Photobromination of Carbohydrate Derivatives. Part 4.[1] Observations on Some Glucopyranoside Esters; a Simple Route to Aryl α-L-Idopyranosides

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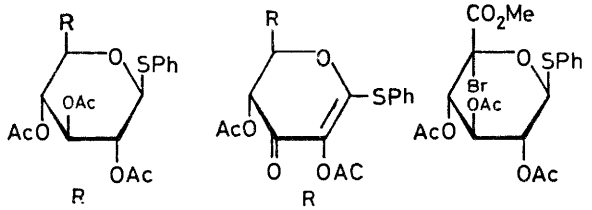
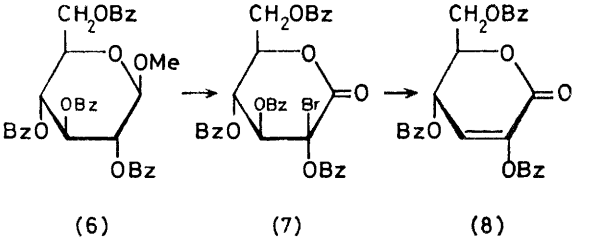
Photobromination of methyl tetra-*O*-benzoyl-β-D-glucopyranoside gives 2,3,4,6-tetra-*O*-benzoyl-2-bromo-D-glucono-1,5-lactone as the main product following hydrogen abstraction at C-1, but similar treatment of aryl β-D-glucopyranoside esters causes abstraction at C-5 and leads to 5-bromo-derivatives. Reduction of these latter products offers a simple route to aryl α-L-idopyranosides which provide means of access to analytical substrates for L-iduronidase.

OUR first studies [2] on the photobromination of carbohydrate derivatives were carried out on phenyl 1-thio-β-D-glucopyranoside esters [*e.g.* (1)], and indicated that the products of reaction [*e.g.* (2)] were derived from free radicals generated by hydrogen abstraction at the anomeric centre, the sulphur atoms stabilising uncoupled electrons at that position. When the reaction was then applied to an analogous uronic acid thioglycoside derivative (3), the corresponding enone (4) was produced, but concurrently, an unexpected product of bromination



at C-5 (5) was obtained, in consequence, it was suggested, of competitive stabilisation of a radical at this position by the carbonyl group at C-6.[3] In order to favour this unusual latter reaction, related compounds devoid of sulphur at the anomeric centre were examined; these led to high yields of 5-bromouronic acid esters.[3] Subsequent observations [1,4] have shown that such bromination does not require that C-6 be in the carboxy oxidation state, and highly efficient substitution can be effected at C-5 with glucopyranose peresters. Furthermore, the centre undergoing reaction need not give a tertiary radical since xylopyranose analogues also take part in this process.[5] It is therefore concluded that an acyloxy-group at the anomeric centre of pyranoid compounds is less effective in stabilising radicals at positions adjacent to the ring oxygen atom than is a carboalkoxy, or an acyloxymethyl group, or even a hydrogen atom. Thus the radical-stabilising effect of the bonded oxygen atom which is usually strong, since it permits delocalisation of the unpaired electron,[6] appears to be very substantially diminished by its acylation. In order to explore further the relative reactivities of C-1 and C-5 under photobromination conditions, studies have now been carried out on glucopyranoside peresters, in which the unshared electrons of the glycosidic oxygen atom would be expected to be more readily available for stabilising radicals at C-1 than is the case with glycosyl esters.

When a solution of methyl tetra-*O*-acetyl-β-D-glucopyranoside in carbon tetrachloride was heated under reflux in the presence of bromine and under bright light, the carbohydrate reacted completely within 10 min to give a complex mixture of products, and since the reaction of penta-*O*-acetyl-β-D-glucopyranose to give the 5-bromo-derivative is much slower,[4] it was concluded that the anomeric centre had taken part in the reaction. Following the observation that penta-*O*-benzoyl-β-D-glucopyranose [1] reacts more specifically than does its acetylated analogue,[4] methyl tetra-*O*-benzoyl-β-D-glucopyranoside (6) was then subjected to this procedure, and in 20 min gave a less complex mixture from which the highly crystalline 2-bromolactone (7) was isolated in 48% yield (Scheme 1). The ^{1}H n.m.r. spectrum of



SCHEME 1

this compound was devoid of resonances for a methoxy-group and the H-1 and H-2, and the H-6 and H-6′ signals were almost unchanged by the process. However, H-5 was deshielded by 0.9 p.p.m. consequent upon the introduction of the carbonyl group at C-1, which is comparable with the deshielding of 1.5 p.p.m. that occurs to H-1 of methyl tetra-*O*-benzoyl-β-D-glucopyranoside when the methyl is replaced by a benzoyl group. H-3 and H-4 resonated as a broad doublet and triplet, respectively, the values for $J_{3,4}$ and $J_{4,5}$ (10 Hz) establishing that the pyranoid ring retained the $^4C_1$ chair form. In the infrared spectrum

an absorption at 1 765 cm^{-1} was consistent with the presence of a δ-lactone, and the ^{13}C n.m.r. spectrum provided further evidence for the assigned structure. The signal for C-1 of the starting material (δ 102.1 p.p.m.) had been replaced by a carbonyl carbon resonance at 163.0 p.p.m., and C-2 had been deshielded by *ca.* 15 p.p.m. (δ 84.1), which is similar to the effect noted for C-5 following bromination at this position in a comparable uronate derivative.[3] The resonances of the other carbon atoms had been affected to a much smaller extent. On the grounds that the compound is slightly more laevorotatory ($[\alpha]_D$ +107°) than tetra-*O*-benzoyl-D-glucono-1,5-lactone ($[\alpha]_D > +113°$) [7] it is tentatively assigned the *S* configuration at C-2 as shown.* This follows from the facts that the orientation of the hydrogen and oxygen atoms at this centre in the starting material leads to a dextrorotatory contribution to the molecular rotation,[8] and that only reversal of the relative rotational ranks of the two substituents at this position in the product would lead to a laevorotatory effect.[9] Treatment of the 2-bromolactone with sodium iodide in acetone solution afforded the known [10] 2,4,6-tri-*O*-benzoyl-3-deoxy-D-*erythro*-hex-2-enono-1,5-lactone (8) in good yield, presumably either by nucleophilic attack by iodide on bromine followed by ejection of the benzoyloxy-group at C-3, or by iodide displacement of bromide followed by an elimination process comparable to well known reactions of carbohydrate α-halogeno-esters which lead to alkenes.[11] When an attempt was made to remove hydrogen bromide from the lactone by use of 1,5-diazabicyclo[5.4.0]undec-5-ene in *NN*-dimethylformamide the only product isolated was the same unsaturated lactone, but the yield was only 27% and other reactions presumably competed with this unexpected elimination.

No information is available on the mechanism of the processes by which the methyl glycoside (6) was converted into the bromolactone (7), but, in the light of the known sensitivity of acetals to reaction with free radicals,[12,13] the initial step is assumed to be hydrogen abstraction from C-1. Following this, bromine could bond to C-1 and the product could react by bromide attack at the more accessible of the acetal's two alkyl carbon atoms to give methyl bromide and tetra-*O*-benzoyl-D-glucono-1,5-lactone, which then could give the bromo-derivative by substitution at the site adjacent to the carbonyl group (this last step has not been independently tested). Production of the intermediate lactone would be consistent with the behaviour of acetals with *N*-bromosuccinimide [12] and with the conversion of 2-methoxytetrahydropyran into the corresponding lactone by a radical process initiated by hydrogen abstraction from the acetal centre.[13] Otherwise, in the production of the bromolactone, a 1-bromo-intermediate could have lost hydrogen bromide to give a 1-enose derivative which, on addition of bromine and loss of methyl bromide, following nucleophilic attack on the methyl group, could have given the same product, and this process therefore initially parallels that postulated for the conversion of phenyl 1-thiohexoside esters into 1-en-3-ulose derivatives.[2] However, if a substituted glycal intermediate was involved, it underwent electrophilic addition rather than allylic bromination, conceivably because the methoxy-group activates the double bond more than the phenyl-thio-group does.

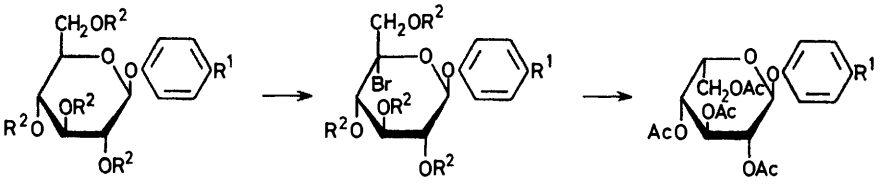
In an attempt to direct this type of reaction, phenyl tetra-*O*-acetyl-β-D-glucopyranoside (9) was next studied with the expectation that lactone formation would be inhibited since phenyl–oxygen bond cleavage by a nucleophilic process would be an improbable step. It gave a product which, although obtained crystalline after column chromatography, underwent decomposition before elemental analysis could be carried out. The ^1H n.m.r. spectrum was entirely consistent with that expected for compound (10): H-5 had been removed, H-6 and H-6′ resonated as an AB pair of doublets and the H-1 and H-3 signals, although not fully resolved, were seen to be deshielded by *ca.* 0.5 p.p.m. as is expected for axial protons *syn*-related to an axial bromine atom.[1,3,4] Consistent with the configuration assigned at C-5, the product ($[\alpha]_D$ −90°) was more laevorotatory than the starting material ($[\alpha]_D$ −21°). Seemingly, therefore, the phenoxy-group stabilises a radical at C-1 less well than does the methoxy-group and has an effect similar to that of an acyloxy-group; and since the *p*-nitrophenyloxy-group would be less likely to lead to reaction at C-1, *p*-nitrophenyl tetra-*O*-acetyl-β-D-gluco pyranoside (11) was photobrominated and gave the syrupy and somewhat unstable 5-bromo-analogue (12) (57% isolated after preparative t.l.c.) which was structurally assigned by ^1H n.m.r. spectroscopy and by reduction (see below).

To ensure that alteration of the ester groups from benzoate to acetate was not responsible for the change in the reaction, phenyl tetra-*O*-benzoyl-β-D-glucopyranoside (13) was tested, and it too underwent substitution to afford a product which gave a ^1H n.m.r. spectrum and a product of reduction consistent with it being the 5-bromide (14).

Earlier application of the photobromination reaction led to a synthesis of alkyl α-L-idopyranosides by way of 5-bromo-D-glucose peresters,[1] but this procedure, although offering an alternative approach to such compounds,[14,15] was inapplicable for aryl glycosides since phenols, in our hands, did not take part in the critical glycosidation step. Such aryl idosides are of value as precursors of substrates for the assay of α-L-iduronidase, a mammalian enzyme involved in the biosynthesis of sulphated mucopolysaccharides.[16] The bromination of the aryl glycosides described above offers a convenient approach to these compounds. There is precedent for expecting the aryl 5-bromoglucopyranosides to undergo reductive cleavage of the carbon–bromine bond with inversion of configuration since analogous acylated

* For discussions of the stereochemistry of related 2-halogeno-compounds see F. W. Lichtenthaler, T. Sakakibara, and E. Oeser, *Cariohydrate Res.*, 1977, **59**, 47; *Chem. Ber.*, 1980, **113**, 471.

ketopyranosyl halides [17] and 5-chloro-D-glucoside esters [1] react mainly in this fashion, and when the crude product of photobromination of phenyl tetra-*O*-benzoyl-β-D-glucopyranoside (13) was treated with lithium aluminium hydride and then acetylated, syrupy phenyl tetra-*O*-acetyl-α-L-idopyranoside (15) was isolated in 26% yield after column chromatography (Scheme 2). Proof of structure was obtained by acetolysis to the crystalline penta-*O*-acetyl-α-L-idopyranose. Likewise, the crude product of photobromination of *p*-nitrophenyl tetra-*O*-acetyl-β-D-glucopyranoside on reduction and acetylation gave crystalline *p*-acetamidophenyl tetra-*O*-acetyl-α-L-idopyranoside (16). During the reduction reaction considerable degradation occurred and the crude product of acetylation was black, so that the required compound was obtained in only 12% yield. Nevertheless, the starting material is simple to obtain and the reactions are easily and quickly carried out. The product was characterised by comparison with its enantiomer, which was prepared by condensation between penta-*O*-acetyl-α-D-idopyranose and *p*-acetamidophenol, and also by reduction of the *p*-nitrophenyl analogue, which again proved to be an inefficient process.



	R^1	R^2
(9)	H	Ac
(11)	NO_2	Ac
(13)	H	Bz

	R^1	R^2
(10)	H	Ac
(12)	NO_2	Ac
(14)	H	Bz

	R^1
(15)	H
(16)	NHAc

SCHEME 2

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; ^{13}C n.m.r. spectra were measured on a Varian CFT-20 instrument for similar solutions. Optical rotations were measured in chloroform solutions within the concentration range 1—3%, unless otherwise stated.

2,3,4,6-*Tetra*-O-*benzoyl*-2-*bromo*-D-*glucono*-1 5-*lactone* (7).—A solution of methyl tetra-*O*-benzoyl-β-D-glucopyranoside (6) (2 g) in carbon tetrachloride (60 ml) containing bromine (1.2 g, 2.3 mol. equiv.) was heated under reflux over a 275-W heat lamp for 20 min. The solvent was removed and the residue was triturated with carbon tetrachloride (10 ml) to give the crystalline *bromolactone* (1.06 g, 48%). Recrystallised from carbon tetrachloride and then chloroform–light petroleum it had m.p. 96—98 °C, $[\alpha]_D$ +97°, (+107°, acetone) (Found: C, 60.8; H, 3.7; Br, 11.3. $C_{34}H_{25}BrO_{10}$ requires C, 60.6; H, 3.7; Br, 11.9%); $\nu_{max.}$ 1 765 cm^{-1} (lactone) and 1 725 (ester); δ 4.51 (1 H, dd, $J_{6,6'}$ 12, $J_{5,6}$ 4 Hz, H-6), 4.82 (1 H, dd, $J_{5,6'}$ 3 Hz, H-6′), 5.15 (1 H, m, $J_{4,5}$ 10 Hz, H-5), 6.28 (1 H, t, $J_{3,4}$ 10 Hz, H-4), 6.52 (1 H, d, H-3), and 7.1—8.3 (20 H, aromatic).

2,4,6-*Tri*-O-*benzoyl*-3-*deoxy*-D-erythro-*hex*-2-*enono*-1,5-*lactone* (8).—(a) *By use of sodium iodide.* Sodium iodide (0.2 g) was added to a solution of the 2-bromolactone (7) (0.2 g) in dry acetone (3 ml) and the solution was stirred for 6 h at room temperature. Chloroform was added to the dark mixture, which was then washed with aqueous sodium thiosulphate and water and then dried. Removal of the solvent gave a pale yellow syrup which afforded the crystalline enone (0.1 g, 68%) on trituration with ethanol. Recrystallised from ethanol it had m.p. 111—112 °C, $[\alpha]_D$ +97° (lit.,[10] m.p. 111—112 °C, $[\alpha]_D$ +105°), m.p. undepressed on admixture with the compound prepared by the method of Lederkremer *et al.*; [10] δ 4.70 (2 H, d, $J_{5,6} = J_{5,6'} = 5$ Hz, H-6 and -6′), 5.10 (1 H, q, $J_{4,5}$ 5 Hz, H-5), 6.00 (1 H, dd, $J_{3,4}$ 4 Hz, H-4), 6.72 (1 H, d, H-3), and 7.2—8.2 (15 H, aromatic).

(b) *By use of DBU.* A solution of the 2-bromolactone (7) (1.0 g) in *NN*-dimethylformamide (10 ml) was stirred at 0 °C during the slow addition of DBU (0.25 g, 1.1 mol. equiv.) in this solvent (5 ml) and stirring was continued for 15 h at room temperature. The resulting black solution was diluted with dichloromethane and washed with dilute hydrochloric acid and then water, and dried. Removal of the solvent gave a dark residue which was resolved on silica gel to give the crystalline enone (0.19 g, 27%). Recrystallised from ethanol it had m.p. and mixed m.p. 111—112 °C, $[\alpha]_D$ +94°.

Photobromination of Phenyl Tetra-O-*acetyl*-β-D-*glucopyranoside* (9).—Phenyl tetra-*O*-acetyl-β-D-glucopyranoside (9) {m.p. 125—126 °C, $[\alpha]_D$ −21° (lit.,[18] m.p. 125—126 °C, $[\alpha]_D$ −22°)} was prepared from penta-*O*-acetyl-β-D-glucopyranose by treatment for 3 h in chloroform solution with phenol (1.1 mol. equiv.) in the presence of boron trifluoride–ether (5 mol. equiv.).[19] A solution of the acetylated glycoside (2 g) in dry carbon tetrachloride (60 ml) was heated under reflux over a 275-W heat lamp for 1.5 h in the presence of bromine (2 g, 2.6 mol. equiv.). The solvent was removed and the residue was separated on a column of silica gel to give a chromatographically more mobile syrup (1.08 g, 46%). Trituration with ether–light petroleum allowed the isolation of the crystalline product (0.63 g, 27%) which on recrystallisation from this solvent was homogeneous on t.l.c. and had m.p. 100—101 °C, $[\alpha]_D$ −90°; δ 2.01, 2.05, 2.07, and 2.07 (12 H, 3 s, 4 Ac), 4.33 (1 H, d, $J_{6,6'}$ 12 Hz, H-6), 4.61 (1 H, d, H-6′), 5.15—5.78 (4 H, m, H-1, -2, -3, and -4), and 6.85—7.5 (5 H, m, phenyl). These spectroscopic data are consistent with the compound being the bromide (10); it decomposed on standing.

Phenyl Tetra-O-*acetyl*-α-L-*idopyranoside* (15).—Phenyl

tetra-*O*-benzoyl-β-D-glucopyranoside (13) {m.p. 177—178 °C, $[\alpha]_D$ +28° (lit.,[20] m.p. 177 °C, $[\alpha]_D$ +27.5°)} was prepared by successive deacetylation and benzoylation of the acetylated analogue, and a portion (1 g) in suspension in carbon tetrachloride (30 ml) containing bromine (0.8 g, 3.4 mol. equiv.) was heated under reflux over a 275-W heat lamp for 1 h. The residue obtained by removal of the volatile materials was fractionated on a column of silica gel to give a chromatographically homogeneous syrup (0.24 g, 21%), $[\alpha]_D$ +2°; δ 4.63 (1 H, d, $J_{6,6'}$ 12 Hz, H-6), 4.96 (1 H, d, H-6'), 5.7—6.3 (4 H, m, H-1, -2, -3, and -4), and 6.9—8.2 (25 H, aromatic). T.l.c. and ^{1}H n.m.r. indicated that this same compound was the main component of the impure fractions; it is assumed, on the basis of the spectroscopic data, to be the 5-bromo-compound (14).

The unfractionated product of photobromination of the glycoside (4.0 g) in dry ether (30 ml) was then added slowly to a stirred suspension of lithium aluminium hydride (2 g) in ether (25 ml) and stirring was continued at room temperature for 1 h. The excess of hydride was removed using ethyl acetate and then water. The mixture was filtered, the solids were washed with water, and the aqueous solutions were neutralised with cationic resin and then taken to dryness with repeated additions of ethanol. Acetylation of the residue under standard conditions with acetic anhydride in pyridine gave a syrup which was fractionated on a column of silica gel to give phenyl tetra-*O*-acetyl-α-L-idopyranoside (15) (0.65 g, 26% based on phenyl tetra-*O*-benzoyl-β-D-glucopyranoside), $[\alpha]_D$ −79° (lit.,[14] −80°); δ 1.82, 2.04, 2.08 (12 H, 3 s, 4 Ac), 4.0—4.6 (3 H, m, H-5, -6, and -6'), 4.8—5.1 (3 H, m, H-2, -3, and -4), 5.47br (1 H, s, H-1), and 6.8—7.4 (5 H, m, aromatic).

A solution of the glycoside (0.25 g) in acetic acid containing acetic anhydride (5 ml; 3 : 7 v/v, containing sulphuric acid 2%) was allowed to stand at room temperature for 15 h and then poured into ice–water. Extraction with chloroform and neutralisation and drying of the extracts gave a syrup which was indistinguishable from penta-*O*-acetyl-α-D-idopyranose (t.l.c.). Crystallised and recrystallised from ethanol it had m.p. 94—95 °C, $[\alpha]_D$ −61° (lit.,[22] 95—96 °C, $[\alpha]_D$ −57°), and was identical (^{1}H n.m.r.) to the product of similar acetolysis of methyl tetra-*O*-acetyl-α-L-idopyranoside.[1]

p-*Acetamidophenyl Tetra*-O-*acetyl*-α-L-*idopyranoside* (16).—*p*-Nitrophenyl tetra-*O*-acetyl-β-D-glucopyranoside (11) {m.p. 173—174 °C, $[\alpha]_D$ −39° (lit.,[21] m.p. 175 °C, $[\alpha]_D$ −39°)} was prepared using boron trifluoride as catalyst (see above), and a suspension (1 g) in carbon tetrachloride (30 ml) containing bromine (1.5 g, 4.4 mol. equiv.) was heated under reflux over a 275-W heat lamp for 1.5 h. Removal of the solvent gave a syrupy residue which on preparative t.l.c. gave a chromatographically homogeneous syrupy product (0.67 g, 57%), $[\alpha]_D$ −57°; δ 2.05, 2.07 (12 H, 2 s, 4 Ac), 4.36 (1 H, d, $J_{6,6'}$ 12 Hz, H-6), 4.64 (1 H, d, H-6'), 5.2—5.85 (4 H, m, H-1, -2, -3, and -4), 7.05 (2 H, d, *J* 9.5 Hz, aromatic), and 8.14 (2 H, d, aromatic), assumed to be the 5-bromide (12).

A solution of the crude photobromination product, derived from the *p*-nitrophenyl glycoside (2 g), in dry ether (25 ml) was added slowly to a stirred suspension of lithium aluminium hydride (1.5 g) in ether (20 ml). Stirring was continued at room temperature for 2 h and the mixture was worked up as for the phenyl compound to give a black syrup. Preparative t.l.c. gave the acetylated L-acetamidophenyl glycoside (0.25 g, 12%) which, recrystallised from chloroform–light petroleum, had m.p. 164—166 °C, $[\alpha]_D$ −99°. The ^{1}H n.m.r. spectrum was identical to that of the D-enantiomer (see below).

p-*Acetamidophenyl Tetra*-O-*acetyl*-α-D-*idopyranoside*.—Penta-*O*-acetyl-α-D-idopyranose (2 g) in dry acetonitrile (20 ml) containing *p*-acetamidophenol (0.81 g, 1.05 mol. equiv.) and boron trifluoride–ether (3.5 g) was allowed to stand at room temperature for 7 h. Chloroform was added and the solution was washed with saturated aqueous sodium hydrogencarbonate and water and then dried. Removal of the solvent and trituration of the residue with ethanol gave the D-*acetamidophenyl glycoside* (0.75 g, 30%), m.p. 165—166 °C (from chloroform–light petroleum), $[\alpha]_D$ +102° (Found: C, 54.8; H, 5.8; N, 3.2. $C_{22}H_{27}NO_{11}$ requires C, 54.9; H, 5.6; N, 2.9%); δ 1.9 (3 H, s, Ac), 2.11 (12 H, s, 4 Ac), 4.1—4.35 (2 H, m, H-6, and -6'), 4.50 (1 H, m, H-5), 4.8—5.1 (3 H, m, H-2, -3, and -4), 5.42br (1 H, s, H-1), 6.92 (2 H, d, *J* 9 Hz, aromatic), 7.40 (2 H, d, aromatic), and 8.20br (1 H, s, NH).

p-*Nitrophenyl Tetra*-O-*acetyl*-α-D-*idopyranoside*.—Penta-*O*-acetyl-α-D-idopyranose[23] (2 g) in chloroform (30 ml) containing *p*-nitrophenol (0.85 g, 1.2 mol. equiv.) and boron trifluoride–ether (1.1 g) was allowed to stand at room temperature for 24 h. The solution was processed as usual and the residue on trituration with ethanol gave the crystalline p-*nitrophenyl glycoside* (1.26 g, 52%), m.p. 119—120 °C (from ethanol), $[\alpha]_D$ +131° (Found: C, 50.8; H, 5.0; N, 3.0. $C_{20}H_{23}NO_{12}$ requires C, 51.2; H, 4.9; N, 3.0%); δ 1.86, 2.12, and 2.15 (12 H, 3 s, 4 Ac), 4.0—4.3 (2 H, m, H-6, and -6'), 4.40 (1 H, m, H-5), 4.75—5.15 (3 H, m, H-2, -3, and -4), 5.60 (1 H, s, H-1), 7.08 (2 H, d, *J* 9 Hz, aromatic), and 8.11 (2 H, d, aromatic).

Reduced with lithium aluminium hydride and then acetylated and purified by preparative t.l.c., the compound gave, in low yield, *p*-acetamidophenyl tetra-*O*-acetyl-α-D-idopyranoside, identical (^{1}H n.m.r.) with the previous sample.

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