Photo-bromination of Carbohydrate Derivatives. Part 3.[1] C-5 Bromination of Penta-*O*-benzoyl-α- and -β-D-glucopyranose; a Route to D-*xylo*-Hexos-5-ulose Derivatives and α-L-Idopyranosides

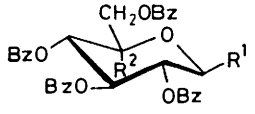
By **Robert J. Ferrier** * and **Peter C. Tyler**, Department of Chemistry, Victoria University of Wellington, Private Bag, Wellington, New Zealand

Photo-bromination of penta-*O*-benzoyl-β-D-glucopyranose with bromine gives good yields of the 5-bromo-derivative; the α-anomer reacts less well but also gives a crystalline 5-bromide. Hydrolysis gives D-*xylo*-hexos-5-ulose tetrabenzoate, which exists as the cyclic hydrate and reacts readily with alcohols and thiols to give tetra-*O*-benzoyl-5-hydroxy-β-D-glucopyranosides and 1-thio-analogues. These 5-hydroxy products can be methylated and the 'diglycosides' react with hydrogen chloride to afford 5-chloroglycoside esters from which α-D-idopyranosides are obtainable by reduction. Acetylation of a 5-hydroxyglycoside gives an acyclic product; a 5-hydroxythioglycoside gives some cyclic and some acyclic products.

In the preceding paper the photo-bromination of penta-*O*-acetyl-β-D-glucopyranose was described in detail, and it was shown that while molecular bromine and *N*-bromosuccinimide can both be used to effect introduction of bromine at C-5, both reagents can also lead to the formation of by-products. With the former the hydrogen bromide produced ultimately causes displacement of the anomeric ester group, whereas reaction with *N*-bromosuccinimide gives products containing brominated acetyl groups, and since sugar benzoates would be less subject to such diversity of reaction the anomeric perbenzoates of D-glucopyranose were examined. The findings are reported here together with observations on the chemistry of the products obtained.

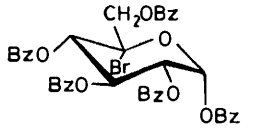
RESULTS AND DISCUSSION

Initially, penta-*O*-benzoyl-β-D-glucopyranose (1) was brominated using *N*-bromosuccinimide, and the crystalline product (2) was isolated directly in 43% yield. As has been noted previously,[2] however, bromine can be a superior reagent for this reaction, and when used in this case gave the 5-bromide (2) readily and in 77% yield. The ^{1}H n.m.r. spectrum of the product was devoid of a



	R^1	R^2		R^1	R^2
(1)	OBz	H	(8)	Cholesteryl	OH
(2)	OBz	Br	(9)	OMe	OMe
(3)	H	OAc	(10)	OEt	OMe
(4)	OH	OH	(11)	OEt	Cl
(5)	OEt	OH	(12)	OMe	Cl
(6)	OMe	OH	(13)	SEt	OAc
(7)	SEt	OH			

signal for H-5 and showed an AB pair of doublets for H-6 and -6′, and the resonance for H-4 appeared as a broad doublet. Substitution had therefore occurred at C-5 in a ring which was not thereby conformationally disturbed ($J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ 8, 10, and 10 Hz, respectively). The configuration at C-5 is assigned (*S*), as indicated, since the bromo-product is more levorotatory ($[\alpha]_D$ −12°) than its precursor ($[\alpha]_D$ +24°) [1,3] and, in agreement with this, H-1 and H-3 (δ 6.84 and 6.44) were deshielded by *ca.* 0.5 p.p.m. with respect to these protons of the starting material (1) (δ 6.32 and 6.0 ± 0.1) by the introduction of the bromine atom.[1] Had the introduction of bromine occurred with inversion of configuration, a conformational distortion would have been expected in the product since 2-*O*-acetyl-1,3,4,5-tetra-*O*-benzoyl-α-L-sorbose (3) exists as illustrated with the anomeric acetoxy-group axial and the other groups



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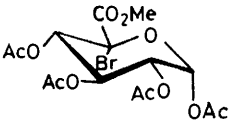


(15)

equatorial, whereas the β-L-anomer is conformationally inverted.[4]

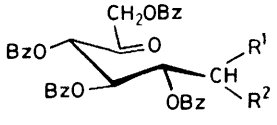
Photo-bromination of the α-isomer of compound (1) occurs more slowly and does not give a specific product,[2] the reaction at H-5 being hindered by steric protection by the axial benzoyloxy-group at C-1. However, the 5-bromide (14) was isolated as a stable, crystalline solid in 22% yield. Again, the n.m.r. spectrum showed that substitution had occurred at C-5 and also that the $^4C_1$ chair conformation had been retained ($J_{2,3}$ and $J_{3,4}$ 10.5 and 10 Hz, respectively). As for the β-anomer (2) it was less dextrorotatory ($[\alpha]_D$ +46°) than its precursor ($[\alpha]_D$ +132°), and again H-3 was specifically deshielded (δ 6.67; *cf.* 6.39 for penta-*O*-benzoyl-α-D-glucopyranose).

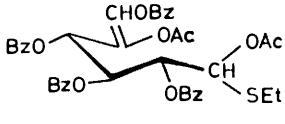
To assess further the photo-bromination of compounds with axial ester groups at C-1, the reaction of methyl tetra-*O*-acetyl-α-D-glucopyranuronate with bromine was examined. Again it was slower than that of the β-anomer,[3] and again more than one compound was formed. In this case there were two major products, one giving a ^{1}H n.m.r. spectrum which indicated that it was the analogue (15) of the 5-bromide formed in high

yield from the β-anomer. It was more levorotatory ($[\alpha]_D$ −6°) than its precursor ($[\alpha]_D$ +98°), and H-3 was again specifically deshielded by introduction of the bromine atom (δ 5.78; 5.49 for methyl tetra-*O*-acetyl-α-D-glucopyranuronate). The second product of bromination gave a similar ^{1}H n.m.r. spectrum except for the replacement of an acetyl resonance by a 2-proton singlet indicative of a bromoacetyl ester group. This type of product has been observed previously during photobromination of acetylated compounds with *N*-bromosuccinimide,[1,3] but not with bromine, and is assumed to have arisen following the establishment of an acetoxonium ion or radical by participation of the ester group at C-4.

Methanolysis of the bromine (2) in the presence of silver oxide gave a product which appeared homogeneous in t.l.c. plates, but which was shown by ^{1}H n.m.r. spectroscopy to comprise at least three methoxy-containing products, some formed, conceivably, by way of benzoxonium ions, and it was not further investigated. Hydrolysis in aqueous acetone in the presence of silver oxide gave a syrupy product which was seen from its ^{1}H n.m.r. spectrum to be largely the diol (4) formed from the 5-hydroxypenta-ester which, in aqueous solution, would equilibrate with the corresponding 5-ulose and spontaneously undergo loss of the benzoyloxygroup at C-1. Values for $J_{1,2}$, $J_{2,3}$, and $J_{3,4}$ of 8, 9, and 9 Hz, respectively, indicated that the hydroxy group at C-1 was equatorial on a conformationally undisturbed ring, and the configuration at C-5 was assumed to be as shown, on the grounds that L-sorbose exists at equilibrium almost entirely in the α-pyranose form with the anomeric hydroxygroup axial and all other ring substituents equatorial.[5]

Heating of the diol (4) in refluxing benzene caused loss of water and the formation of the aldos-5-ulose compound (16) which gave a formyl singlet resonance at δ 9.72 in place of the H-1 doublet, and had $J_{2,3}$ and $J_{3,4}$ values





(22)

	R^1	R^2
(16)	O	
(17)	S—CH_2CH_2—S	
(18)	S—$CH_2CH_2CH_2$—S	
(19)	SPh	SPh
(20)	OMe	OAc
(21)	SEt	OAc

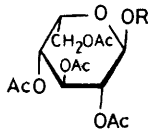
of 4 Hz, which is consistent with the existence of a *xylo*-acyclic compound.[6] With 2,4-dinitrophenylhydrazine a bishydrazone was obtained from the diol (4) which also reacted readily with alcohols to afford specific monoalkylmonohydroxy-products, the ethyl compound (5), for example, being obtained even on dissolution in chloroform containing traces of ethanol. Treated with pure ethanol and methanol the diol afforded good yields of the 5-hydroxyglycosides (5) and (6) and, similarly, the ethylthio-analogue (7) was obtained by use of ethanethiol.

Acyclic dialdehydes can hydrate to give dihydroxyoxygen-heterocyclic compounds and react with alcohols to give analogous monoalkoxyalcohols,[7] and the above observations indicate that the aldehydoketone (16) behaves in a similar fashion. To test whether complex alcohols would react, the aldulose (16) was treated in dichloromethane with cholesterol at room temperature and a crystalline product was obtained in high yield. Elemental analysis indicated that the adduct (8) had been produced, but the product appeared to contain two components (t.l.c. analysis), and the ^{1}H n.m.r. spectrum, although generally consistent with the production of a 1 : 1 adduct, also suggested that the product was not specifically the β-compound (8) and may have contained some of the α-anomer.

In an effort to obtain a 'double glycoside' with methoxy-groups at C-1 and C-5 related to recently reported 4'-methoxynucleosides,[8] the diol (4) was treated with methanolic hydrogen chloride, but the first product (6) underwent decomposition rather than specific further substitution at the tertiary centre. Reaction, under acidic conditions, with ethane-1,2-dithiol likewise did not cause substitution at both carbonyl centres (to give a possible 10-oxa-2,5-dithiabicyclo[4.3.1]decane), but resulted in the production of the aldehydo-ethylene dithioacetal (17) which contained a ketonic carbonyl group (^{13}C n.m.r.) and an appropriate H-1 resonance. Values for $J_{2,3}$ and $J_{3,4}$ were similar to those for the aldehyde (16), and the value for $J_{1,2}$ (8.5 Hz) indicated that H-1 and H-2 were *anti* in the favoured rotamer state. In a similar fashion, propane-1,3-dithiol and thiophenol gave the analogous aldehyde dithioacetals (18) and (19).

Methylation of the methyl and ethyl 5-hydroxyglycosides (6) and (5) with methyl iodide in the presence of silver oxide gave the fully substituted compounds (9) and (10), respectively, but similar treatment of the thio-analogue (7) was not successful, presumably because the silver ions reacted with sulphur. A possible route to L-sorbopyranosides which would have followed from desulphurisation of the fully substituted products was therefore frustrated. Treatment of the ethyl methyl compound (10) with hydrogen chloride in acetic acid led to replacement of the methoxy-substituent at the tertiary centre and production of the crystalline ethyl 5-chloroglycoside (11). Likewise, the dimethyl derivative (9), afforded the crystalline analogue (12) and reduction of it and compound (11) with lithium aluminium hydride gave ethyl and methyl α-L-idopyranoside respectively. The latter gave crystalline methyl tetra-*O*-acetyl-α-L-idopyranoside (23) (39% from the chloride), the enantiomer of which is known, and the syrupy ethyl glycoside, after acetylation to give compound (24) (46%), was identical chromatographically and by ^{1}H n.m.r.

spectroscopy to the acetylated glycoside made from penta-*O*-acetyl-α-D-idopyranose. The optical rotations were the same in magnitude but opposite in sign. Treatment of tetra-*O*-acetyl-α-D-idopyranosyl bromide with ethanol and silver oxide did not give an ethyl glycoside as anticipated, but rather an ethyl 1,2-ortho-acetate.[9] However, mercury-catalysed rearrangement of this did give access to the required 1,2-*trans*-ethyl



(23) R = Me
(24) R = Et

glycoside.[10] The acetylated methyl glycoside was further characterised by acetolysis to penta-*O*-acetyl-α-L-idopyranose. Reduction of the 5-chloro-compounds (11) and (12) thus occurred with inversion of configuration, as is consistent with the observation that tetra-*O*-benzoyl-β-D-fructopyranosyl bromide is reduced with lithium aluminium hydride mainly to 1,5-anhydro-L-gulitol,[11] and a new route to α-L-idopyranosides has therefore been opened.

A further route to β-D-glucopyranosides or, if inversion occurred during reduction, α-L-idopyranosides, would be provided by specific and direct removal of the hydroxy-groups at C-5 of the alcohol and thiol adducts, *e.g.* (5)—(8), and to this end the acetylations of the methyl and ethyl 1-thio-derivatives (6) and (7) were examined since a procedure has been reported [12] for the alkyl-oxygen reductive fission of tertiary esters specifically. Reaction of the methyl compound (6) with acetic anhydride in pyridine solution at 4 °C gave substantially one product, but it had been formed by acylation of the ring oxygen atom rather than the tertiary hydroxy-group, and was the acyclic compound (20). (By analogy, ketohexoses frequently give acyclic acetates under these conditions.[13]) This was established by the intermediate nature (*ca.* 4 Hz) of the proton–proton coupling constants and the characteristics of resonance of the protons at the primary centre (singlet, δ 5.09) [δ 5.35—5.08 for compounds (16)—(19); δ 4.65—4.50 for compounds (4)—(6)] as well as from ^{13}C n.m.r. evidence (see below).

Reaction of the ethyl 1-thio-derivative (7) under similar conditions with acetic anhydride was more complex, leading to a mixture of the analogous acyclic derivative (21) and the product of direct esterification (13), together with small amounts of the enol acetate (22) derived from the former. Conceivably this complex situation arises because the thio-substituent at C-1 is less effective than is the methoxy-group [in compound (6)] in drawing charge onto the ring oxygen atom of the ambident nucleophile, thus rendering it more susceptible to acylation.

The characterisation of the ketonic products (20) and (21) of the acetylation of the methyl and ethylthio-glycosides (6) and (7) confirms the positions of the alkoxy- and alkylthio-groups in these initial materials, and establishes therefore that the diol (4) reacts with nucleophiles at the aldehydic centre. Had reaction with alcohols and thiols occurred preferentially at C-5, acetylation of the products would have given glycosyl acetates and aldehyde compounds with mixed acetal functionality at C-5 and no such compounds were found. Further proof of the site of the alkoxy-groups in compound (5) and (6) follows from the observation that methylation of the residual hydroxy-groups caused the protons at C-6 to become magnetically non-equivalent, presumably by inhibiting rotation about the C-5–C-6 bond.

^{13}C N.m.r. spectroscopy (Table) confirmed many of the above conclusions. Bromination of penta-*O*-benzoyl-β-D-

^{13}C N.m.r. chemical shifts (measured in $CDCl_3$, downfield from internal $SiMe_4$)

Compound	C-1	C-2—C-4	C-5	C-6	Other carbons [a]
(1)	92.8	73.2, 70.9, 69.2	72.9	62.7	
(2) [b]	92.6	71.5, 70.1, 69.7	96.9	66.7	
(4)	91.5	74.3, 71.4, 70.1	95.8	67.2	
(5)	96.7	72.3, 72.0, 70.5	95.5	67.4	Et, 65.6, 15.1
(6)	97.7	72.1, 71.7, 70.5	95.5	67.1	Me, 56.8
(7)	77.3	71.9, 71.4, 70.8	96.6	67.5	Et, 23.8, 14.9
(9)	97.9	72.0, 71.9, 70.2	97.9	62.7	1-Me, 56.9, 5-Me, 49.3
(10) [b]	96.9	72.2, 72.0, 70.3	97.9	62.9	Me, 49.3, Et, 65.7, 15.1
(11)	99.5	71.3, 70.6, 70.2	100.0	66.3	Et, 66.3, 14.9
(12)	99.8	71.1, 70.4, 70.1	100.7	66.2	Me, 57.6
(13)	79.2	71.2, 71.0, 70.4	101.5	63.7	Ac, 21.7, Et, 24.4, 14.6
(14)	90.5	69.7, 69.3, 68.1	94.8	67.3	
(17)	53.3	74.9, 74.6, 71.0	197.4	67.2	CH_2, 38.6, 38.0
(18)	44.4	74.5, 71.2, 70.6	197.6	67.2	CH_2, 27.1, 26.6, 25.0
(19)	60.7	74.5, 72.6, 71.1	196.8	67.0	
(20)	95.5	75.2, 71.1, 68.7	197.4	67.2	Ac, 20.7, Me, 57.5
(21)	77.3	74.4, 71.8, 69.5	197.3	67.2	Ac, 20.7, Et, 25.3, 14.8
(22)	77.2	71.0, 70.9, 69.6	*ca.* 130		Ac, 20.9, 20.3, Et, 25.3, 14.8

[a] Ester carbonyl and aromatic resonances were observed as expected. [b] C-1 and C-5 distinguished by single-frequency off-resonance decoupling.

glucopyranose resulted in deshielding of C-5 by 23 p.p.m. and produced a smaller β-effect (4 p.p.m.) at C-6.[14] Like the bromo-product (2) all the other derivatives with electronegative groups at C-5 [compounds (4)—(7) and (9)—(14)] showed deshielded resonances for C-1 and C-5, and in several cases these were distinguishable by their relative peak heights, the broader being assigned to C-1. In the cases of compounds (2) and (10) these resonances were further assigned by single-frequency off-resonance decoupling experiments, which gave doublets for the C-1 resonances. For the diol (4) small resonances were observed which indicated that it was not anomerically discrete, although the proton spectrum was in good agreement with the assigned structure. On replacement of the hydroxy-group at C-1 by methoxy, C-1 [compound (6)] was, as expected,[15] deshielded by *ca.* 6 p.p.m. and the remaining resonances were largely unaffected, and methylation of O-5 [compound (9)] then deshielded C-5 (2.4 p.p.m.), but shielded C-6,[16] and the second methoxy- group resonated 7.6 p.p.m. upfield from the first, which is consistent with their being axial and equatorial, respectively.[14,15] A similar shielding effect on C-6 was observed on acetylation of O-5 in the ethylthio-compound (7) and again C-5 was deshielded, but when a chlorine atom was present at this last centre [compounds (11) and (12)] it had the effect of deshielding (4.5 p.p.m.) C-5 relative to this atom of the hydroxy-analogues [(5) and (6)] and also causing C-1 to resonate at lower fields (3 p.p.m.). In the case of the α-bromo-compound (14) all carbons except C-6 were shielded with respect to those of the β-isomer which suggests a conformational change, but the ^{1}H n.m.r. spectrum unambiguously shows that no such change occurred. Rather, the effect can be ascribed to steric compression within the molecule.[17]

In the acyclic compounds (17)—(21) ketonic carbonyl resonances were observed near δ 197 and in the spectrum of the enol acetate (22) no resonances for either C-5 or C-6 were detected. These are assumed to be amongst the aromatic carbon signals as is to be expected for enol ester vinylic carbons.[18]

EXPERIMENTAL

^{1}H N.m.r. spectra were measured at 60 MHz for solutions in deuteriochloroform with tetramethylsilane as internal reference on a Perkin-Elmer–Hitachi R-20 spectrometer. The ^{13}C n.m.r. spectra were recorded in the pulse Fourier-transform mode using the Varian CFT-20 instrument for solutions in $CDCl_3$ with $SiMe_4$ as internal standard and at 308 K. Typically spectral widths of 4 505 or 4 000 Hz were examined using pulse intervals of 1 s and flip angles of *ca.* 40°. Fourier transformations were carried out over 16 000 points. Optical rotations were measured in chloroform solution within the concentration range 1—3%.

1,2,3,4,6-*Penta*-O-*benzoyl*-5-*bromo*-β-D-*glucopyranose* (2).—A suspension of penta-*O*-benzoyl-β-D-glucopyranose (1) (10 g) [19] and bromine (6.8 g, 3.0 mol. equiv.) in carbon tetrachloride (300 ml) was heated under reflux over a 275-W heat lamp for 2 h. Evaporation of the solvent left a light yellow syrup which on trituration with ethanol–chloroform (185 ml, 3 : 1) gave a white solid (8.6 g, 77%). Recrystallised (×3) from methanol–chloroform (1 : 1) the *bromo-derivative* had m.p. 169.5—171 °C, $[\alpha]_D$ −11°. A sample purified by preparative t.l.c. and recrystallised from ethanol–carbon tetrachloride (4 : 1) had m.p. 171—172 °C, $[\alpha]_D$ −12° (Found: C, 62.9; H, 3.8; Br, 10.1. $C_{41}H_{31}BrO_{11}$ requires C, 63.2; H, 4.0; Br, 10.3%); δ 4.70 (1 H, d, $J_{6,6'}$ 12 Hz, H-6), 5.03 (1 H, d, H-6′), 6.02 (1 H, d, $J_{3,4}$ 10 Hz, H-4), 6.10 (1 H, dd, $J_{1,2}$ 8 and $J_{2,3}$ 10 Hz, H-2), 6.45 (1 H, t, H-3), 6.85 (1 H, d, H-1), and 7.1—8.2 (25 H, phenyl). The compound may also be recrystallised advantageously from aqueous acetone.

The photo-bromination was repeated with the penta-benzoate (10 g) and *N*-bromosuccinimide (12.8 g, 5.0 mol equiv.) in refluxing carbon tetrachloride (300 ml) for 8.5 h. The solids and solvent were removed and the residue was taken up in chloroform and washed with water (1 × hot, 1 × cold). The solution was then dried and the solvent again removed to give a yellow syrup which on trituration with ethanol–chloroform gave the 5-bromo-derivative in 43% yield. Recrystallised from methanol–chloroform (1 : 1) it had m.p. 171—172 °C, $[\alpha]_D$ −13° and gave the same n.m.r. spectrum as the product obtained using bromine.

Penta-O-*benzoyl*-5-*bromo*-α-D-*glucopyranose* (14).—A suspension of penta-*O*-benzoyl-α-D-glucopyranose [19] (1.0 g) in carbon tetrachloride (20 ml) containing bromine (0.8 g, 3.5 mol. equiv.) was heated under reflux over a 275-W heat lamp for 4 h to give a series of products, there being two main compounds of similar chromatographic mobility, which were more mobile than the starting material. Removal of the volatile materials gave a solid (from ethanol at −20 °C) which was resolved on a column of silica gel to afford the *α-bromo-product* (0.25 g, 22%) after recrystallisation from ethanol, m.p. 126—128 °C, $[\alpha]_D$ +46° (Found: C, 62.3; H, 3.8; Br, 11.2. $C_{41}H_{31}BrO_{11}$ requires C, 63.2; H, 4.0; Br, 10.3%); δ 4.53 (1 H, d, $J_{6,6'}$ 12 Hz, H-6), 4.92 (1 H, d, H-6′), 5.73 (1 H, dd, $J_{1,2}$ 4 and $J_{2,3}$ 10.5 Hz, H-2), 5.92 (1 H, d, $J_{3,4}$ 10 Hz, H-4), 6.67 (1 H, t, H-3), 7.02 (1 H, d, H-1), and 7.1—8.2 (25 H, phenyl).

Photo-bromination of Methyl Tetra-O-*acetyl*-α-D-*glucopyranuronate*.—A suspension of the uronate [20] (1.0 g) in carbon tetrachloride (30 ml) containing bromine (1.0 g, 2.35 mol. equiv.) was heated under reflux over a 275-W heat lamp for 1.25 h when the starting material had been replaced by two chromatographically more mobile products in similar proportions. After removal of the volatile components the residue (1.3 g) was partially fractionated on a column of silica gel to give, as an unstable syrup, *methyl tetra*-O-*acetyl*-5-*bromo*-α-D-*glucopyranuronate* (15) (0.2 g, 16%), $[\alpha]_D$ −6°; δ 2.04 (6 H, s, 2 Ac), 2.09 (3 H, s, Ac), 2.19 (3 H, s, Ac), 3.79 (3 H, s, OMe), 5.16 (1 H, dd, $J_{1,2}$ 4 and $J_{2,3}$ 10 Hz, H-2), 5.27 (1 H, d, $J_{3,4}$ 9 Hz, H-4), 5.78 (1 H, t, H-3), and 6.48 (1 H, d, H-1). The more mobile component (0.45 g, 32%) gave an almost identical spectrum but one of the acetyl resonances had been replaced by a 2-proton singlet at δ 3.8.

Methanolysis of Penta-O-*benzoyl*-5-*bromo*-β-D-*glucopyranose*.—Silver oxide (0.3 g) was added to a solution of the bromo-compound (2) (0.3 g) in dichloromethane–methanol (8 ml, 3 : 1) and the mixture was stirred at room temperature for 24 h. The solids and solvent were removed and the residue was dissolved in chloroform, treated with activated charcoal, and the charcoal and solvent removed to give a colourless syrup (0.28 g) which was homogeneous on t.l.c. plates. The ^{1}H n.m.r. spectrum was complex and showed sharp singlet resonances at δ 3.13, 3.23, and 3.41 which

were taken to indicate the presence of three methoxy-containing products.

2,3,4,6-*Tetra*-O-*benzoyl*-5-*hydroxy*-β-D-*glucopyranose* (4).—A suspension of silver oxide (5 g) and penta-*O*-benzoyl-5-bromo-β-D-glucopyranose (2) (5 g) in aqueous acetone (150 ml, 1 : 5) was stirred for 18 h at room temperature. Decolourising charcoal (5 g) was then added, and the mixture shaken thoroughly and filtered through Celite. Ethanol-free chloroform (100 ml) was added to the filtrate and the solution was washed with water (600 ml), dried, and solvent removed to leave a glass (3.86 g, 98%) which was the *diol*, $[\alpha]_D$ −1.6° (Found: C, 66.4; H, 4.6. $C_{34}H_{28}O_{11}$ requires C, 66.7; H, 4.6%); δ 4.50 (2 H, s, H-6 and -6′), 5.48 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 5.55 (1 H, t, $J_{2,3}$ 9 Hz, H-2), 5.77 (1 H, d, $J_{3,4}$ 9 Hz, H-4), 6.22 (1 H, t, H-3), and 7.0—7.9 (20 H, phenyl).

On standing for 16 h in methanol (30 ml containing concentrated sulphuric acid, 2 ml) with 2,4-dinitrophenylhydrazine (1.0 g), the diol (0.5 g) gave the *bis*(*dinitrophenylhydrazone*), m.p. 113—116 °C (Found: C, 57.5; H, 3.6; N, 10.9. $C_{46}H_{34}N_8O_{16}$ requires C, 57.9; H, 3.6; N, 11.7%). It decomposed on attempted recrystallisation.

2,3,4,6-*Tetra*-O-*benzoyl*-D-xylo-*hexos*-5-*ulose* (16).—Heating of the diol in refluxing benzene for 8 h with the separation of the water evolved gave the *dicarbonyl anhydride* in quantitative yield, $[\alpha]_D$ +4° (*c* 3% in dichloromethane); δ [$(CD_3)_2CO$] 5.35 (2 H, s, H-6 and -6′), 5.98 (1 H, d, *J* 4 Hz, H-2 or H-4), 6.30 (1 H, d, *J* 4 Hz, H-2 or H-4), 6.50 (1 H, t, H-3), 7.2—8.1 (20 H, phenyl), and 9.72 (1 H, s, H-1).

Ethyl 2,3,4,6-*Tetra*-O-*benzoyl*-5-*hydroxy*-β-D-*glucopyranoside* (5).—When, in the preparation of the diol, the chloroform used contained small proportions of ethanol a small amount of the *monoethyl glycoside* was obtained. Recrystallised from ethanol it had m.p. *ca.* 110—125 °C, $[\alpha]_D$ −15° (Found: C, 67.2; H, 5.1. $C_{36}H_{32}O_{11}$ requires C, 67.5; H, 5.0%); δ 1.08 (3 H, t, *J* 7 Hz, Me), 3.75 (2 H, q, CH_2), 4.50 (2 H, s, H-6 and -6′), 4.68 (1 H, s, OH), 5.32 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 5.53 (1 H, t, $J_{2,3}$ 9 Hz, H-2), 5.72 (1 H, d, $J_{3,4}$ 9 Hz, H-4), 6.18 (1 H, t, H-3), and 7.1—8.0 (20 H, phenyl). This compound was also readily prepared from the diol (4) using ethanol.

Methyl 2,3,4,6-*Tetra*-O-*benzoyl*-5-*hydroxy*-β-D-*glucopyranoside* (6).—A solution of 2,3,4,6-tetra-*O*-benzoyl-5-hydroxy-D-glucopyranose (4) (2.3 g) in methanolic hydrogen chloride [acetyl chloride (3 ml) and dry methanol (30 ml)] was allowed to stand at room temperature for 2 h, after which the solvent was removed and the residue crystallised from ether–light petroleum to give the *monomethyl derivative* (1.7 g, 72%). Recrystallised from methanol it had m.p. *ca.* 110—120 °C, $[\alpha]_D$ −16° (Found: C, 67.3; H, 4.9. $C_{35}H_{30}O_{11}$ requires C, 67.1; H, 4.8%); δ 3.42 (3 H, s, OMe), 4.65 (2 H, s, H-6 and -6′), 5.12 (1 H, s, OH), 5.32 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 5.67 (1 H, t, $J_{2,3}$ 9 Hz, H-2), 5.90 (1 H, d, $J_{3,4}$ 9 Hz, H-4), 6.33 (1 H, t H-3), and 7.0—8.0 (20 H, phenyl).

Heating the diol (3.0 g) in dry methanol under reflux for 4 h, then removal of the solvent, gave a gum which crystallised from ether–light petroleum to give the same monomethyl compound (2.23 g, 73%). Recrystallised from methanol it gave identical n.m.r. and i.r. spectra to those of the above product.

Ethyl 2,3,4,6-*Tetra*-O-*benzoyl*-5-*hydroxy*-1-*thio*-β-D-*glucopyranoside* (7).—Ethanethiol (1.0 g) and the diol (4) (1.0 g) were heated in refluxing chloroform (20 ml) for 4 h under nitrogen and the volatile components were removed. Trituration with ether–light petroleum gave the crystalline *thio-compound* (0.85 g, 79%) which, recrystallised from the same solvent, had m.p. 113—117 °C, $[\alpha]_D$ +1° (Found: C, 65.5; H, 4.9; S, 4.7. $C_{36}H_{32}O_{10}S$ requires C, 65.8; H, 4.9; S, 4.9%); δ 1.15 (3 H, t, Me), 2.68 (2 H, q, CH_2), 4.55 (2 H, s, H-6 and -6′), 5.0 (1 H, br s, OH), 5.35 (1 H, d, $J_{1,2}$ 10 Hz, H-1), 5.62 (1 H, t, $J_{2,3}$ 10 Hz, H-2), 5.75 (1 H, d, $J_{3,4}$ 9 Hz, H-4), 6.26 (1 H, t, H-3), and 7.0—8.0 (20 H, phenyl).

Cholesteryl 2,3,4,6-*Tetra*-O-*benzoyl*-5-*hydroxy*-D-*glucopyranoside* (8).—Tetra-*O*-benzoyl-5-hydroxy-D-glucopyranose (4) (1 g) was heated under reflux in benzene for 8 h with removal of water. The solvent was evaporated and the dicarbonyl product was dissolved in dichloromethane (15 ml) containing cholesterol (0.62 g, 1 mol. equiv.). After 3 days at room temperature the solution was taken to dryness and trituration of the residue with ether–light petroleum gave the *cholesteryl compound* as a white solid (1.1 g, 68%). Recrystallised from di-isopropyl ether it had m.p. 134—136 °C, $[\alpha]_D$ +4° (Found: C, 74.5; H, 7.4. $C_{61}O_{74}O_{11}$ requires C, 74.5; H, 7.6%).

2,3,4,6-*Tetra*-O-*benzoyl*-D-xylo-*hexos*-5-*ulose Ethylene Dithioacetal* (17).—Ethane-1,2-dithiol (0.18 g, 1.2 mol equiv.) and boron trifluoride–ether (0.47 g, 2 mol. equiv.) were sequentially added to the diol (4) (1.0 g) in dry chloroform (20 ml) and after 2 h at room temperature the solution was washed with saturated aqueous sodium hydrogencarbonate and water. After drying and removal of the solvent the resulting syrup was purified by preparative t.l.c. to give the syrupy *dithioacetal* (0.7 g, 65%), $[\alpha]_D$ −40° (Found: C, 64.3; H, 4.5. $C_{36}H_{30}O_9S_2$ requires C, 64.5; H, 4.5); δ 3.10 (4 H, s, 2 × CH_2), 4.76 (1 H, d, $J_{1,2}$ 8.5 Hz, H-1), 5.12 (2 H, s, H-6 and -6′), 5.60 (1 H, dd, $J_{2,3}$ 3 Hz, H-2), 5.95 (1 H, d, $J_{3,4}$ 5 Hz, H-4), 6.29 (1 H, dd, H-3), and 7.0—8.1 (20 H, phenyl).

2,3,4,6-*Tetra*-O-*benzoyl*-D-xylo-*hexos*-5-*ulose* 1,3-*Propylene Dithioacetal* (18).—The method used for the ethylene analogue afforded a syrup which was purified by preparative t.l.c. to give the *propylene dithioacetal* [0.4 g, 71% from 0.5 g of the diol (4)], $[\alpha]_D$ −34° (Found: C, 64.5; H, 4.9; S, 8.7. $C_{37}H_{32}O_9S_2$ requires C, 64.9; H, 4.7; S, 9.4%); δ 1.7—2.1 (2 H, m, CH_2), 2.3—3.2 (4 H, m, 2 × CH_2), 4.10 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 5.16 (2 H, s, H-6 and -6′), 6.01 (1 H, d, $J_{3,4}$ 4.5 Hz, H-4), 6.10 (1 H, dd, $J_{2,3}$ 4 Hz, H-2), 6.50 (1 H, t, H-3), and 7.0—8.1 (20 H, phenyl).

2,3,4,6-*Tetra*-O-*benzoyl*-D-xylo-*hexos*-5-*ulose Diphenyl Dithioacetal* (19).—The diol (4) (0.5 g) was treated with thiophenol in chloroform in the presence of boron trifluoride and gave the *diphenyl dithioacetal* (0.47 g, 72% after preparative t.l.c.), $[\alpha]_D$ −2° (Found: C, 68.8; H, 4.4; S, 7.5. $C_{46}H_{36}O_9S_2$ requires C, 69.3; H, 4.5; S, 8.0%); δ 4.75 (1 H, d, $J_{1,2}$ 3.5 Hz, H-1), 5.08 (2 H, s, H-6 and -6′), 6.01 (1 H, d, $J_{3,4}$ 3 Hz, H-4), 6.06 (1 H, dd, $J_{2,3}$ 6.5 Hz, H-2), 6.64 (1 H, dd, H-3), and 6.75—8.0 (30 H, phenyl).

Methyl 2,3,4,6-*Tetra*-O-*benzoyl*-5-*methoxy*-β-D-*glucopyranoside* (9).—Silver oxide (0.5 g) was added to a solution of methyl 2,3,4,6-tetra-*O*-benzoyl-5-hydroxy-β-D-glucopyranoside (6) (0.5 g) in methyl iodide (20 ml) at 0 °C and the mixture was stirred at this temperature for 24 h. After removal of the solids and the solvent the residue was taken up in chloroform, treated with activated charcoal, and the solids and solvent were again removed to give the *dimethyl compound* as a clear, chromatographically (t.l.c.) homogeneous syrup (0.5 g, 98%), $[\alpha]_D$ −1.5° (Found: C, 67.2; H, 5.2. $C_{36}H_{32}O_{11}$ requires C, 67.5; H, 5.0%); δ 3.46 (3 H, s, OMe), 3.49 (3 H, s, OMe), 4.38 (1 H, d, $J_{6,6'}$ 12 Hz, H-6), 4.62 (1 H, d, H-6′), 4.90 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 5.48 (1 H,

t, $J_{2,3}$ 9 Hz, H-2), 5.75 (1 H, d, $J_{3,4}$ 9 Hz, H-4), 6.09 (1 H, t, H-3), and 7.0—7.9 (20 H, phenyl).

Ethyl 2,3,4,6-*Tetra*-O-*benzoyl*-5-*methoxy*-β-D-*glycopyranoside* (10).—Methylation of compound (5) (1.0 g) was effected as for the methyl analogue (6) and the product was treated with activated charcoal before crystallisation from ethanol to give the *methoxy ethyl glycoside* (0.82 g, 79%). Recrystallised from chloroform–light petroleum it had m.p. 151—152 °C, $[\alpha]_D$ −7° (Found: C, 68.0; H, 5.2. $C_{37}H_{34}O_{11}$ requires C, 67.9; H, 5.2%); δ 1.17 (3 H, t, Me), 3.50 (3 H, s, OMe), 3.62 (2 H, q, CH_2), 4.41 (1 H, d, $J_{6,6'}$ 12 Hz, H-6), 4.67 (1 H, d, H-6'), 5.03 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 5.56 (1 H, t, $J_{2,3}$ 9 Hz, H-2), 5.82 (1 H, d, $J_{3,4}$ 9.5 Hz, H-4), 6.17 (1 H, t, H-3), and 6.9—8.1 (20 H, phenyl).

Ethyl 2,3,4,6-*Tetra*-O-*benzoyl*-5-*chloro*-β-D-*glucopyranoside* (11).—The 5-methoxy-compound (10) (4.0 g) was suspended in dry acetic acid (30 ml) and dry hydrogen chloride was passed in for 10 min, by which time the starting material had dissolved. After standing at room temperature for 2 days the solution was diluted with chloroform (50 ml), washed with ice–water (300 ml), saturated aqueous sodium hydrogencarbonate, and again with ice–water, and dried. Removal of the solvent gave a syrupy residue (4.06 g) which, by t.l.c., was shown to contain mainly a single, more mobile product but also two slower moving compounds with the same mobilities as the ethyl glycoside (5) and the diol (4). Chromatography on a column of silica gel gave the 5-*chloro-compound* as a clear syrup (1.81 g, 45%) which crystallised from chloroform–light petroleum. Recrystallised from this solvent it had m.p. 116—118 °C, $[\alpha]_D$ +11° (Found: C, 65.4; H, 4.7; Cl, 5.0. $C_{36}H_{31}ClO_{10}$ requires C, 65.6; H, 4.7; Cl, 5.4%); δ 1.13 (3 H, t, Me), 3.70 (2 H, q, CH_2), 4.49 (1 H, d, $J_{6,6'}$ 12 Hz, H-6), 4.83 (1 H, d, H-6'), 5.35 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 5.60 (1 H, t, $J_{2,3}$ 9 Hz, H-2), 5.96 (1 H, d, $J_{3,4}$ 9 Hz, H-4), 6.18 (1 H, t, H-3), and 7.0—8.1 (20 H, phenyl).

Methyl 2,3,4,6-*Tetra*-O-*benzoyl*-5-*chloro*-β-D-*glucopyranoside* (12).—The syrupy dimethyl compound (9) (9.0 g) was dissolved in dry acetic acid (70 ml) and hydrogen chloride was bubbled through, the solution for 0.5 h. The solution was left for 2 days and processed as for the ethyl analogue (11) to give a syrupy product from which the *methyl chloro-compound* (5.01 g, 55%) was obtained by separation on a column of silica gel. Crystallised (×2) from chloroform–light petroleum it had m.p. 134—136 °C, $[\alpha]_D$ +15° (Found: C, 65.0; H, 4.6; Cl, 5.7. $C_{35}H_{29}ClO_{10}$ requires C, 65.2; H, 4.5; Cl, 5.5); δ 3.48 (3 H, s, OMe), 4.50 (1 H, d, $J_{5,6'}$ 12 Hz, H-6), 4.85 (1 H, d, H-6'), 5.25 (1 H, d, $J_{1,2}$ 8 Hz, H-1), 5.60 (1 H, t, $J_{2,3}$ 8.5 Hz, H-2), 5.95 (1 H, d, $J_{3,4}$ 9.5 Hz, H-4), 6.20 (1 H, t, H-3), and 7.0—8.1 (20 H, phenyl).

Methyl 2,3,4,6-*Tetra*-O-*acetyl*-α-L-*idopyranoside* (23).—A solution of the benzoylated 5-chloroglycoside (12) (4.0 g) in dry ether (25 ml) was added slowly to a stirred suspension of lithium aluminium hydride (2.0 g) in ether (20 ml) and the mixture was stirred for 1 h. Excess of hydride was destroyed, water was added, the solids were removed and washed, and the filtrate and washings were neutralised with acidic resin and taken to dryness. The syrupy residue was acetylated with acetic anhydride in pyridine and after filtration the solution was taken to dryness with occasional addition of toluene. The residue was dissolved in chloroform, was washed with dilute hydrochloric acid, aqueous sodium hydrogencarbonate, and water before drying and removal of the solvent. Trituration with ethanol gave the crystalline *acetylated methyl idoside* (total 0.87 g, 39%; two crops, mother-liquors fractionated on a column of silica gel). Recrystallised from chloroform-light petroleum it had m.p. 107—108 °C, $[\alpha]_D$ −53° (lit.,[21] for the D-isomer, m.p. 107—108 °C, $[\alpha]_D$ +55°).

Ethyl 2,3,4,6-*Tetra*-O-*acetyl*-α-L-*idopyranoside* (24).—The ethyl 5-chloroglucoside tetrabenzoate (11) (1.54 g) was reduced with lithium aluminium hydride and acetylated as for the methyl analogue to give a syrup (0.65 g) from which the *ethyl glycoside tetra-acetate* (0.41 g, 46%), $[\alpha]_D$ −56°, was obtained from a column of silica gel (Found: C, 51.4; H, 6.7. $C_{16}H_{24}O_{10}$ requires C, 51.1; H, 6.4%).

Ethyl 2,3,4,6-*Tetra*-O-*acetyl*-α-D-*idopyranoside*.—Penta-*O*-acetyl-α-D-idopyranose [22] (2.0 g) was converted into the acetylated glycosyl bromide by treatment with hydrogen bromide in acetic acid (25 ml, 24%) for 0.5 h. The product (1.82 g, 87%) had m.p. 119—121 °C, $[\alpha]_D$ +170° (lit.,[23] m.p. 120.5—121 °C, $[\alpha]_D$ +172°). Stirring of this compound (4.5 g) in dry dichloromethane (50 ml) with ethanol (50 ml) and silver oxide (4.0 g) for 3 h, followed by removal of the solids and solvent, gave a syrup which on trituration with ether–light petroleum gave 3,4,6-tri-*O*-acetyl-β-D-idopyranosyl ethyl 1,2-orthoester (1.02 g, 25%), m.p. 112—114 °C, $[\alpha]_D$ +32° (lit.,[23] m.p. 113—115 °C, $[\alpha]_D$ +34°). The crystalline orthoester (0.7 g) was heated with mercury(II) bromide (0.7 g) and ethanol (0.7 g) in dry refluxing nitromethane (15 ml) for 0.75 g.[10b] The solution was diluted with chloroform, washed with water, dried, and the solvent removed to give a syrup which was acetylated using acetic anhydride (5 ml) and pyridine (5 ml), and the product was purified on a column of silica gel to give the ethyl glycoside tetra-acetate (0.45 g, 64%, $[\alpha]_D$ +56°) having identical t.l.c. and ^1H n.m.r. characteristics to those of the L-compound (above).

Penta-O-*acetyl*-α-L-*idopyranose*.—Methyl tetra-*O*-acetyl-α-L-idopyranoside (23) (0.25 g) was allowed to stand in acetic acid and acetic anhydride (5 ml, 3 : 7 v/v, containing 2% sulphuric acid) [24] for 16 h and the solution was poured into water. The product was extracted with chloroform in the usual way and crystallised from ethanol (yield 0.11 g, 41%), m.p. 94—95 °C, $[\alpha]_D$ −60° (lit.,[25] m.p. 95—96 °C, $[\alpha]_D$ −57°),and was identical by t.l.c. and ^1H n.m.r. spectroscopy with the D-isomer.

1-O-*Acetyl*-2,3,4,6-*tetra*-O-*benzoyl*-1-O-*methyl*-D-xylo-*hexos*-5-*ulose Aldehydohydrate* (20).—Methyl 2,3,4,6-tetra-*O*-benzoyl-5-hydroxy-β-D-glucopyranoside (6) (0.5 g) was kept in acetic anhydride (2.5 ml) and pyridine (2.5 ml) at 4 °C for 24 h. Chloroform was added and the solution was washed with water, dilute hydrochloric acid (×2), saturated aqueous sodium hydrogencarbonate, and water, dried, and the solvent removed. The syrupy residue (0.55 g, 100%) was purified by preparative t.l.c. to give the *acyclic acetate* (0.36 g, 68%), $[\alpha]_D$ +25° (Found: C, 66.3; H, 5.0. $C_{37}H_{32}O_{12}$ requires C, 66.5; H, 4.8%); δ 2.00 (3 H, s, OAc), 3.35 (3 H, s, OMe), 5.09 (2 H, s, H-6 and -6'), 5.76 (1 H, dd, *J* 4 and 6 Hz, H-2 or H-3), 5.96 (1 H, d, *J* 4 Hz, H-1 or H-4), 6.02 (1 H, d, *J* 4 Hz, H-4 or H-1), 6.30 (1 H, dd, *J* 4 and 6 Hz, H-2 or H-3), and 7.1—8.1 (20 H, phenyl).

Acetylation of Ethyl Thioglycoside (7).—A solution of the thio-compound (7) (1.0 g) in pyridine (15 ml) was treated with acetic anhydride (5 ml) at 4 °C for 40 h. Usual processing gave a dark syrup (0.9 g) which was resolved on a column of silica gel to give: (a) *ethyl* 5-*acetoxy*-2,3,4,6-*tetra*-O-*benzoyl*-1-*thio*-β-D-*glucopyranoside* (13) (0.13 g, 12%) which on crystallisation from ethanol had m.p. 168.5—170 °C, $[\alpha]_D$ −22° (Found: C, 65.1; H, 4.7; S, 4.7. $C_{38}H_{34}O_{11}S$ requires C, 65.3; H, 4.9; S, 4.6%); δ 1.22 (3 H, t, Me), 2.30 (3 H, s, Ac), 2.71 (2 H, q, CH_2), 4.80 (1 H, d,

$J_{6,6'}$ 12 Hz, H-6), 5.05 (1 H, d, $J_{1,2}$ 9 Hz, H-1), 5.07 (1 H, d, H-6'), 5.55 (1 H, t, $J_{2,3}$ 9 Hz, H-2), 5.78 (1 H, d, $J_{3,4}$ 9 Hz, H-4), 6.10 (1 H, t, H-3), and 7.0—8.0 (20 H, phenyl); (b) 1-O-*acetyl*-2,3,4,6-*tetra*-O-*benzoyl*-S-*ethyl*-1-*thio*-D-xylo-*hexos*-5-*ulose aldehydohydrate* (21) (0.17 g, 16%), $[\alpha]_D$ +12° (Found: C, 65.7; H, 5.2; S, 4.6%); δ 1.18 (3 H, t, Me), 1.94 (3 H, s, Ac), 2.66 (2 H, q, CH_2), 5.10 (2 H, s, H-6 and -6'), 5.7—6.3 (4 H, m, H-1, -2, -3, and -4, several couplings of *ca.* 4 Hz were observed but not assigned), and 7.0—8.1 (20 H, phenyl); and (c) 1,5-*di*-O-*acetyl*-2,3,4,6-*tetra*-O-*benzoyl*-S-*ethyl*-1-*thio*-D-xylo-*hex*-5-*enose aldehydohydrate* (22) (0.05 g, 5%) which on crystallisation from ethanol had m.p. 140—142 °C, $[\alpha]_D$ −81° (Found: C, 64.9; H, 4.9; S. 4.4. $C_{40}H_{36}O_{12}S$ requires C, 64.9; H, 4.9; S, 4.3%); δ 1.18 (3 H, t, Me), 1.97 (3 H, s, Ac), 2.27 (3 H, s, Ac), 2.71 (2 H, q, CH_2), 5.75—6.3 (5 H, m, H-1, -2, -3, -4, and -6), and 7.1—8.1 (20 H, phenyl).

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