to protons on C-2 to C-4.

# Preparation of 6-Acetamido-1,2,3,4-tetra-O-acetyl-6-deoxy-L-idothiapyranose[1]

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Reaction of 5,6-anhydro-3-O-benzyl-1,2-O-isopropylidene-D-glucofuranose (I) with benzylmercaptide ion afforded 3-O-benzyl-6-S-benzyl-1,2-O-isopropylidene-6-thio-D-glucofuranose (II) that, with thionyl chloride, yielded 3-O-benzyl-5-S-benzyl-6-chloro-6-deoxy-1,2-O-isopropylidene-5-thio-L-idofuranose (IV) *via* the benzylepisulfonium ion (VIII). Reaction of IV with sodium azide gave the 6-azido-5-benzylthio sugar (VII) that was reduced to the 6-amino-5-benzylthio derivative (V), easily converted to the N-acetate (VI). Reduction of V or VI with sodium and liquid ammonia afforded the 6-amino-5-thiol (IX) and the 6-acetamido-5-thiol (X), respectively. Acid hydrolysis of the isopropylidene group resulted in the formation of a thiapyranose sugar, that was acetylated to the pentaacetate (XII), one anomer of which was isolated as a crystalline solid.

Since 1961 a number of articles have appeared describing sugars that contain sulfur[2] or nitrogen[3] as the heterocyclic atom of the sugar ring. In studying the relative abilities of thiol, hydroxyl, and amino groups to interact with C-1 to form a cyclic sugar it will be advantageous to have a number of sugars containing these groups properly situated for potential cyclization. This manuscript reports the preparation of a derivative (XII) of 6-amino-6-deoxy-5-thio-L-idose, such a sugar. The pentaacetate (XII) is also a derivative of a vicinal aminomercapto sugar which is of interest for comparison with other such compounds which have recently been prepared.[4]

The conversion of 1,2:5,6-di-O-isopropylidene-D-glucofuranose to 5,6-anhydro-3-O-benzyl-1,2-O-isopropylidene-D-glucofuranose (I) was carried out using the sequence described by Meyer and Reichstein.[5] Reaction of the epoxide (I) with sodium benzyl mercaptide afforded the 6-benzylthio sugar (II) (Chart I) as an oil purified by chromatography over silica gel. Previously it had been determined that treatment of I with sodium hydroxide gave 3-O-benzyl-1,2-O-isopropylidene-D-glucofuranose predominantly, if not exclusively,[5] indicating nucleophilic attack at C-6. Similar 5,6-anhydro sugars have been shown to undergo nucleophilic attack by ammonia at C-6[6]; structure II is written on the basis of these considerations. The benzylthio sugar (II) was characterized as the crystalline phenylurethan (III) and was converted to the crystalline chloro sugar (IV) by treatment with thionyl chloride. The structure of IV was assigned on the assumption of opening of an episulfonium ion intermediate (VIII, formed by the way of the chlorosulfite of II) at C-6[5,6] and on the basis of n.m.r. information. Thus, the C-6 methylene group of IV appeared as a four-peak multiplet centered at $\gamma$ 6.45 as compared

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