Carbohydrate Research
Elsevier Publishing Company, Amsterdam
Printed in Belgium

MIGRATION OF THE METHYLTHIO GROUP IN THE SOLVOLYSIS OF SOME METHYL 1-THIO-6-*O*-TOLUENE-*p*-SULPHONYL-β-D-GLYCOPYRANOSIDES

E V E ROBERTS, J C P SCHWARZ, AND (IN PART) CAROL A MCNAB
Chemistry Department, University of Edinburgh, West Mains Road, Edinburgh 9 (Great Britain)
(Received December 29th, 1967)

ABSTRACT

The hydrolysis and methanolysis of methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside proceeds with migration of the methylthio group to C-6 Acetolysis of methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside triacetate and of the corresponding galactoside likewise gives 6-*S*-methyl-6-thio compounds The stereochemical outcome at C-1 of these reactions is discussed

Replacement of the methylthio group of the methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-α- and -β-D-glucopyranosides by an acetoxyl group, using mercuric acetate in acetic acid, proceeds mainly with inversion of configuration at C-1

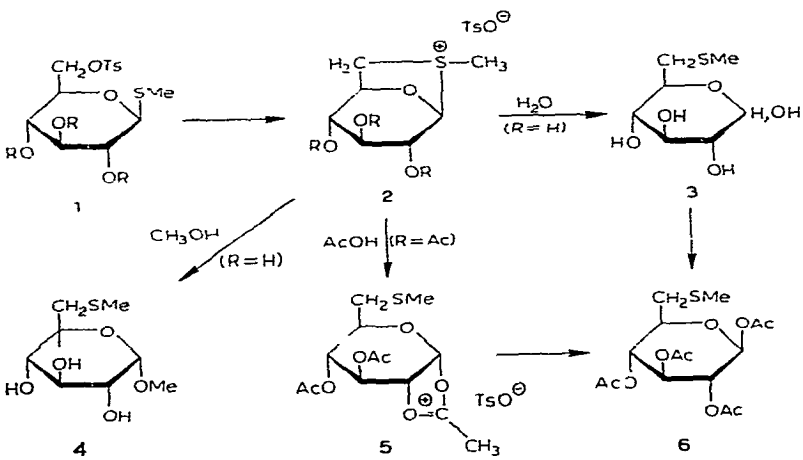
INTRODUCTION

During kinetic studies[1] of the alkaline cyclisation of glycoside 6-toluene-*p*-sulphonates to 3,6-anhydro compounds, it was found that methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside (**1**, R = H) decomposed with the liberation of toluene-*p*-sulphonate ions even in a neutral aqueous solution, the half-life for the reaction being about 30 h at room temperature By contrast, the corresponding α-D-thioglucoside and the oxygen analogues (the methyl 6-*O*-toluene-*p*-sulphonyl-α- and -β-D-glucopyranosides) were unreactive under the same conditions These results suggest that the reactivity of the β-thioglucoside **1** (R = H) is due to neighbouring-group participation by the methylthio group, and the behaviour of this compound was therefore examined further

As detailed below, the reaction was found to involve migration of the methylthio group to C-6, presumably *via* a 1,6-cyclic sulphonium intermediate Migration reactions through a three-membered sulphonium ring had already been observed in carbohydrate chemistry before this work was begun[2] More recently, other interesting migration and rearrangement reactions have been encountered in solvolyses of carbohydrate sulphonates, involving participation by alkylthio groups[3], alkoxyl groups[4,5], and even ring oxygen atoms[5,6]

RESULTS AND DISCUSSION

Chromatographic evidence showed that the decomposition of the toluene-*p*-sulphonate **1** (R = H) in aqueous solution yielded a single product On acetylation, this gave crystalline 6-*S*-methyl-6-thio-β-D-glucopyranose tetra-acetate (**6**), identified by its n m.r spectrum (see Experimental section) and by desulphurisation to the known 6-deoxy-β-D-glucopyranose tetra-acetate[7] The formation of 6-*S*-methyl-6-thio-D-glucopyranose (**3**) clearly confirms that the reaction of the toluene-*p*-sulphonate proceeds with neighbouring-group participation by sulphur *via* the cyclic sulphonium compound **2** (R = H) The ready occurrence of this reaction, even although it must proceed through an unstable conformation of the toluene-*p*-sulphonate, is a striking illustration of the efficacy of alkylthio groups in neighbouring-group reactions[8] A cyclic sulphide related to the above sulphonium compound has been reported[9] The fact that the sulphonium compound reacts exclusively at C-1 may be ascribed to the mesomeric effect of the ring oxygen atom



Since the reaction of the toluene-*p*-sulphonate **1** (R = H) with water gives no information about the stereochemistry of the opening of the sulphonium ring, the reaction with methanol was examined, calcium carbonate being added to prevent anomerisation by the toluene-*p*-sulphonic acid liberated The main product was methyl 6-*S*-methyl-6-thio-α-D-glucopyranoside (**4**), formed with inversion at C-1, this was isolated as its triacetate, which was characterised by n m r and by desulphurisation to the known methyl 6-deoxy-α-D-glucopyranoside triacetate[10] Chromatographic evidence indicated the presence of a second compound, presumably methyl 6-*S*-methyl-6-thio-β-D-glucopyranoside

The methanolysis of the triacetate (**1**, R = Ac) of methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside was then examined to see if participation by the acetoxy group at C-2 in the opening of the sulphonium ring would influence the course of the reaction Unfortunately, this compound was relatively unreactive and had

only partly reacted in boiling methanol after 5 h However, the compound reacted smoothly at 100° with anhydrous acetic acid containing sodium acetate, giving mainly 6-*S*-methyl-6-thio-β-D-glucopyranose tetra-acetate (**6**) and about 10% of a second compound The latter was chromatographically identical with the corresponding α-D tetra-acetate, an authentic sample of which was obtained by anomerisation of the β-D tetra-acetate with zinc chloride

The preferential formation of the β-D tetra-acetate suggests that the acetolysis involves the opening of the sulphonium ring of the intermediate (**2**, R = Ac) by the acetoxy group at C-2, giving the acetoxonium ion **5**, which then reacts with inversion at C-1 Formation of the acetoxonium ion was supported by the fact that, in acetic acid containing 1% of water, the main products were partially acetylated compounds (presumably triacetates of 6-*S*-methyl-6-thio-D-glucose, since they gave the tetraacetates of this compound on acetylation) Such behaviour is characteristic of acetoxonium ions[11]

Acetolysis of methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-D-galactopyranoside triacetate also proceeded with migration of the methylthio group and gave mainly 6-*S*-methyl-6-thio-β-D-galactopyranose tetra-acetate, recognised by its n m r spectrum Since the rearrangement reactions described here must occur *via* an unstable conformation of the toluene-*p*-sulphonates, the relative reactivities of stereoisomeric methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-D-glycopyranosides would be of interest

Attempted acetolysis of methyl 6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside triacetate under the conditions used for the thioglycosides gave only unchanged starting material

The toluene-*p*-sulphonates mentioned above were prepared by conventional methods The position of the toluene-*p*-sulphonyl group in the methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-α-D-glucopyranoside was confirmed by treatment with mercuric acetate in acetic acid, followed by acetylation of the product to the known 6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranose tetra-acetate[7] Under similar conditions, methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside also reacted mainly with inversion at C-1, giving 6-*O*-toluene-*p*-sulphonyl-α-D-glucopyranose tetra-acetate, an authentic sample of which was prepared by anomerisation of the β-D tetra-acetate with perchloric acid in acetic anhydride Surprisingly, methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside triacetate was recovered unchanged when treated with mercuric acetate under the same conditions

The n m r spectrum of methyl 6-*S*-methyl-6-thio-α-D-glucopyranoside triacetate showed an interesting effect On one occasion, the peaks at τ 7 82 ($-SCH_3$) and τ 7 39 ($-SCH_2-$) were found to be greatly broadened, although the other peaks in the spectrum were quite sharp It is probable that this was due to contamination by copper ions, since addition of a trace of cupric chloride gave the same effect The selective broadening of the signals from protons α- to the sulphur atom can be ascribed to relaxation in a paramagnetic copper complex, we have observed the same phenomenon for a number of simple thioethers[12] An interesting feature is that, in the spectrum of diethyl sulphide, for example, the β-CH_3 gives a recognisable triplet even

when the α-CH_2 has been broadened by the addition of cupric chloride so as to be indistinguishable from the base-line Selective broadening by copper ions is clearly a useful adjunct in the interpretation of the spectra of thioethers, *e g*, it provided a ready distinction between SCH_3 and CH_3CO O peaks for some of the compounds studied here (see Experimental section)

EXPERIMENTAL

General — Evaporations were carried out under diminished pressure on a rotatory evaporator at *ca* 30°, unless otherwise stated Chloroform extracts were dried with anhydrous sodium sulphate The light petroleum used had b p 60–80° Optical rotations were measured at *ca* 20° in 1- or 2-dm tubes. N m r spectra were obtained at 60 MHz on a Perkin-Elmer R 10 spectrometer by using 10–20% solutions in deuterochloroform with tetramethylsilane as internal standard

Chromatographic methods — Paper chromatography was done on Whatman No 1 paper with the following solvent systems (*i*) butyl alcohol–ethanol–water (4.1 5, upper layer), (*ii*) methyl sulphoxide as stationary phase and isopropyl ether as mobile phase[13] (in the application of the stationary phase, the paper was dried at 85–90° instead of 60°) Sprays used were (*a*) silver nitrate–sodium hydroxide[14], (*b*) a saturated solution of aniline oxalate in methanol, followed by heating for 15 min at 110° (to detect free sugars)

Thin-layer chromatography was done on Kieselgel G (Merck) with benzene–ethanol (2 1) Sprays used were (*c*) anisaldehyde–sulphuric acid[15] and (*d*) 1% diphenylamine in ethanol followed by exposure to ultraviolet light[16]

Methyl 1-thio-6-O-toluene-p-sulphonyl-α-D-glucopyranoside. — Toluene-*p*-sulphonyl chloride (0 2 g) in anhydrous pyridine (2 ml) was added dropwise to methyl 1-thio-α-D-glucopyranoside[17] (0 2 g) in pyridine (2 ml) at −10° The mixture was kept at −10° for 2 h and then at room temperature overnight After addition of a little water, the pyridine was removed by repeated evaporation with ethanol The residue was dissolved in chloroform and washed with 2N sulphuric acid and sodium hydrogen carbonate solution Evaporation and crystallisation from ethyl acetate–light petroleum gave the toluene-*p*-sulphonate (0 15 g) A dried sample had m p 114° (dec), $[\alpha]_D$ +169 5° (*c* 1 3, ethanol) On standing in air, the compound (60 mg) absorbed water (1 5 mg), corresponding to the formation of a hemihydrate, m p 80–82° (dec) (Found C, 45 1, H, 5 6, S, 16 85 $C_{14}H_{20}O_7S_2$ 0 5 H_2O calc C, 45 0, H, 5.6, S, 17 2%) After drying, m p 114° (dec) was again obtained

Methyl 1-thio-6-O-toluene-p-sulphonyl-β-D-glucopyranoside — Toluene-*p*-sulphonyl chloride (2 2 g) in anhydrous pyridine (20 ml) was added dropwise, during 2 h, with stirring to methyl 1-thio-β-D-glucopyranoside[17,18] (2 1 g) in pyridine (20 ml) at −10° The mixture was kept at −10° for a further 2 h and at room temperature overnight It was then poured into light petroleum (250 ml) The clear, supernatant liquid was decanted, and the residual syrup was dissolved in chloroform (30 ml) and poured, with vigorous stirring, into ice-cold 2N sulphuric acid (100 ml) The white precipitate which separated was filtered off and washed thoroughly with water

Crystallisation from chloroform–light petroleum gave the toluene-*p*-sulphonate (1 6 g), m p 108° (dec), $[\alpha]_D$ −10° (*c* 2, ethanol) (Found C, 46 1, H, 5 5; S, 17 6 $C_{14}H_{20}O_7S_2$ calc C, 46 1, H, 5 5, S, 17 6%) The above material was fairly stable, but samples prepared by using a different work-up, which included crystallisation from ethanol, decomposed with blackening in a few days

*Methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-*D*-glucopyranoside triacetate* — (*a*) Methyl 1-thio-β-D-glucopyranoside (2 1 g) was treated with toluene-*p*-sulphonyl chloride as described above After the reaction mixture had stood overnight, it was again cooled to −10°, and acetic anhydride (5 ml) was added dropwise After 15 h at room temperature, the solution was poured with vigorous stirring into ice-cold water (300 ml), yielding a precipitate of the triacetate, which was crystallised from ethanol to give needles (3 1 g), m p 146–148° (dec), $[\alpha]_D$ +9° (*c* 1, chloroform) (Found C, 49 0, H, 5 3, S, 12 5 $C_{20}H_{26}O_{10}S_2$ calc C, 49 0, H, 5 3, S, 13 1%)

(*b*) The same triacetate, m p and mixed m p 146–148° (dec), $[\alpha]_D$ +9° (*c* 1, chloroform) was obtained in 85% yield when methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside in pyridine was treated with acetic anhydride

*Treatment of methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-*D*-glucopyranoside with water.* — The toluene-*p*-sulphonate (1 2 g) in water (50 ml) was heated for 2 h at 70–75°. T l c with spray *d* showed that the starting material (R_F 0 45) had reacted; spray *c* revealed the product (R_F 0 19) Paper chromatography (solvent *i*, spray *b*) showed the presence of a free sugar (R_G 3 0), no additional products were revealed by spray (*a*) The solution was buffered with sodium acetate (0 5 g) and evaporated The residue was dried over phosphorus pentoxide and then heated for 140 min at 100° with anhydrous sodium acetate (0 5 g) and acetic anhydride (20 ml) The solution was poured into ice-cold water, and the product obtained by using chloroform Paper chromatography (solvent *ii*, spray *a*) showed it to be mainly 6-*S*-methyl-6-thio-β-D-glucopyranose tetra-acetate (see below), together with some of the α-D anomer Four crystallisations from ethanol gave the pure β-D anomer (0 75 g), m p 103–104°

*Methanolysis of methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-*D*-glucopyranoside* — The toluene-*p*-sulphonate (1 2 g), calcium carbonate (1 0 g), and anhydrous calcium sulphate (1 0 g) in anhydrous methanol (50 ml) were heated under reflux for 5 h T l c (sprays *c* and *d*) indicated complete conversion into a product having R_F 0 35 The product, after filtration, and evaporation of the methanol, was chromatographed[19] on a column (70 × 2 cm) of Dowex-1X2 (OH^-, 200–400 mesh) by elution with water. The fractions (5 ml) were examined polarimetrically and, in some cases, by paper chromatography in solvent (*ii*) after acetylation

Fractions 125–161 contained only the α-D-glucoside (0 40 g), acetylation of this compound (0 32 g) with acetic anhydride (5 ml) and pyridine (10 ml) gave methyl 6-*S*-methyl-6-thio-α-D-glucopyranoside triacetate, which crystallised from ethanol as needles (0.40 g), m p 119°, $[\alpha]_D$ +144° (*c* 1 6, chloroform) (Found C, 48 2, H, 6.0; S, 9 0 $C_{14}H_{22}O_8S$ calc C, 48 0, H, 6 3, S, 9 1%) The n m r spectrum included peaks at τ 6 55 (3-proton singlet, $-OCH_3$), τ *ca* 7 39 (2-proton multiplet, $-CH_2S-$), τ 7 82, 7 93, 7 97, and 8 00 [12 protons, $-SCH_3$ and three acetoxyl groups, the peak

at τ 7 82 is assigned to -SCH_3 as it is selectively broadened by Cu^{II}, see Discussion]

Fractions 162–180 (0.14 g) were acetylated to give a product which was shown by paper chromatography (solvent *u*, spray *a*) to consist of the above triacetate (R_F 0 78) and a slower-moving compound (R_F 0 62), presumably the β-D-anomer

Desulphurisation of the methyl 6-*S*-methyl-6-thio-α-D-glucopyranoside triacetate (0.4 g) with Raney nickel in boiling ethanol, followed by crystallisation of the product from light petroleum (b p 40–60°), gave methyl 6-deoxy-α-D glucopyranoside triacetate (0 2 g), m.p 76–77°, $[\alpha]_D$ +153° (*c* 1 6, chloroform) (lit [10], m p 77–78°, $[\alpha]_D$ +153 6° in chloroform) The n m r spectrum included peaks at τ 8 80 (3-proton doublet, separation 6 5 Hz, C-CH_3), τ 7 93, 7 97, and 8 00 (9 protons, three acetoxyl groups), and τ 6 59 (3 protons, OCH_3)

*Acetolysis of methyl 1-thio-6-O-toluene-*p*-sulphonyl-β-D-glucopyranoside triacetate* — (*a*) *In anhydrous acetic acid* A solution of the toluene-*p*-sulphonate (0 9o g) and anhydrous sodium acetate (0 53 g) in acetic acid (50 ml, dried by using triacetyl borate)[20] was heated on an oil-bath for 2 h at 100° with the exclusion of moisture After evaporation of the acetic acid at 50°, the residue was extracted with chloroform, and the extract was washed with sodium hydrogen carbonate solution and water Evaporation of the chloroform gave a syrup (0 73 g) which was shown by paper chromatography (solvent *u*, spray *a*) to be mainly 6-*S*-methyl-6-thio-β-D-glucopyranose tetra-acetate (R_F 0 62), together with a little of the α-D anomer (R_F 0 74, see below) and traces of two slower-moving materials The syrup had $[\alpha]_D$ +17 8° (chloroform), suggesting that the proportion of β-D anomer was >90%. Two crystallisations from ethanol gave the pure β-D-tetra-acetate as needles (0 56 g), m p 104°, $[\alpha]_D$ +10° (*c* 2 75, chloroform) (Found C, 47 6, H, 5 7, S, 8 7 $C_{15}H_{22}O_9S$ calc C, 47.6; H, 5 8, S, 8 5%) The n m r spectrum included peaks at τ 4 30 (1-proton doublet, separation 7 Hz, anomeric proton), τ *ca* 7 35 (2-proton multiplet, -CH_2S-), τ 7 87, 7 90, 7 97, 7 98, and 7 99 [15-protons, -SCH_3 and four acetoxyl groups, the peak at 7 87 τ is assigned to -SCH_3 as it is selectively broadened by Cu^{II}, see Discussion]

Desulphurisation of the β-D tetra-acetate (0 3 g) with Raney nickel in boiling ethanol, followed by crystallisation of the product from ethanol, gave 6-deoxy-β-D-glucopyranose tetra-acetate (0 18 g), m p 149–150°, $[\alpha]_D$ +22° (*c* 1 4, chloroform) (lit [7], m p 151°, $[\alpha]_D$ +22° in chloroform) N m r spectrum τ 8 77 (3-proton doublet, separation 6 Hz, C-CH_3), τ 7 90, 7 96, 7 98, and 8 00 (12-protons, four acetoxyl groups), and τ 4 28 (1-proton doublet, separation 7 5 Hz, anomeric proton)

(*b*) *In acetic acid containing 1% of water* The toluene-*p*-sulphonate (0 98 g) was treated as in (*a*), but with acetic acid containing 1% of water On working up as above, evaporation of the chloroform gave a syrup (0 55 g) which, when examined by paper chromatography (solvent *u*, spray *a*), gave intense spots having R_F less than 0 25 and only faint spots corresponding to the two tetra-acetates of 6-*S*-methyl-6-thio-D-glucopyranose After acetylation of the syrup with acetic anhydride and sodium acetate, as described above for the parent sugar, only the two tetra-acetates were present Crystallisation of the acetylation product from ethanol gave 6-*S*-methyl-6-thio-β-D-glucopyranose tetra-acetate (0 49 g), m p and mixed m p 103–104°

6-S-Methyl-6-thio-α-D-glucopyranose tetra-acetate — 6-*S*-Methyl-6-thio-β-D-glucopyranose tetra-acetate (0.4 g) and zinc chloride (0 1 g) in acetic anhydride (5 ml) were heated for 30 min at 100° The mixture was then poured, with stirring, into ice-cold water (25 ml) The product was isolated by using chloroform Crystallisation from ethanol gave the α-D-tetra-acetate as needles (0 15 g), m p 132–134°, $[\alpha]_D$ +115° (*c* 1 6, chloroform) (Found. C, 47.5; H, 5 5; S, 8 5 $C_{15}H_{22}O_9S$ calc: C, 47 6, H, 5 8, S, 8 5%) N m r spectrum· 3 70 τ (1-proton doublet, separation *ca* 3.5 Hz, anomeric proton), τ 7 39 (2-proton multiplet, $-CH_2S-$), τ 7 82, 7 86, 7 95, and 7.98 (15-protons, $-SCH_3$ and four acetoxyl groups, the peak at τ 7 86 was selectively broadened in one spectrum and is assigned to $-SCH_3$, that at τ 7 98 represents two acetoxyl groups)

Methyl 1-thio-6-O-toluene-p-sulphonyl-β-D-galactopyranoside triacetate — Methyl 1-thio-β-D-galactopyranoside[21] (4 0 g) in pyridine was treated with toluene-*p*-sulphonyl chloride as described above for the corresponding glucoside. After the reaction mixture had stood overnight at 0–5°, it was treated with acetic anhydride and worked up as described above Four crystallisations from ethanol gave the toluene-*p*-sulphonate as needles (2 9 g), m p 115°, $[\alpha]_D$ *ca* 0° (*c* 2 0, chloroform) (Found C, 49 0, H, 5 3, S, 12 9 $C_{20}H_{26}O_{10}S_2$ calc C, 49 0, H, 5 3; S, 13 1%)

Acetolysis of methyl 1-thio-6-O-toluene-p-sulphonyl-β-D-galactopyranoside triacetate — The toluene-*p*-sulphonate (0 98 g) was treated as described above for the corresponding glucoside (procedure *a*) Paper chromatography (solvent *u*, spray *a*) indicated that the resulting crude product was mainly 6-*S*-methyl-6-thio-β-D-galactopyranose tetra-acetate (R_F *ca* 0 28), together with a small amount of material having R_F *ca* 0 55, presumably the α-D anomer The crude product had $[\alpha]_D$ +7 1° (c 1 0, chloroform), calculation using Hudson's Rules of Isorotation suggests that the proportion of the α-D anomer was *ca* 8%. Three crystallisations from ethanol gave the pure β-D-tetra-acetate as prisms (0 52 g), m p 104–106°, $[\alpha]_D$ +1° (*c* 2 0, chloroform) (Found. C, 47 8, H, 5 9, S, 7 9 $C_{15}H_{22}O_9S$ calc C, 47 6, H, 5 8, S, 8 5%) The structure of the tetra-acetate was confirmed by the following signals in its n m r spectrum τ 4 20–4 80 (4-proton complex multiplet, a doublet at τ 4 27 with separation 7 Hz was assigned to the anomeric proton), τ 6 00 (1-proton triplet, H-5), 7 37 τ (2-proton quartet, $-CH_2S-$), τ 7 83, 7 89, 7 97, and 8 02 (15-protons, $-SCH_3$ and four acetoxyl groups, the signal at 7 89 τ had twice the intensity of the others)

6-O-Toluene-p-sulphonyl-α-D-glucopyranose tetra-acetate — 6-*O*-Toluene-*p*-sulphonyl-β-D-glucopyranose tetra-acetate (0 5 g) was added in portions to acetic anhydride (10 ml) containing 60% perchloric acid (0 2 ml) at 30–40° After 30 min at the same temperature, the mixture was poured into ice–water (50 ml) Processing with chloroform gave a product (0 48 g) which was dissolved in warm carbon tetrachloride Some starting material was filtered off from the cooled solution, and the filtrate was evaporated Two similar treatments of the residue gave chromatographically pure α-D tetra-acetate, which crystallised from ethanol as needles (0 37 g), m p 128–129°, $[\alpha]_D$ +92° (*c* 2 0, chloroform) (Found C, 50 4, H, 5 3; S, 6 4 $C_{21}H_{26}O_{12}S$ calc C, 50 2, H, 5 2, S, 6.4%) Ohle and Vargha[22] described

a hydrate, m p 129–130°, $[\alpha]_D$ +105.7°, obtained from the mother liquors from the acetylation of 6-*O*-toluene-*p*-sulphonyl-D-glucose

*Treatment of methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranoside with mercuric acetate.* — The toluene-*p*-sulphonate (0 34 g) was dissolved at room temperature in acetic acid (10 ml, anhydrous) containing mercuric acetate (1.1 g) After 1 h at room temperature, the acetic acid was evaporated at 50° The dried residue in pyridine (10 ml) was treated at 0° with acetic anhydride (5 ml) added dropwise The reaction mixture was left overnight at room temperature when a yellow precipitate separated The entire mixture was poured into ice-cold potassium iodide (10 g) in water (50 ml), most of the precipitate dissolved Processing with chloroform gave a syrup (0 4 g) which was shown by paper chromatography (solvent *u*, spray *a*) to be mainly 6-*O*-toluene-*p*-sulphonyl-α-D-glucopyranose tetra-acetate (R_F 0 24), with a small proportion of the β-D anomer (R_F 0 12) The syrup was dissolved in warm carbon tetrachloride and, after cooling, the solution was filtered to remove some β-D anomer. The filtrate was evaporated, and the above process was repeated until the product dissolved completely in carbon tetrachloride Evaporation and crystallisation from ethanol then gave the pure α-D-tetra-acetate as needles (0 30 g), m p and mixed m p 128–129°, $[\alpha]_D$ +91 5° (*c* 1 2, chloroform)

*Treatment of methyl 1-thio-6-*O*-toluene-*p*-sulphonyl-α-D-glucopyranoside with mercuric acetate* — The toluene-*p*-sulphonate (0 1 g), dissolved in anhydrous acetic acid (10 ml) containing mercuric acetate (0 4 g), was treated as described above for the β-D anomer The yellow precipitate which formed during the acetylation was filtered off, and the filtrate was poured with stirring into ice-cold water Chromatography (solvent *u*, spray *a*) of the crude product showed it to be mainly 6-*O*-toluene-*p*-sulphonyl-β-D-glucopyranose tetra-acetate, with traces of the α-D anomer. One crystallisation from ethanol gave the pure β-D anomer as needles (0 09 g), m p 204–205° (dec), $[\alpha]_D$ +23 7° (*c* 1 1, chloroform) (lit [7,23], m p 203–205°, $[\alpha]_D$ +23 9°)

ACKNOWLEDGMENTS

We express our gratitude to Professor Sir Edmund Hirst, C B E, F R S, for continued guidance and encouragement, and thank the Sugar Research Foundation Inc for financial support

REFERENCES

1 R BAKER, G R INGLIS, E V E ROBERTS, AND J C P SCHWARZ, unpublished work
2 C D ANDERSON, L GOODMAN, AND B R BAKER, *J Am Chem Soc*, 81 (1959) 3967, C D ANDERSON, W W LEE, L GOODMAN, AND B R BAKER, *ibid*, 83 (1961) 1900, G CASINI AND L GOODMAN, *ibid*, 86 (1964) 1427
3 N A HUGHES AND R ROBSON, *J Chem Soc (C)*, (1966) 2366
4 N A HUGHES AND P R H SPEAKMAN, *J Chem Soc (C)*, (1967) 1182
5 C L STEVENS, R P GLINSKI, K G TAYLOR, P BLUMBERGS, AND F SIROKMAN, *J Am Chem Soc*, 88 (1966) 2073
6 P W AUSTIN, J G BUCHANAN, AND R M SAUNDERS, *J Chem Soc (C)*, (1967) 372 P W AUSTIN J G BUCHANAN, AND D G LARGE, *Chem Commun*, (1967) 418, N A HUGHES, *ibid*, (1967) 1072, S HANESSIAN, *ibid*, (1966) 796

7 E HARDEGGER AND R M MONTAVON, *Helv Chim Acta*, 29 (1946) 1199
8 B CAPON, *Quart Rev* (London), 18 (1964) 65, K D GUNDERMANN, *Angew Chem, Intern Ed Engl*, 2 (1963) 674
9 M AKAGI, S TEJIMA, AND M HAGA, *Chem Pharm Bull* (Tokyo), 11 (1963) 58
10 J COMPTON, *J Am Chem Soc*, 60 (1938) 395
11 R M ROBERTS, J CORSE, R BOSCHAN, D SEYMOUR, AND S WINSTEIN, *J Am Chem Soc*, 80 (1958) 1247, R U LEMIEUX AND J D T CIPERA, *Can J Chem*, 34 (1956) 906
12 J C P SCHWARZ AND P F SWINTON, unpublished work
13 B WICKBERG, *Acta Chem Scand*, 12 (1958) 615
14 W E TREVELYAN, D P PROCTER, AND J S HARRISON, *Nature*, 166 (1950) 444
15 E STAHL AND U KALTENBACH, *J Chromatogr*, 5 (1961) 351
16 M JACKSON AND L D HAYWARD, *J Chromatogr*, 5 (1961) 166
17 J F CLAPPERTON, E V E ROBERTS, AND J C P SCHWARZ, unpublished work
18 W SCHNEIDER, J SEPP, AND O STIEHLER, *Ber*, 51 (1918) 220, M ČERNY AND J PACÁK, *Collection Czech Chem Commun*, 24 (1959) 2566, 26 (1961) 2084
19 P W AUSTIN, F E HARDY, J G BUCHANAN, AND J BADDILEY, *J Chem Soc*, (1963) 5350, J F CLAPPERTON, E V E ROBERTS, AND J C P SCHWARZ, unpublished work
20 A PICTET AND A GELEZNOFF, *Ber*, 36 (1903) 2219
21 B HELFERICH, H GRUNEWALD, AND F LANGENHOFF, *Ber*, 86 (1953) 873, M ČERNY, J STANĚK, AND J PACÁK, *Monatsh Chem*, 94 (1963) 290
22 H OHLE AND L v VARGHA, *Ber*, 62 (1929) 2425
23 B HELFERICH AND W KLEIN, *Ann*, 450 (1926) 219