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THE CHEMISTRY OF SOME 1-MERCURY(II)THIO-D-GLUCOSE COMPOUNDS; A NEW SYNTHESIS OF 1-THIO SUGARS*

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ABSTRACT

Treatment of tetra-*O*-acetyl-β-D-glucopyranosyl *N*,*N*-dimethyldithiocarbamate (1) with phenylmercury(II) acetate gives tetra-*O*-acetyl-1-phenylmercury(II)thio-β-D-glucopyranose (3), which can also be made in high yield from other dithiocarbamates, from tetra-*O*-acetyl-1-thio-β-D-glucopyranose, and from its *S*-acetyl derivative. The *p*-diethylamino derivative (7) of compound 3 displays significantly different properties and is readily convertible into bis(tetra-*O*-acetyl-1-thio-β-D-glucopyranosyl)mercury-(II) (8), which is also obtainable by treatment of tetra-*O*-acetyl-1-thio-β-D-glucopyranose with mercury(II) acetate. Aspects of the chemistry of compounds 3, 7, and 8 are reported; demercuration of 3 affords a convenient synthesis of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose.

INTRODUCTION

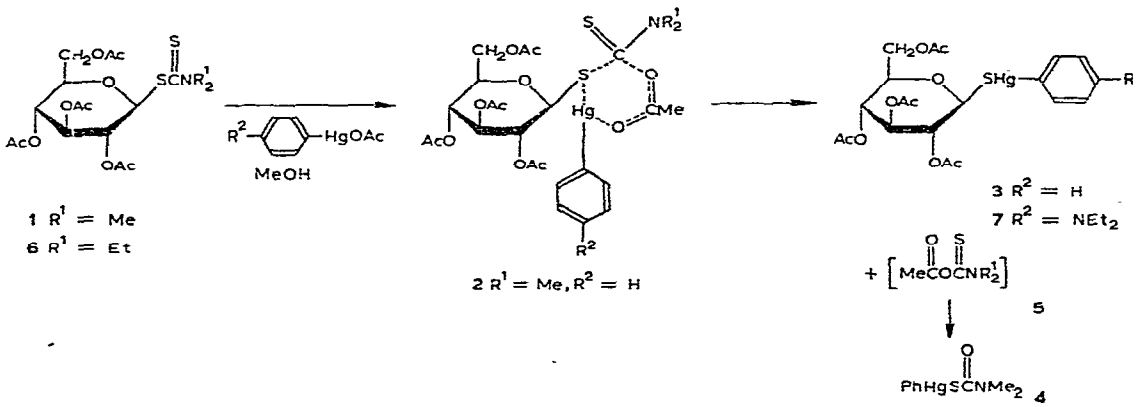
In connection with the use of the mercury(II)–sulphur soft acid–soft base affinity for synthetic purposes in carbohydrate chemistry[1], especially in the synthesis of glycosides[1a], we have encountered some 1-mercury(II)thio-D-glucose derivatives and now report on their synthesis and some of their chemical characteristics. Several carbon-bonded mercury derivatives of carbohydrates are known, usually as the products of mercuration of unsaturated compounds[2]. However, not many sulphur-bonded mercury derivatives of thiocarbohydrates seem to have been reported[3], despite their potential value as diuretics[4], and the use of other metal derivatives of thio sugars in medicine, *e.g.*, that of the gold salt of 1-thio-β-D-glucose in the treatment of some types of arthritis and in many biochemical studies[5]. Alkali-metal salts of 1-thioaldoses are used frequently in thioglucoside syntheses[6].

RESULTS AND DISCUSSION

Tetra-*O*-acetyl-1-phenylmercury(II)thio-β-D-glucopyranose (3) was initially encountered on treatment of tetra-*O*-acetyl-β-D-glucopyranosyl *N*,*N*-dimethyldithio-

*Dedicated to the memory of Sir Edmund Hirst, C.B.E., F.R.S.

carbamate (**1**) with two molar equivalents of phenylmercury(II) acetate in refluxing methanol, and is envisaged as having been formed by way of the transition state **2** (Scheme 1). Reaction by way of a sulphur–mercury-bonded complex which underwent solvolytic attack at C-1 would have led to a new approach to glycoside synthesis. Mercury(II) sulphide was formed concurrently with **3**, and examination of the mother liquors of the reaction yielded diphenylmercury and triphenylmethanol, which provide evidence for the presence of phenyl radicals in the reaction. In addition, *S*-phenylmercury(II) *N,N*-dimethylthiocarbamate (**4**) was isolated; **4** conceivably arose by reaction of phenylmercury(II) acetate with the first by-product, *i.e.*, the mixed anhydride (**5**) of acetic acid and *N,N*-dimethylthionocarbamic acid.

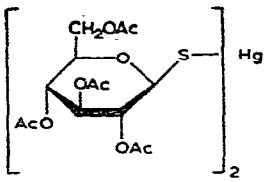


Scheme 1.

Compound **3** was similarly obtained in high yield from the diethyl compound **6** and also, again using phenylmercury(II) acetate, from 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose and, further, from the *S*-acetyl derivative of this compound. In each case, the mercury–sulphur association led to cleavage of the bond joining the sulphur atoms to the groups other than the carbohydrate. In related fashion, penta-*O*-acetyl-1-thio-β-D-glucopyranose reacts with bromine to give the glucosylsulphenyl bromide[7], whereas corresponding 1-thioglycosides afford the acetylated glycosyl bromide[8].

(*p*-Diethylaminophenyl)mercury(II) acetate (prepared in high yield from mercury(II) acetate and *N,N*-diethylaniline), on treatment with compound **1** in methanol at room temperature, gave the substituted phenylmercury(II)thio-compound **7** in high yield, and it was also obtained smoothly from 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose under similar conditions. However, when these reactions were repeated in refluxing methanol, *i.e.*, in conditions used for the preparation of compound **3**, a black precipitate formed and bis(tetra-*O*-acetyl-1-thio-β-D-glucopyranosyl)-mercury(II) **8** was isolated in good yield. This was the first of several reactions noted for the diethylamino compound **7** which exhibited facile rupture of the mercury–phenyl bond following nucleophilic attack by sulphur at the mercury atom. This

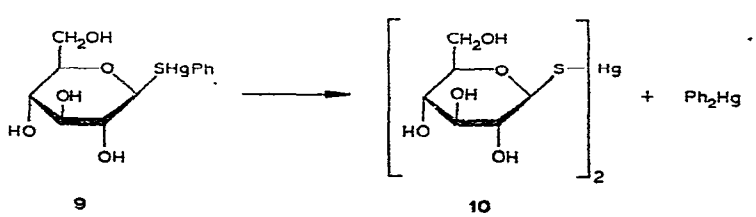
susceptibility has been noted for related (*N,N*-dialkylaminophenyl)mercury(II) compounds[9] and represented the reason for preparing compound **7**. Compound **8** was also obtainable in high yield from tetra-*O*-acetyl-1-thio-β-D-glucopyranose and mercury(II) acetate (0.5 mol. equiv.).



8

In an effort to prepare tetra-*O*-acetyl-1-thio-β-D-glucopyranosylmercury(II) acetate, the thio sugar and mercury(II) acetate (now in equimolar proportions) were again treated in methanol, but none of the anticipated compound was obtained. Instead, the dimeric species **8** was again isolated (46% yield), and the other carbohydrate products were identified by n.m.r. spectroscopy as methyl α-D-glucopyranoside tetra-acetate and the corresponding *endo*- and *exo*-1,2-(orthoacetates) in the ratios 3:2:10. It appears, therefore, that the thioglycosylmercury(II) acetate is unfavoured relative to the di(thioglycosyl)mercury compound **8**, and also that some glycosyl–sulphur bond fission can occur in this series–even in the presence of ester groups which are known to inhibit such reactions[1a]. In contrast, treatment of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose with mercury(II) chloride in alcohol gives the thioglycosylmercury(II) chloride[3], which exemplifies the stability of mercury–chlorine bonds relative to mercury–oxygen analogues[10].

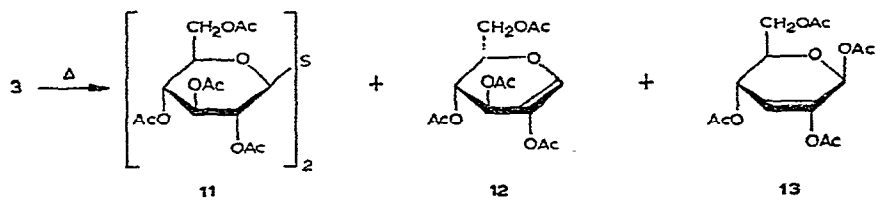
Compounds **3** and **8** are stable in refluxing methanol, can be recrystallised from this solvent, and undergo smooth deacetylation and reacetylation. 1-*S*-Phenylmercury(II)thio-β-D-glucopyranose (**9**), obtained by deacetylation of compound **3**, can also be recrystallised from methanol, but is unstable in water, undergoing disproportionation to give di(1-thio-β-D-glucopyranosyl)mercury(II) (**10**, *i.e.*, the product of deacetylation of compound **8**) and diphenylmercury (Scheme 2), which can be separated efficiently by carrying out the reaction in water–chloroform. Such disproportionations of simpler thiomercury compounds are well established[11].



9 **10**

Scheme 2.

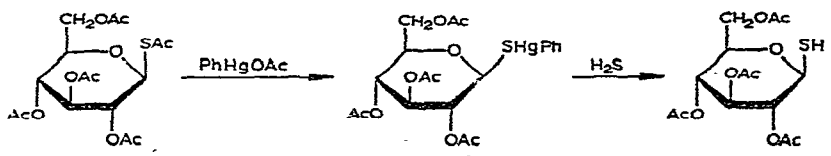
With the intention of seeing whether mercury(II) sulphide might be thermally extruded from compound **3**, to provide a new route to *C*-glycosides, the compound was heated in refluxing nitrobenzene, whereupon a black precipitate and some metallic mercury were formed. No tetra-*O*-acetyl-β-D-glucopyranosylbenzene was the detected in the products; instead, the only carbohydrate product isolated was the β-D-glucopyranosyl 1-thio-β-D-glucopyranoside ester (**11**, 14%), and the mother liquors were shown by n.m.r. spectroscopy to be a mixture of tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**12**) and its product of thermal rearrangement[12], tetra-*O*-acetyl-3-deoxy-β-D-*erythro*-hex-2-enopyranose (**13**), in the ratio 1:3 (Scheme 3).



11 12 13

Scheme 3.

Investigation of the reactions undergone by the 1-mercurythio-D-glucose compounds **3**, **7**, and **8** with hydrogen sulphide showed that each was converted into 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose. This reaction of compound **3** in ethanol allows an especially simple and efficient means of obtaining the thio sugar by specific *S*-deacetylation of the penta-acetyl derivative **14** (Scheme 4), which is obtainable by standard means from tetra-*O*-acetyl-α-D-glucopyranosyl bromide, or directly from penta-*O*-acetyl-β-D-glucopyranose by treatment with thiolacetic acid in the presence of boron trifluoride[13]. The by-product of the demercuration step was a yellow solid, assumed to be di[phenylmercury(II)] sulphide, which was obtained in 85% yield. From **7** and **8**, mercury(II) sulphide was produced, together with diethylaniline in the case of **7**. Again, therefore, the mercury–carbon bond in **7** is more labile than that in the unsubstituted analogue **3**, and this accords with the observation that, whereas dialkylaminophenylmercury(II) acetates give mercury(II) sulphide[9] on treatment with hydrogen sulphide, phenylmercury(II) acetate affords di[phenylmercury(II)] sulphide[14]. In similar fashion, when compound **3** was treated with thiophenol in refluxing methanol, it gave phenylmercury(II) thiophenate in high yield and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose (n.m.r. and t.l.c. identification), whereas the



14 3

Scheme 4.

diethylamino compound 7 gave mercury(II) thiophenate and the diglycosyl compound 8, presumably by way of a mixed glycosylthio–phenylthiomercury(II) intermediate. Acetic acid was used to catalyse this latter reaction, after it had been shown to have little affect on 3, and to catalyse the transformation of 7 into the dimer 8 in the absence of thiol.

With excess of thiolacetic acid, compounds 7 and 8 both gave 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose in high yield, conceivably by way of tetra-*O*-acetyl-1-thio-β-D-glucopyranosylmercury(II) thioacetate for 7.

EXPERIMENTAL

Unless otherwise noted, optical rotations were measured for 1–5% solutions in chloroform.

Tetra-O-acetyl-1-phenylmercury(II)thio-β-D-glucopyranose (3). — (*a*) *From tetra-O-acetyl-β-D-glucopyranosyl* N,N-*dimethyldithiocarbamate.* The carbamate[15] (1, 10 g) and phenylmercury(II) acetate (14.9 g, 2.0 mol. equiv.) were heated under reflux in methanol (150 ml) for 30 min. The resulting black precipitate was shown by X-ray diffraction to be mercury(II) sulphide, which has *d*-spacings of 3.38, 2.07, and 1.76 Å (Found: 3.35, 2.06, and 1.76 Å). After filtration, 3 crystallised (9.1 g, 64%) and, on recrystallisation from methanol, had m.p. 147–148.5°, $[\alpha]_D$ −85.5°.

Anal. Calc. for $C_{20}H_{24}HgO_9S$: C, 37.5; H, 3.8; S, 5.0. Found: C, 37.3; H, 3.9; S, 5.3.

Cooling of the mother liquors to −20° gave a crude, white solid (3.9 g, 26%), which was purified on a column of silica gel and recrystallised from methanol to give diphenylmercury, m.p. 124–125°; lit.[16] m.p. 122–124. The n.m.r. spectrum showed only aromatic resonances.

Anal. Calc. for $C_{12}H_{10}Hg$: C, 40.6; H, 2.8. Found: C, 40.6; H, 2.8.

Fractionation of the remainder by preparative t.l.c. gave triphenylmethanol, m.p. and mixture m.p. 161–162°; lit.[17] m.p. 161–162°. The n.m.r. and infrared spectra were identical with those of authentic material. A second component crystallised from light petroleum to give *S*-phenylmercury(II) *N,N*-dimethylthiocarbamate (4), m.p. 74–76°; n.m.r. data: δ 2.99 (6 H, NMe_2) and 7.23 (5 H, phenyl); ν_{max} 1587 cm^{-1}.

Anal. Calc. for $C_9H_{11}HgNOS$: C, 28.4; H, 2.9; N, 3.7. Found: C, 28.9; H, 3.5; N, 3.9.

(*b*) *From tetra-O-acetyl-β-D-glucopyranosyl* N,N-*diethyldithiocarbamate* (6). The carbamate[15] (1.20 g) and phenylmercury(II) acetate (1.69 g, 2.0 mol. equiv.) were heated under reflux in methanol (40 ml) for 30 min. The resulting black precipitate was removed by filtration through Celite, and the liquors, on cooling, deposited 3 (1.32 g, 82%); after recrystallisation (×2) from methanol, 3 had m.p. 147–148°, $[\alpha]_D$ −85°. The n.m.r. and i.r. spectra were identical with those of the product from (*a*).

(*c*) *From 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucose.* The thio sugar (1.0 g) in

warm ethanol (20 ml) was mixed with phenylmercury(II) acetate (0.815 g, 1.0 mol. equiv.) in the same solvent (25 ml). On cooling of the solution to 0°, the thiomercury product **3** (1.34 g, 76%) precipitated. Without recrystallisation, **3** had m.p. 146–148°, $[\alpha]_D$ −85°, and the infrared spectrum was identical with that given by the samples prepared by methods (*a*) and (*b*).

(*d*) *From pentaacetyl-1-thio-β-*D*-glucopyranose.* The penta-acetate (1.1 g) and phenylmercury(II) acetate (0.91 g, 1.0 mol. equiv.) were heated under reflux in ethanol (25 ml) for 40 min, and a small amount of yellow precipitate was then removed from the hot solution. On cooling, the filtrate gave the thiomercury product **3** (1.30 g, 75%). Recrystallised from methanol, **3** had m.p. and mixture m.p. 147–149°, $[\alpha]_D$ −83°, and gave the same n.m.r. spectrum as the earlier samples.

(*e*) *From 1-phenylmercurythio-β-*D*-glucopyranose* (**9**). Compound **9** (0.115 g; obtained by deacetylation of the tetra-acetate **3**) was treated with acetic anhydride (3 ml) in pyridine (3 ml) to give **3** (0.130 g, 84%), which, after recrystallisation from methanol, had m.p. and mixture m.p. 146–148°, $[\alpha]_D$ −85°.

(p-*Diethylaminophenyl*)*mercury(II) acetate.* — Mercury(II) acetate (15.5 g) in water (90 ml) was added to *N,N*-diethylaniline (8.0 g, 1.1 mol. equiv.) in ethanol (20 ml) to give a solution from which separated the arylmercury salt (14.8 g, 74%). Recrystallised (×2) from benzene–light petroleum, it had m.p. 103–105°; lit.[18] m.p. 105°; and gave a consistent n.m.r. spectrum.

*Tetra-*O*-acetyl-1-*(p-*diethylaminophenyl*)*mercury(II)thio-β-*D*-glucopyranose* (**7**). — (*a*) *From tetra-*O*-acetyl-β-*D*-glucopyranosyl* N,N-*dimethyldithiocarbamate* (**1**). The carbamate (1.66 g) and (*p*-diethylaminophenyl)mercury(II) acetate (3.0 g, 2.0 mol. equiv.) were dissolved in methanol (50 ml). After the solution had stood at 20° for 2 h and 0° for 0.5 h, the white product **7** (2.21 g, 85%) was removed in two crops by filtration of the black mixture. Recrystallised from methanol (×2), **7** had m.p. 150–152°, $[\alpha]_D$ −86°.

Anal. Calc. for $C_{24}H_{33}HgNO_9S$: C, 40.5; H, 4.7; N, 2.0; S, 4.5. Found: C, 40.6; H, 5.0; N, 2.1; S, 4.8.

(*b*) *From 2,3,4,6-tetra-*O*-acetyl-1-thio-β-*D*-glucose.* The thiol (5.0 g) and (*p*-diethylaminophenyl)mercury(II) acetate (5.6 g, 1.0 mol. equiv.) were separately dissolved in methanol (100 ml) containing triethylamine (2 ml). The solutions were mixed, and **7** (8.65 g, 88%) separated as white platelets. Recrystallised from methanol, **7** had m.p. 148–150°, $[\alpha]_D$ −85°, and gave an infrared spectrum identical with that of the product from (*a*).

*Bis(tetra-*O*-acetyl-1-thio-β-*D*-glucopyranosyl)mercury(II)* (**8**). — (*a*) *From tetra-*O*-acetyl-β-*D*-glucopyranosyl* N,N-*dimethyldithiocarbamate* (**1**). The carbamate (13.6 g) and (*p*-diethylaminophenyl)mercury(II) acetate (12.0 g, 1.0 mol. equiv.) were heated under reflux in methanol (150 ml) for 2.5 h. Removal of the solvent gave a black syrup which was extracted with ether (200 ml); from the extract, compound **8** (10.7 g, 77%) was obtained after cooling to −20°. Recrystallised from methanol (×3), **8** had m.p. 95° (difficult to determine because a highly viscous liquid was formed), $[\alpha]_D$ −59°.

Anal. Calc. for $C_{28}H_{38}HgO_{18}S_2$: C, 36.3; H, 4.1. Found: C, 36.0; H, 4.1.

(*b*) *From 2,3,4,6-tetra-*O*-acetyl-1-thio-β-*D*-glucose and (p-diethylaminophenyl)-mercury(II) acetate.* The thiol (1.0 g) and the mercury compound (0.56 g, 0.5 mol. equiv.) were heated under reflux in methanol (25 ml) containing acetic acid (0.5 ml) for 0.5 h. When the solution was then cooled to 0°, compound **8** (0.80 g, 60%) precipitated. Recrystallised from methanol, **8** had m.p. and mixture m.p. 95°, $[\alpha]_D$ −60°; the infrared spectrum and melting characteristics were identical with those of the compound produced by method (*a*).

(*c*) *From 2,3,4,6-tetra-*O*-acetyl-1-thio-β-*D*-glucose and mercury(II) acetate.* Hot solutions of the thiol (10.0 g) in methanol (50 ml), and mercury(II) acetate (4.37 g, 0.5 mol. equiv.) in methanol (20 ml), were mixed, and a small amount of a dark precipitate was removed. On cooling the filtrate to 0°, compound **8** (10.0 g, 83%) crystallised. Recrystallised from methanol, **8** had m.p. 95°, $[\alpha]_D$ −59°; the melting characteristics were identical with those of the earlier sample.

(*d*) *From di(1-thio-β-*D*-glucopyranosyl)mercury(II)* (**10**). Compound **10** (0.165 g; obtained by deacetylation of the octa-acetate **8**) was treated with acetic anhydride (5 ml) in pyridine (5 ml) to give **8** (0.195 g, 75%). Recrystallised from methanol, **8** had m.p. 95°, $[\alpha]_D$ −59°; the infrared spectrum was identical with that of the original octa-acetate.

*Reaction of 2,3,4,6-tetra-*O*-acetyl-1-thio-β-*D*-glucose with mercury(II) acetate in methanol.* — (*a*) *In molar ratio 2:1.* See (*c*) above.

(*b*) *In molar ratio 1:1.* The thiol (1.5 g) in methanol (50 ml, dry) was slowly added to a stirred solution of mercury(II) acetate (1.31 g, 1.0 mol. equiv.) in methanol (70 ml, dry). A white solid precipitated, and two chromatographically distinguishable products were formed. Removal of the solid (0.54 g, which was insoluble in all solvents used and was not further studied) and the solvent gave a pale-yellow syrup (1.81 g) which was resolved into two components by preparative t.l.c. The first (0.89 g, 46%), on crystallisation from methanol, gave bis(tetra-*O*-acetyl-1-thio-β-D-glucopyranosyl)-mercury(II), m.p. 95°, $[\alpha]_D$ −59°. The second fraction (0.52 g, 35%) was shown by n.m.r. spectroscopy to be a mixture of methyl tetra-*O*-acetyl-α-D-glucopyranoside and 3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl *endo*- and *exo*-1,2-(methyl orthoacetate) in the ratios 3:2:10. N.m.r. data: δ 1.57, 1.70 (CMe); 3.26, 3.40, 3.42 (OMe); lit. for the *endo*-orthoester[19], 1.57 and 3.46 (CMe, OMe); for the *exo*-orthoester[19], 1.72 and 3.30 (CMe, OMe); for the α-glycoside[20], 3.42 (OMe); measured for an authentic sample of the α-glycoside, 3.40 (OMe). The intensities of the resonances were consistent with the assignments and the above ratios.

*1-Phenylmercury(II)thio-β-*D*-glucopyranose* (**9**). — The tetra-acetate **3** (3.69 g) was deacetylated with catalytic amounts of sodium methoxide in methanol; on completion of the reaction, the sodium was removed with cationic resin and the volume was decreased to 15 ml. Cooling to 0° gave **9** (1.45 g, 53%); recrystallised from methanol, **9** had m.p. 173–174° (dec.), $[\alpha]_D$ −8° (*c* 1, methanol).

Anal. Calc. for $C_{12}H_{16}HgO_5S$: C, 30.5; H, 3.4; S, 6.8. Found: C, 30.8; H, 3.5; S, 6.6.

Di(1-thio-β-D-glucopyranosyl)mercury(II) (**10**). — The octa-acetate **8** (7.5 g) was deacetylated with catalytic amounts of sodium methoxide in methanol (100 ml). When the reaction solution was kept at 0°, **10** (4.2 g, 88%) crystallised as a white solid. Recrystallised from aqueous methanol, **10** had m.p. 184–187° (dec.), $[\alpha]_D$ −6° (*c* 5, water).

Anal. Calc. for $C_{12}H_{22}HgO_{10}S_2$: C, 24.4; H, 3.8; S, 10.9. Found: C, 24.5; H, 3.7; S, 11.7.

Disproportionation of 1-phenylmercury(II)thio-β-D-glucopyranose (**9**). — Compound **9** (0.68 g) was shaken with a mixture of water (40 ml) and chloroform (5 ml) for 85 h, during which time the solid dissolved. Further chloroform was then added and the phases were separated. After drying, the chloroform was removed to give diphenylmercury (0.25 g, 97%) which, on recrystallisation from methanol, had m.p. and mixture m.p. 122–124°; lit.[16] m.p. 122–124°. The infrared spectrum was identical with that of an authentic sample.

Removal of the water from the aqueous phase gave di(1-thio-β-D-glucopyranosyl)mercury(II) (**10**; 0.42 g, 98%); on recrystallisation from aqueous methanol, **10** had m.p. ~180° (dec.), $[\alpha]_D$ −5.4° (*c* 3, water), and was further characterised by conversion into the octa-acetate, m.p. 95°, $[\alpha]_D$ −60°.

Thermolysis of tetra-O-acetyl-1-phenylmercury(II)thio-β-D-glucopyranose. — Compound **3** (1.46 g) in nitrobenzene (10 ml) was boiled under reflux for 1.25 h, causing the formation of a black precipitate and metallic mercury. The nitrobenzene was removed under reduced pressure, the black residue was extracted with ethanol, and the solution was treated with charcoal. From this solution, β-D-glucopyranosyl 1-thio-β-D-glucopyranoside octa-acetate (0.11 g, 14%) crystallised. Recrystallised from methanol, it had m.p. 174–176°, $[\alpha]_D$ −40°; lit.[21] m.p. 175–176°, $[\alpha]_D$ −38°.

Anal. Calc. for $C_{28}H_{28}O_{18}S$: C, 48.4; H, 5.5; S, 4.6. Found: C, 48.7; H, 5.3; S, 4.5.

Purification of the mother liquors by chromatography on a column of silica gel gave a syrup which was shown by n.m.r. spectroscopy to be a mixture (1:3) of tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol [δ 6.63 (s, 1 H, H-1), 5.56 (d, 1 H, $J_{3,4}$ 4 Hz, H-3), 5.25 (m, 1 H, H-4), 4.3 (m, 3 H, H-5,6,6'), 2.10 and 2.15 (12 H, Ac); lit.[12] 6.69 (s, 1 H), 5.62 (d, 1 H, *J* 4 Hz), 5.26 (m, 1 H), 4.3 (m, 3 H), and 2.1 (12 H)] and tetra-*O*-acetyl-3-deoxy-β-D-*erythro*-hex-2-enopyranose [δ 6.40 (s, 1 H, H-1), 5.97 (d, 1 H, $J_{3,4}$ 5 Hz, H-3), 5.30 (m, 1 H, H-4), 4.3 (m, 3 H, H-5,6,6'), 2.10 and 2.15 (12 H, Ac); lit.[12] 6.44 (s, 1 H); 6.01 (d, 1 H, *J* 5.5 Hz), 5.35 (m, 1 H), 4.3 (m, 3 H), and 2.1 (12 H)].

Thermolysis of bis(tetra-O-acetyl-1-thio-β-D-glucopyranosyl)mercury(II). — Compound **8** (1.39 g) was heated in boiling nitrobenzene (5 ml) for 5 h, and removal of the solvent *in vacuo* then gave a black syrup which was extracted with ether. Removal of the ether left a red syrup (0.93 g) which was shown by t.l.c. to contain several products. Preparative t.l.c. yielded only one pure product, bis(tetra-*O*-acetyl-β-D-glucopyranosyl) disulphide (0.07 g, 7%), m.p. 142–143°; lit.[22] m.p. 142–143°.

The melting point was undepressed on admixture with an authentic sample; the t.l.c. mobility was identical with that of the authentic material.

Reactions of tetra-O-acetyl-1-phenylmercury(II)thio-β-D-glucopyranose (3). — (*a*) *With hydrogen sulphide.* Hydrogen sulphide was passed into a solution of 3 (5.0 g) in hot ethanol (60 ml) for 1 h; yellow di[phenylmercury(II)] sulphide (1.95 g, 85%; decomposes on heating) was precipitated and was removed. The filtrate was taken to dryness, and the resulting syrup was crystallised from ethanol (20 ml) to give 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose (2.31 g, 81%). Recrystallised (×2) from methanol, it had m.p. and mixture m.p. 114–115°, $[\alpha]_D$ +3°; lit.[23] m.p. 115°, $[\alpha]_D$ +5°.

(*b*) *With thiophenol.* A solution of compound 3 (1.0 g) in methanol (25 ml) containing thiophenol (3.2 ml, 20 mol. equiv.) was boiled under reflux for 0.5 h. Phenylmercury(II) thiophenate (0.52 g, 86%) crystallised from the cooled solution as white plates with m.p. and mixture m.p. 101–104°; lit.[24] m.p. 103.5°; the infrared spectrum was identical with that of an authentic sample. Removal of the solvent from the mother liquors gave a syrup which contained (n.m.r. spectroscopy and t.l.c.) 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose as the sole carbohydrate component; it resisted satisfactory crystallisation because of contaminating phenylmercury(II) thiophenate.

(*c*) *With acetic acid.* A solution of compound 3 (0.43 g) in ethanol (10 ml) and acetic acid (2 ml) was boiled under reflux. After 30 h, at least three products had been formed (t.l.c.) and some of 3 remained; 11% of 3 was recovered by direct crystallisation from methanol.

Reactions of tetra-O-acetyl-1-(p-diethylaminophenyl)mercury(II)thio-β-D-glucopyranose (7). — (*a*) *With hydrogen sulphide.* Hydrogen sulphide was passed into a solution of compound 7 (2.4 g) in chloroform (50 ml), causing an immediate blackening of the solution. After 15 h, the black precipitate (assumed to be mercury(II) sulphide) had settled and the supernatant solution was passed through a short column of silica gel to give diethylaniline (0.46 g, 98%; t.l.c. identification), and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose (0.80 g, 65%), m.p. 114–117°, $[\alpha]_D$ +6.5°.

(*b*) *With thiophenol.* A solution of compound 7 (1.0 g) in methanol (25 ml) containing acetic acid (0.43 ml) and thiophenol (0.15 g, 1 mol. equiv.) was boiled under reflux for 20 min. When the solution was cooled to 20°, mercury(II) thiophenate crystallised (0.24 g, 82%) and, after recrystallisation from chloroform–methanol, had m.p. 149–150°; lit.[25] m.p. 150–152°; the infrared spectrum was identical with that of authentic material. The filtrate, on cooling to 0°, yielded bis-(tetra-*O*-acetyl-1-thio-β-D-glucopyranosyl)mercury(II) (8; 0.46 g, 71%) which, after recrystallisation from methanol (×2), had m.p. 95°, $[\alpha]_D$ −65° (infrared and n.m.r. spectra identical with those of authentic material).

(*c*) *With thiolacetic acid.* Compound 7 (1.0 g) was dissolved in methanol (50 ml) containing thiolacetic acid (0.5 g, 5.0 mol. equiv.); on storage, the solution deposited a small amount of a yellow solid. Removal of this and of 40 ml of solvent gave a solution from which 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose (0.44 g, 86%) crystallised. Recrystallised from methanol, it had m.p. 118–119°, $[\alpha]_D$ +9°.

(*d*) *With acetic acid.* A solution of compound 7 (2.0 g) in methanol (20 ml) containing acetic acid (0.4 g) was boiled under reflux for 0.5 h. A grey precipitate was then removed by filtration, and the filtrate was cooled to −20° to yield bis(tetra-*O*-acetyl-1-thio-β-D-glucopyranosyl)mercury(II) (8; 0.59 g, 45%). Recrystallised from aqueous methanol, 8 had m.p. 95° (indefinite), $[\alpha]_D$ −60°.

Reactions of bis(tetra-O-acetyl-1-thio-β-D-glucopyranosyl)mercury(II) (8). — (*a*) *With hydrogen sulphide.* Compound 8 (1.7 g) in chloroform–ethanol (100 ml, 1:1) decomposed to give a black solid, assumed to be mercury(II) sulphide, on treatment with hydrogen sulphide. After the mixture had been kept for 15 h, it was passed down a short column of silica gel, and the clear eluate was taken to dryness to give a residue which crystallised from methanol to give 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose (0.94 g, 70%). Recrystallised from methanol, it had m.p. 74–75°, $[\alpha]_D$ +5°; lit.[23] m.p. 75°, $[\alpha]_D$ +5°; the infrared and n.m.r. spectra were identical with those of an authentic sample; this compound is reported to be dimorphic[23].

(*b*) *With thiolacetic acid.* Compound 8 (1.0 g) in methanol (25 ml) containing thiolacetic acid (0.25 ml, 3.3 mol. equiv.) was kept at 20° for 2 h and 0° for 15 h, whereupon 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucose (0.34 g) precipitated. A further crop (0.33 g, 86% total) was obtained after cooling of the mother liquors to −20°. Recrystallised from methanol, it had m.p. ~73° and then 113–114°, $[\alpha]_D$ +5°; the infrared and n.m.r. spectra were identical with those of an authentic sample.

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