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THE METHOXYMERCURATION OF A 6-DEOXYHEX-5-ENOPYRANOSIDE DERIVATIVE AND REACTIONS OF THE PRODUCTS*†

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ABSTRACT

Methoxymercuration of methyl 3,4-di-*O*-benzoyl-6-deoxy-2-*O*-toluene-*p*-sulphonyl-α-D-*xylo*-hex-5-enopyranoside (**5**) at room temperature with mercury(II) acetate afforded the direct product of addition (**8**) with mercury bonded to the exocyclic carbon atom. Acetylation of **8** gave the acyclic vinyl ether **11**, from which the methyl ketone **12** was prepared. On the other hand, treatment of the alkene **5** with phenylmercury acetate in boiling methanol gave the bis(glycos-6-yl)mercury compound **13** with inverted stereochemistry at the anomeric centre. This compound, on acetylation, gave the C-1 epimer (**15**) of compound **11**, together with the anomer (**14**) of the initial alkene **5**. Compounds **11** and **15** underwent methoxymercuration to give the acyclic adducts **16** and **17**, and these, together with the methyl ketone **12**, were tested as sources of functionalised cyclopentanes.

INTRODUCTION

The synthesis by Stork and his collaborators of prostaglandins (PG) from carbohydrates[2–4], most notably his route to prostaglandin $F_{2\alpha}$ from D-glucose[4], illustrates the potential of readily available carbohydrates as starting materials for synthesis of highly functionalised and optically pure non-carbohydrate compounds[5]. However, while the $PGF_{2\alpha}$ goal has already been attained, and while several routes for conversion of carbohydrates to inositols have been developed[6], no general and efficient method of preparing functionalised cyclopentanes from carbohydrates has been proposed**. Compound **1**, however, by way of the derived 5-deoxypent-4-enofuranose and then the 5-deoxypent-4-ulose derivative, has recently been converted into the *Streptomyces* antibiotic pentenomycin[7] (**2**) to illustrate the value of this approach, but the aldol reaction used to effect ring closure was less than wholly satisfactory.

In this laboratory, the reactions of compound **3** with base were studied in the hope of effecting nucleophilic displacement of the sulphonyloxy group at C-2 with

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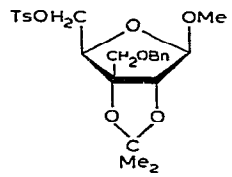

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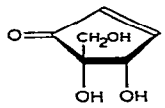

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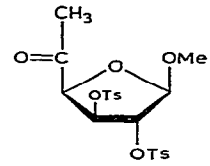

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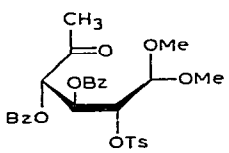
the carbanion at C-6 to give a cyclopentane ring having a potential formyl group amongst its substituents[8]. Although a product having spectroscopic characteristics consistent with an appropriate bicyclic compound was obtained, the main reaction undergone by the ketone **3** was *β*-elimination of toluene-*p*-sulphonic acid and subsequent formation of a substituted furan. In the hope that elimination reactions would be relatively less favoured with acyclic compounds, an attempt was then made to prepare the 6-deoxyhexos-5-ulose dimethyl acetal (**4**) by methanolysis of the 6-deoxy-5-enopyranoside[6] (**5**), but, rather than the hoped-for ring-opening, acid-catalysed addition of methanol together with anomerisation took place at the vinyl ether centre to give the 5-methoxyglycoside **6**. However, compound **5**, treated with mercury(II) chloride in aqueous acetone, reacted by way of a 6-deoxy-6-mercuri intermediate to give the inosose derivative **7**, following attack by the carbanionic C-6 at the released carbonyl group at C-1 rather than at C-2, and thus a route to cyclohexane rather than to cyclopentane derivatives was developed. In the present work, mercuration of compound **5** was conducted in dry methanol to give stable products having mercury bonded to C-6, and from these, acyclic compounds related to the initial target-compound **4** were obtained. Aspects of the chemistry of the adducts and derived acyclic derivatives were examined — in particular to determine whether cyclic products having C-2 bonded to C-6 could be obtained.



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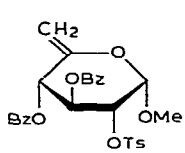

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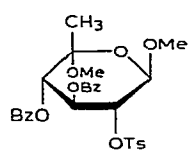

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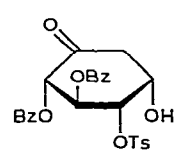

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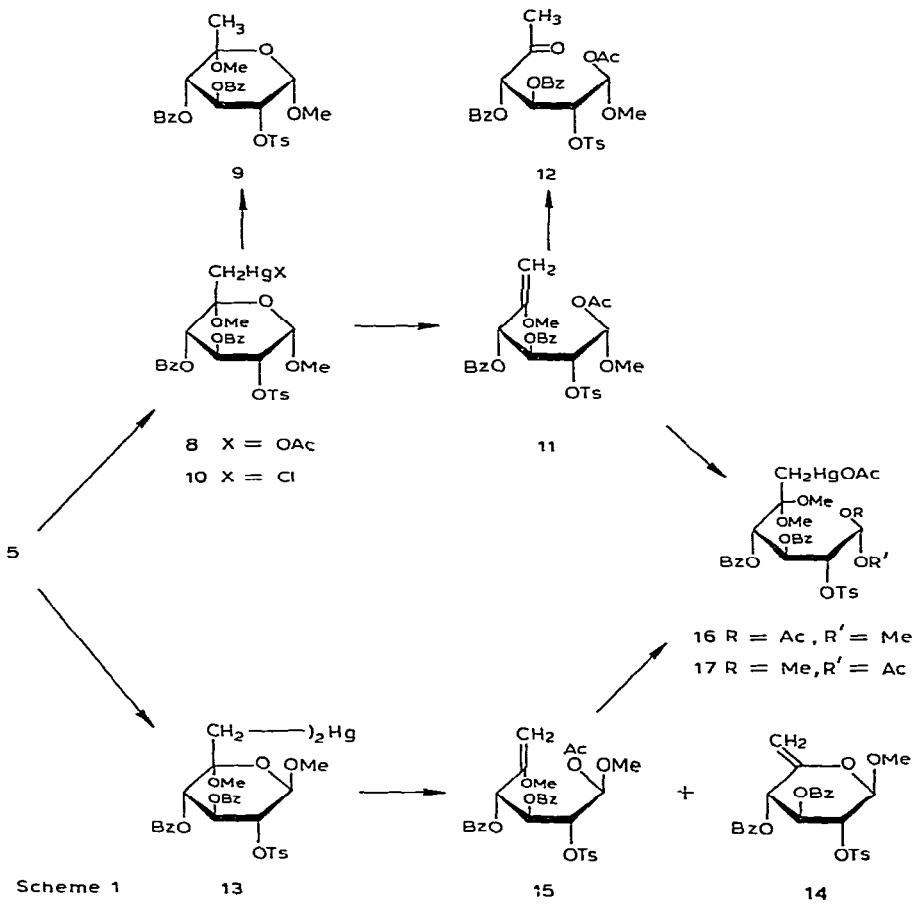
RESULTS AND DISCUSSION

Pyranosyl products having mercury bonded to C-2, and formed by additions to glycals and their derivatives, have received considerable attention[9], but there has been little work on other carbohydrate carbon–mercury-bonded compounds, although 2,3,4-tri-*O*-acetyl-1,5-anhydro-6-deoxy-D-*xylo*-hex-5-enitol afforded crystalline methyl 3,4,5-tri-*O*-acetyl-1-chloromercuri-1-deoxy-α-L-sorbopyranoside[10] by a methoxy-

mercuration process followed by treatment with chloride ion*. The alkene **5** reacted at room temperature in methanol with mercury(II) acetate to give a stable, crystalline product (**8**) having mercury bonded at C-6 (Scheme 1), as expected on account of the starting alkene being a vinyl ether[9] and its having an exocyclic double bond[11]. Reduction of the adduct **8** with sodium borohydride gave the 6-deoxy product **9**, which was assigned the α-D-*gluco* configuration on the basis of $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ values of 4.5, 10, and 10 Hz, respectively, and from the observation that it was more dextrorotatory than the β anomer **6** by ~360° (molecular rotation), in line with the closely related methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-α- and -β-D-glucopyranosides[12,13], which differ by ~450°. Furthermore, compound **9** ($[\alpha]_D$ −32°) is appreciably more levorotatory than is methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-α-D-glucopyranoside ($[\alpha]_D$ +57°). Both of these points are consistent only with the presence in compound **9** of an *R* centre at C-5, as illustrated[14–16]. Were the configuration at C-5 different, ring distortion might have been expected, since an axial methyl group and equatorial methoxyl group at this centre would have introduced substantial strain, and, in addition, the C-6 protons would have been deshielded relative to those in the β anomer[17] **6**; in practice they resonate 0.12 p.p.m. upfield. Similarly, C-6 of the α compound (**9**) resonated 1.3 p.p.m. downfield from this atom of compound **6**, and had it been axial, it would have been relatively shielded[18]. Also, in keeping with the configurational assignment at C-5, H-3 of compound **9** is specifically deshielded with respect to this proton of methyl 3,4-di-*O*-benzoyl-2,6-di-*O*-toluene-*p*-sulphonyl-α-D-glucopyranoside and the 6-deoxy-6-iodo analogue[19]. Likewise, this proton is relatively deshielded in the adduct **8**, and this observation, together with the assignment already made for the reduced product **9**, establish that methoxymercuration of the alkene occurred by a process involving attack by methanol from the axial side at C-5. This is not consistent with observations made with cyclohexane derivatives, which indicate that electrophilic mercury might approach the double bond of the alkene **5** from the α side[20], and that subsequent solvolysis would lead to the introduction of methanol from the more accessible, equatorial, β side, regardless of the configuration of the mercurinium intermediate[21].

Several reactions reported for the products of oxymercuration of glycals[9] indicate that the carbon atoms bonded to the metal have carbanionic activity that can initiate elimination processes, and their ability to take part as nucleophiles in substitution reactions is indicated by the conversion of a mercury adduct of the alkene **5** into the carbocyclic compound **7** (ref. 6). To assess whether this could be utilised to effect alkylation or acylation at C-6, compound **8** was treated separately at room temperature with allyl chloride in pyridine and with acetyl chloride in *N*,*N*-dimethylformamide and pyridine. In the former case, the product was simply the chloromercuri analogue (**10**) of the starting material, but with the latter reagent a crystalline acetylated product was isolated in good yield. Small coupling-constants

*A referee has kindly pointed out that the addition of mercury(II) azide to an exocyclic alkene has been used in the synthesis of branched-chain amino sugar derivatives[10a].



Scheme 1

in the ^{1}H-n.m.r. spectrum indicated that the compound was acyclic, and were consistent with its having the structure **11**; the ^{13}C-n.m.r. spectrum (Table I) confirmed this assignment, C-5 and C-6 resonating at 157.0 and 85.7 p.p.m., respectively, values that are consistent with expectations for a vinyl ether[22]. Instead, therefore, of the mercurial derivative reacting nucleophilically at C-6, it had undergone acylation at the ring oxygen atom, and it is assumed that the stereochemical integrity of the anomeric centre was retained during substitution, and therefore that the acyclic product had the *S* configuration at C-1. Compound **11**, on mild acidic hydrolysis, gave the methyl ketone **12** in quantitative yield, and this sequence therefore affords access to the type of acyclic compound initially sought by attempted, direct ring-opening of the alkene **5**. With several basic reagents, the ketone **12** underwent non-specific degradation reactions, presumably following β-eliminations, but potassium carbonate in *N*,*N*-dimethylformamide at room temperature afforded a discrete compound. N.m.r. spectroscopy (both ^{1}H and ^{13}C) indicated that C-6 had participated in the reaction, that the toluene-*p*-sulphonyloxy group had been displaced, and that metho-

xyl and acetoxyl groups remained, but other data were not consistent with those expected for the anticipated cyclopentanone derivative, and the compound has not been fully characterised.

In an attempt to cause phenylmercury(II) acetate to react with the initial alkene (**5**), equimolar proportions of the two compounds were heated together in methanol, there being no observable reaction at room temperature. A stable, crystalline product obtained in high yield proved to be the dimeric species **13**, formed presumably by way of a phenylmercury adduct which then mercurated a second alkene molecule in a process involving cleavage of the labile[23] phenyl–mercury bond. The reaction also, presumably, involved a C-5 carbonium ion sufficiently stable to permit reversible ring-opening to a glyc-5-ulose having carbonium-ion character at C-1, as the product (**13**) had undergone inversion at this position. As is to be expected when a large substituent is present at C-5, equilibration led to a product having an equatorial anomeric group, in a manner similar to that observed with 5-hydroxy-D-glucopyranoside[16] and 6-deoxy-5-methoxy-D-glucopyranoside derivatives[6].

Compound **13**, when heated in methanol with benzenethiol to generate carbanion character at C-6, gave bis(phenylthio)mercury(II) in high yield and, as the main carbohydrate product, the alkene **14** (30% isolated), formed by a process constituting the reversal of oxymercuration. The same alkene was obtained (35% isolated) on treatment of the mercurial derivative **13** with acetyl chloride in *N*,*N*-dimethylformamide and pyridine, but in this instance, the acyclic vinyl ether **15**, the C-1 epimer of compound **11**, was also formed in substantial amount (47% isolated).

No evidence has been found, therefore, to indicate that carbanion activity at C-6 in compounds **8** and **13** can be utilised to eject the sulphonyloxy group at C-2; instead it leads to displacement of the methoxyl group or the ring oxygen atom from C-5 and thence to cyclic 5-enose derivatives or acyclic species having the substituted ring-oxygen atom bonded to C-1. The finding that acetylation of the mercurated α compound (**8**) led to more of the latter type of product than was the case with the β compound (**13**) may indicate that *syn*-diaxial interaction between large groups bonded to C-1 and C-5 favours ring-opening processes.

Both the acyclic vinyl ethers **11** and **15** afforded discrete, syrupy products on further methoxymercuration with mercury(II) acetate. These were difficult to purify and were not analysed, but their ^{1}H-n.m.r. spectra clearly indicated that they were the expected adducts **16** and **17**, respectively. In the hope that these might undergo ring closure by nucleophilic displacement of the sulphonyloxy groups by the metalated C-6, both were heated in boiling xylene, but no specific products were isolated. T.l.c. examination of the mixtures suggested that, on heating, the adducts reverted to the alkenes **11** and **15**, which then reacted further. ^{1}H-N.m.r. analysis indicated that the main products were aromatic, having been formed, conceivably, by initial attack of C-6 or C-1 with removal of the (readily displaceable) acetoxyl groups.

The ^{13}C-spectral data of the alkenes **5** and **14**, the mercury adducts **8** and **13**, the acyclic compounds **11**, **15**, and **12**, and the 6-deoxy compounds **9** and **6** are given in Table I. As expected, the methoxyl resonance and that for C-1 of the β-alkene **14**

TABLE I

^{13}C CHEMICAL-SHIFTS (δ VALUES, MEASURED IN CHLOROFORM-*d*)

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Other carbon atoms*[a]
5	98.6	76.4	69.3	69.8	149.3	98.4	OMe 56.0
6	99.2	79.4	69.3	74.5	97.4	19.7	OMe 48.5, 57.3
8	103.0	76.8	66.4	76.4	99.8	30.0	OMe 49.6, 59.2
9	96.6	77.0	66.4	74.8	100.8	21.0	OMe 49.7, 58.7
11	95.4	78.5	69.7	72.7	157.0	85.7	OMe 55.2, 57.6
12	96.4	78.3	68.3	77.0	200.5	26.4	OMe 58.8
13	104.2	79.8	69.8	76.8	97.6	42.1	OMe 47.8, 57.4
15	95.4	78.5	69.6	72.7	156.9	85.7	OMe 55.2, 57.6

[a]Resonances for all of the ester groups were observed as expected.

were downfield with respect to those resonances for the α anomer[24], and those for C-5 and C-6 were consistent with expectations for 6-deoxyhex-5-enopyranose derivatives[1]. As toluene-*p*-sulphonyloxy groups deshield bonded carbon atoms by about 4 p.p.m. more than do benzoyloxy groups[25], the lowest-field resonances of the sets of three in the region δ 70 are assigned to C-2 in these compounds, and the others in Table I together with the central signals of these sets are assigned to C-4, since when compound **11** was hydrolysed to the ketone **12**, the central signal was specifically deshielded and a ketonic group would have this effect on the α-carbon atom[26]. In the spectra of the mercury adducts **8** and **13**, C-6 was strongly shielded as expected[27], and one of the ring carbon atoms was deshielded by about 6 p.p.m. by introduction of the methoxyl group at C-5. This result is consistent with the β-effect expected of such a group[28], and with the assignment of these resonances to C-4. The resonances for C-5 and C-6 in compounds **11** and **15** indicated the regeneration of vinyl ether functions at these positions, and clearly showed the presence of the *C*-acetyl group in compound **12**.

EXPERIMENTAL

General methods. — ^{1}H-N.m.r. spectra were measured at 60 MHz, for solutions in chloroform-*d* with tetramethylsilane as internal reference, on a Perkin–Elmer–Hitachi R-20 spectrometer. The ^{13}C spectra were recorded in the repetitive-pulse, f.t. mode on a Varian CFT-20 instrument for solutions in the same solvent and with the same reference compound. Typically, spectral widths of 4505 or 4000 Hz were examined, using pulse-intervals of 1 s and flip-angles of about 40°. Fourier transformations were carried out over 16K points. Compounds **6** and **9** were, however, examined with a Jeol JNM-FX60 instrument. Column chromatography was performed with Merck Kieselgel 60 and ether–light petroleum (1:1) as eluting solvent.

*Methyl 6-acetoxymercuri(II)-3,4-di-*O*-benzoyl-6-deoxy-5-methoxy-2-*O*-toluene-*p*-sulphonyl-α-*D*-glucopyranoside* (**8**). — The alkene[6] (**5**, 1.0 g), prepared by using 1,5-diazabicyclo[5.4.0]undec-5-ene in *N*,*N*-dimethylformamide and methyl 3,4-di-*O*-benzoyl-6-deoxy-6-iodo-2-*O*-toluene-*p*-sulphonyl-α-D-glucopyranoside, and mercury(II) acetate (0.6 g, 1 mol equiv.) were kept for 2 h at room temperature in dry methanol (40 mL) to give a crystalline product. Half of the solvent was removed, and the solid was collected and recrystallised from methanol to give the methoxymercuration adduct (0.5 g, 59%); m.p. 163–164°, $[\alpha]_D$ +42° (*c* 0.4, chloroform); n.m.r. ($CDCl_3$): δ 1.98 (s, 3 H, Ac), 2.24 (s, 5 H, $C_6H_4CH_3$, H-6,6′), 3.27, 3.61 (2s, 6 H, OCH_3), 4.68 (dd, 1 H, $J_{1,2}$ 4, $J_{2,3}$ 10.5 Hz, H-2), 5.07 (d, 1 H, H-1), 5.30 (d, 1 H, $J_{3,4}$ 10 Hz, H-4), 6.10 (t, 1 H, H-3), and 6.8–7.9 (m, 14 H, aromatic).

Anal. Calc. for $C_{31}H_{32}HgO_{12}S$: C, 44.9; H, 3.9; Found: C, 44.5; H, 4.1.

*Methyl 3,4-di-*O*-benzoyl-6-deoxy-5-methoxy-2-*O*-toluene-*p*-sulphonyl-α-*D*-glucopyranoside* (**9**). — A solution of sodium borohydride (0.3 g) in aqueous ethanol (12 mL, 1:1) was slowly added to a solution of the mercury derivative (**8**, 0.3 g) in ethanol at 0°. The mixture was kept for 0.5 h at this temperature and then the solid was removed and washed with cold ethanol. It was redissolved in acetone, the solution clarified by filtration, and the solvent was removed to give the deoxy product (0.2 g, 97%). Recrystallised from methanol it had m.p. 117–119°, $[\alpha]_D$ −32° (*c* 1, chloroform); n.m.r. ($CDCl_3$): δ 1.35 (s, 3 H, H-6), 2.12 (s, 3 H, $C_6H_4CH_3$), 3.27, 3.52 (2s, 6 H, OCH_3), 4.62 (dd, 1 H, $J_{1,2}$ 4.5, $J_{2,3}$ 10 Hz, H-2), 5.00 (d, 1 H, H-1), 5.20 (d, 1 H, $J_{3,4}$ 10 Hz, H-4), 6.05 (t, 1 H, H-3), and 6.7–7.9 (m, 14 H, aromatic).

Anal. Calc. for $C_{29}H_{30}O_{10}S$: C, 61.0; H, 5.3; S, 5.6. Found: C, 61.3; H, 5.5; S, 5.7.

*Methyl 3,4-di-*O*-benzoyl-6-chloromercuri(II)-6-deoxy-5-methoxy-2-*O*-toluene-*p*-sulphonyl-α-*D*-glucopyranoside* (**10**). — Allyl chloride (0.6 g) in pyridine (3 mL) was added to the acetoxymercuri compound (**8**, 0.56 g) in pyridine and the mixture was kept for 15 h at room temperature. Chloroform was added and the solution was washed successively with dilute hydrochloric acid, aqueous sodium hydrogencarbonate, and water. After drying, the solvent was removed to give a brown syrup (0.53 g) that was purified by preparative t.l.c. to give the chloromercuri compound as a glass (0.32 g) which crystallised from methanol. The product (0.18 g, 33%) had m.p. 101–103°, $[\alpha]_D$ +53° (*c* 1.4, chloroform); n.m.r. ($CDCl_3$): δ 2.13 (s, 5 H, $C_6H_4CH_3$, H-6,6′), 3.31, 3.52 (2s, 6 H, OCH_3), 4.66 (dd, 1 H, $J_{1,2}$ 5, $J_{2,3}$ 10 Hz, H-2), 5.00 (d, 1 H, H-1), 5.24 (d, 1 H, $J_{3,4}$ 10.5 Hz, H-4), 6.02 (t, 1 H, H-3), and 6.7–7.8 (m, 14 H, aromatic).

Anal. Calc. for $C_{29}H_{29}ClHgO_{10}S$: C, 43.2; H, 3.6. Found: C, 43.1; H, 3.8.

1(S)-*1*-O-*Acetyl-3,4-di-*O*-benzoyl-6-deoxy-1,5-di-*O*-methyl-2-*O*-toluene-*p*-sulphonyl-*D*-xylo-hex-5-enose aldehydrol* (**11**). — Freshly distilled acetyl chloride (0.8 g) in *N*,*N*-dimethylformamide (5 mL) was added to the mercurial derivative (**8**, 2.0 g) in *N*,*N*-dimethylformamide (10 mL) containing pyridine (1 mL). After 2 h at room temperature, the solution was diluted with chloroform (30 mL) and washed successively with dilute hydrochloric acid, aqueous sodium hydrogencarbonate, and water,

and then dried. Removal of the solvent and separation of the residue on a column of silica gel gave the acyclic acetate as a glass (1.09 g, 74%), which was obtained crystalline (0.88 g, 60%) from ether–light petroleum; m.p. 99–100°, $[\alpha]_D$ +91° (*c* 2.4, chloroform); n.m.r. ($CDCl_3$): δ 1.91 (s, 3 H, Ac), 2.25 (s, 3 H, $C_6H_4CH_3$), 3.40, 3.44 (2s, 6 H, OCH_3), 3.98, 4.11 (2d, 2 H, $J_{6,6'}$ 3 Hz, H-6,6'), 4.93 (dd, 1 H, $J_{1,2}$ 4.5, $J_{2,3}$ 6 Hz, H-2), 5.61 (d, 1 H, $J_{3,4}$ 4.5, H-4), 5.88 (d, 1 H, H-1), 6.08 (dd, 1 H, H-3), and 6.9–8.0 (m, 14 H, aromatic).

Anal. Calc. for $C_{31}H_{32}O_{11}S$: C, 60.7; H, 5.2; S, 5.2. Found: C, 60.7; H, 5.2; S, 5.2.

1(S)-*1*-O-*Acetyl-3,4-di*-O-*benzoyl-6-deoxy-1*-O-*methyl-2*-O-*toluene*-p-*sulphonyl*-D-xylo-*hexos-5-ulose aldehydrol* (**12**). — The vinyl ether (**11**, 0.5 g) in 1:5 aqueous acetone (6 mL) was heated under reflux with hydrochloric acid (2M, 0.3 mL) for 1.5 h.

The acid was made neutral with aqueous sodium hydrogencarbonate, the acetone was removed, and the products were partitioned between water and chloroform. After drying, the solvent was removed from the organic phase to leave the glassy methyl ketone (0.48 g, 100%), which was purified by chromatography on a column of silica gel. It had $[\alpha]_D$ +147° (*c* 2, chloroform); n.m.r. ($CDCl_3$): δ 1.81 (s, 3 H, Ac), 2.21 (s, 3 H, H-6), 2.25 (s, 3 H, $C_6H_4CH_3$), 3.47 (s, 3 H, OMe), 5.08 (dd, 1 H, $J_{1,2}$ 3, $J_{2,3}$ 7.5 Hz, H-2), 5.72 (d, 1 H, $J_{3,4}$ 3 Hz, H-4), 5.98 (d, 1 H, H-1), 6.18 (dd, 1 H, H-3), and 6.9–8.2 (m, 14 H, aromatic).

Anal. Calc. for $C_{30}H_{30}O_{11}S$: C, 60.2; H, 5.0; S, 5.4. Found: C, 60.4; H, 5.2; S, 5.4.

Bis(methyl 3,4-di-O-*benzoyl-6-deoxy-5-methoxy-2*-O-*toluene*-p-*sulphonyl*-β-D-*glucopyranosid-6-yl)mercury(II)* (**13**). — Heating of the alkene (**5**, 2.0 g) in refluxing methanol (45 mL) with phenylmercury(II) acetate (1.25 g, 1.0 mol equiv.) for 5 h gave a solution from which the dimeric product crystallised on cooling. Recrystallised from abs. ethanol, the product (1.82 g, 73%) had m.p. 138–139°, $[\alpha]_D$ −38° (*c* 0.8, chloroform); n.m.r. ($CDCl_3$): δ 1.13, 1.50 (2d, 2 H, $J_{6,6'}$ 17 Hz, H-6,6'), 2.13 (s, 3 H, $C_6H_4CH_3$), 3.30, 3.41 (2s, 6 H, OCH_3), 4.58 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 5.08 (t with virtual coupling, 1 H, $J_{2,3}$ ~9 Hz, H-2), 5.8–5.95 (m, 2 H, H-3,4), 6.5–6.9 (m, 5 H, aromatic), 7.1–7.65 (m, 7 H, aromatic), and 7.9–8.15 (m, 2 H, aromatic).

Anal. Calc. for $C_{58}H_{58}HgO_{20}S_2$: C, 52.0; H, 4.4. Found: C, 52.1; H, 4.5.

Reaction of the mercury derivative **13** *with acetyl chloride.* — Acetyl chloride (0.2 g) in *N,N*-dimethylformamide (1 mL) was added dropwise to a solution of **13** (0.5 g) in *N,N*-dimethylformamide (9 mL) and pyridine (0.3 g), and the mixture was kept for 24 h at room temperature. Chloroform was added and the solution was washed with dilute hydrochloric acid, aqueous sodium hydrogencarbonate, and water, and then dried. Removal of the solvent gave a syrup that was resolved on a column of silica gel to give two pure products. Methyl 3,4-di-*O*-benzoyl-6-deoxy-2-*O*-toluene-*p*-sulphonyl-β-D-*xylo*-hex-5-enopyranoside (**14**; 0.14 g, 35%) crystallised from methanol; on recrystallisation from ether–light petroleum it had m.p. 94–95°, $[\alpha]_D$ −48° (*c* 1, chloroform); ν_{max} 1660 cm^{-1} (C=C–O); n.m.r. ($CDCl_3$): δ 2.16 (s, 3 H, $C_6H_4CH_3$), 3.42 (s, 3 H, OMe), 4.50 (bs, 1 H, $J_{6,6'}$ ~2 Hz, H-6), 4.65–4.9 (m, 3 H,

H-1,2,6'), 5.45 (t with "virtual coupling", 1 H, $J_{2,3} \simeq J_{3,4} \simeq 9$ Hz, H-3), 5.92 (d, 1 H, H-4), and 6.9–8.0 (m, 14 H, aromatic).

Anal. Calc. for $C_{28}H_{26}O_9S$: C, 62.5; H, 4.8; S, 5.9. Found: C, 62.2; H, 4.9; S, 6.1.

The second fraction was 1(*R*)-1-*O*-acetyl-3,4-di-*O*-benzoyl-6-deoxy-1,5-di-*O*-methyl-2-*O*-toluene-*p*-sulphonyl-D-*xylo*-hex-5-enose aldehydrol (**15**; 0.22 g, 47%), which crystallised from ether–light petroleum and had m.p. 102°, $[\alpha]_D$ +67° (*c* 3, chloroform); n.m.r. ($CDCl_3$): δ 2.02 (s, 3 H, Ac), 2.25 (s, 3 H, $C_6H_4CH_3$), 3.19, 3.47 (2s, 6 H, OCH_3), 4.05, 4.22 (2d, 2 H, $J_{6,6'}$ 3 Hz, H-6,6'), 5.00 (dd, 1 H, $J_{1,2}$ 5, $J_{2,3}$ 7 Hz, H-2), 5.64 (d, 1 H, $J_{3,4}$ 7 Hz, H-4), 5.76 (d, 1 H, H-1), 5.91 (t, 1 H, H-3), and 6.9–8.0 (m, 14 H, aromatic).

Anal. Calc. for $C_{31}H_{32}O_{11}S$: C, 60.7; H, 5.2; S, 5.2. Found: C, 60.8; H, 5.1; S, 5.2.

Methoxymercuration of the acyclic vinyl ethers **11** *and* **15**. — Compound **11** (0.52 g) was kept for 1 h at room temperature in methanol (15 mL) containing mercury(II) acetate (0.27 g, 1.0 mol equiv.). The solvent was removed and the residue was dissolved in chloroform and washed with aqueous sodium hydrogencarbonate and water, and then dried. Further removal of the solvent gave the adduct, assumed to be the acetal **16** (0.59 g, 75%), $[\alpha]_D$ −11° (*c* 1.2, chloroform), which did not crystallise and could not be further purified; n.m.r. ($CDCl_3$): δ 1.90 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 2.20 (s, 2 H, H-6,6'), 2.33 (s, 3 H, $C_6H_4CH_3$), 2.91 (s, 3 H, OCH_3), 3.32 (s, 6 H, 2 × OCH_3), 5.26 (dd, 1 H, $J_{1,2}$ 6.5, $J_{2,3}$ 3 Hz, H-2), 5.58 (d, 1 H, $J_{3,4}$ 7 Hz, H-4), 5.84 (d, 1 H, H-1), 5.86 (dd, 1 H, H-3), and 7.0–7.9 (m, 14 H, aromatic).

Similar treatment of the isomeric alkene **15** gave an isomeric adduct **17**, $[\alpha]_D$ −1° (*c* 3, chloroform); n.m.r. ($CDCl_3$): δ 1.90 (s, 6 H, 2 × OAc), 2.21 (s, 2 H, H-6,6'), 2.32 (s, 3 H, $C_6H_4CH_3$), 3.04, 3.22, 3.31 (3s, 9 H, 3 × OCH_3), 5.27 (dd, 1 H, *J* 3 and 5 Hz, H-2), 5.6–5.9 (m, 3 H, H-1,3,4), and 6.9–7.9 (m, 14 H, aromatic).

Thermolysis of the acyclic mercurial derivatives **16** *and* **17**. — The mercurial derivatives (0.3 g) were heated separately in dry, refluxing xylene (5 mL) under nitrogen for 1 h. Chloroform was added and the mixtures were filtered through short columns of silica gel to remove coloured decomposition-products. Removal of the solvents gave a syrup that showed no resonances in the region δ 3.7–6.7 p.p.m., suggesting that the products formed had undergone aromatisation[6].

Reaction of the mercury derivative **13** *with benzenethiol.* — The dimeric mercury adduct (0.25 g) in methanol (15 mL) was heated under reflux with benzenethiol (0.1 g) for 1 h. On cooling, bis(phenylthio)mercury(II) (0.07 g, 89%) precipitated. It had m.p. 151–152° (lit.[29] 150–152°) and gave an identical i.r. spectrum to that of an authentic sample. The mother liquor was taken to dryness and the major carbohydrate-product isolated by preparative t.l.c. Crystallisation from ether–light petroleum gave the β-6-deoxy-5-enopyranoside (**14**; 0.06 g, 30%), m.p. 94–95°, n.m.r. spectrum identical to that of the compound obtained by using acetyl chloride.

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