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STEREOSELECTIVE HYDROGENOLYSIS OF DIOXOLANE-TYPE BENZYLIDENE DERIVATIVES: SYNTHESIS OF SOME BENZYL ETHERS OF BENZYL β-D-ARABINOPYRANOSIDE

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ABSTRACT

The following derivatives of benzyl β-D-arabinopyranoside are described: *exo*-3,4-*O*-benzylidene (**2**), *endo*-3,4-*O*-benzylidene (**3**), and the 2-benzyl ether derivatives (**4** and **5**) of **2** and **3**. Hydrogenolysis ($LiAlH_4$–$AlCl_3$) of the *exo*-isomers (**2** and **4**) gave mainly 4-hydroxy-3-*O*-benzyl derivatives (**6** and **11**), whereas the *endo*-isomers (**3** and **5**) gave mainly 3-hydroxy-4-*O*-benzyl derivatives (**7** and **12**). Acid hydrolysis of **4** and **5** yielded the 2-*O*-benzyl derivative (**10**).

INTRODUCTION

In Nature, the L and D enantiomers of arabinose are both frequent constituents of plant polysaccharides[1] and plant glycosides, mainly as sugar components of saponins[2]. Partial hydrolysis of polysaccharides and structural investigation of saponin glycosides led to the recognition of the structure of several branched, complex oligosaccharides. Their syntheses have not yet been accomplished, which is mainly due to the lack of arabinoside derivatives containing suitable protecting groups. Because of the stability of benzyl groups and the ease with which they can be removed[3–9], partially benzylated benzyl glycosides are generally used in the syntheses of complex oligosaccharides.

For the synthesis of partially benzylated carbohydrates, a number of methods have been worked out[10–13], and several new methods of benzylation have been reported[14–18]. The earlier observation that hydrogenolysis of benzylidene derivatives of carbohydrates gives hydroxy-*O*-benzyl derivatives[19–22] and that the regioselectivity of the ring opening of 4,6-*O*-benzylidene derivatives is mainly determined by the steric requirements of the neighbouring groups[23–26] made possible the preparation of partially benzylated derivatives containing HO-6 unsubstituted.

A new, selective blocking is made possible by a stereoselective ring-opening that depends on the steric position of the phenyl group[26–28]; this was recognized in the *exo*- and *endo*-isomers of dioxolane-type benzylidene derivatives. It was proved for a number of 2,3-*O*-benzylidene-D-manno-[26,28] and -L-rhamno-, and 3,4-*O*-benzylidene-D-galacto-, -D-arabino-, and -D-fuco-pyranoside derivatives[27] that the *exo*-isomer yields *axial* hydroxyl, *equatorial* *O*-benzyl derivatives, whereas the *endo*-

isomer gives *equatorial* hydroxyl, *axial* *O*-benzyl derivatives. This regularity was also shown[29] for several D-galactopyranoside derivatives.

We now report the synthesis of benzyl 2-*O*-, 3-*O*-, 4-*O*-, 2,3-di-*O*-, and 2,4-di-*O*-benzyl-β-D-arabinopyranosides.

RESULTS AND DISCUSSION

The first two diastereomeric benzylidene derivatives described were those of methyl 3,4-*O*-benzylidene-β-L-arabinopyranoside[30]. Their absolute configurations were later determined by n.m.r. spectroscopy[31]. Recently, both diastereomers of benzyl 3,4-*O*-benzylidene-α-D-arabinopyranoside[32] and methyl 3,4-*O*-*o*-nitrobenzylidene-β-L-arabinopyranoside[33] have been isolated and their structures proved.

Our investigations, which are part of a programme on oligosaccharide synthesis, started with benzyl β-D-arabinopyranoside[34] (**1**) which, in a zinc chloride-catalysed reaction with benzaldehyde, gave an ~1:1 mixture (n.m.r. and g.l.c.) of benzyl *exo*/*endo*-3,4-*O*-benzylidene-β-D-arabinopyranosides (**2** and **3**) in fairly low yield; **2** and **3** were isolated by fractional crystallisation. A much better yield and the same isomer ratio were obtained[35] by using α,α-dimethoxytoluene in *N*,*N*-dimethylformamide and catalysis by toluene-*p*-sulphonic acid at 80°. Benzylation of **2** and **3** gave crystalline 2-*O*-benzyl derivatives (**4** and **5**).

The structures of **2**–**5** were proved by ^{1}H-n.m.r. spectroscopy, and those of **2** and **3** were checked by ^{13}C-n.m.r. spectroscopy. The benzylidene protons of *exo*-isomers (**2** and **4**) resonate at lower fields (δ 6.18 and 6.02) than those of *endo*-isomers (**3** and **5**, δ 5.84 and 5.89). The analysis of the signals for the ring protons indicates that the compounds have a strained $^1C_4$ conformation ($J_{4,5e} = J_{4,5a} =$ 1.8 Hz). Significant deformation of the chair conformers is indicated by the coupling constants of the protons of the bridgehead atoms forming the dioxolane ring ($J_{3,4}$ 5.5–6.3, $J_{2,3}$ 5.8–7.9 Hz).

In the ^{13}C-n.m.r. spectra of **2** and **3**, which are typical of dioxolane derivatives[36], the acetal carbon of the *endo*-isomer resonates at lower field (103.9 p.p.m.), and the quaternary carbon of the phenyl group at higher field (137.4 p.p.m.), than the corresponding carbon atoms of the *exo*-isomers (103.2 and 139.3 p.p.m., respectively). The regularities observed in the g.l.c. behaviour of *exo*- and *endo*-isomers[37] are also valid for **2**–**5**; on a polar liquid phase (UCW-982), the *endo*-isomers have shorter retention times (R_T values: **3**, 5.27 min; **5**, 3.84 min) than the *exo*-isomers (R_T values: **2**, 5.87 min; **4**, 4.04 min).

Hydrogenolysis of **2** by the $LiAlH_4$–$AlCl_3$ (1:1) reagent in ether–dichloromethane (1:1) at the boiling point gave, after 15 min, two mono-*O*-benzyl derivatives (**6** and **7**), the ratio of which, after acetylation, was found by g.l.c. to be 7:3. Compound **6** is resistant to periodate, whereas **7** is oxidised. In this way, in addition to the structural proof, **6** could be purified: after hydrogenolysis, the mixture of **6** and **7** was oxidized with periodate and then acetylated to give the diacetate (**8**) of **6**. Hydrogenolysis of **3** also gave a mixture of **6** and **7**, with the latter being the major product

(78%, g.l.c.). Acetylation of the mixture and chromatography of the products gave **8** and **9**, from which pure **6** and **7** were obtained by saponification. Benzyl 2-*O*-benzyl-β-D-arabinopyranoside (**10**) was isolated crystalline after hydrolysis of **4** or **5** with acetic acid.

Of the three possible di-*O*-benzyl isomers, two were prepared by the hydrogenolysis of **4** and **5**. Thus, **4** gave benzyl 2,3-di-*O*-benzyl-β-D-arabinopyranoside (**11**, 81%) and the 2,4-dibenzyl ether (**12**, 19%). A reverse product-distribution was found after hydrogenolysis of **5**: namely, **12**, 84%; **11**, 16%. The direction of hydrogenolysis of **2**–**5**, as indicated by the n.m.r. data, is consistent with $^1C_4$ conformations.

In the *exo*-isomers, the reagent attacks the axial oxygen atom to give an *axial* OH, *equatorial* *O*-benzyl derivative, whereas the *equatorial* oxygen of the dioxolane ring in the *endo*-isomers is attacked, giving mainly, or exclusively, an *equatorial* OH, *axial* *O*-benzyl derivative. A chemical method is therefore provided for the determination of absolute configuration of dioxolane-type benzylidene derivatives.

The stereospecificity of the hydrogenolysis of **4** and **5** is somewhat higher than that of **2** and **3**. In contrast to 4,6-*O*-benzylidene derivatives, the direction of ring opening is not influenced by the steric requirements of the neighbouring substituents, and it is thought that the stereoselectivity of the ring opening is significantly influenced by the deformation of the pyranosyl ring. This aspect is being investigated further.

The hydrogenolysis of dioxolane-type benzylidene derivatives makes possible a general method for the selective blocking of glycopyranosides containing vicinal *cis*-hydroxyl groups. The utilisation of this method in oligosaccharide synthesis is being investigated.

EXPERIMENTAL

Melting points were determined with a Kofler apparatus and are uncorrected. Kieselgel G was used for both column chromatography and t.l.c. Detection was effected by charring with sulphuric acid. G.l.c. was carried out on a Hewlett–Packard 5830 A chromatograph incorporating helical stainless-steel columns (0.4 mm i.d.) packed with (*a*) 10% of UCW-982 on Chromosorb WAW-DMCS (80–100 mesh), 2 ft, 220°/2.5°; (*b*) 20% of SE-30 on Chromosorb W (60–80 mesh), 4 ft, 300°, isothermal; (*c*) 10% of UCW-982 on Chromosorb WAW-DMCS (80–100 mesh), 220°, isothermal; and (*d*) 10% of UCW-982 on Chromosorb WAW-DMCS (80–100 mesh), 2 ft, 240°/2.5°; nitrogen flow-rate, 20 ml/min. Values of $[\alpha]_D$ were measured for chloroform solutions with a Perkin–Elmer 241 automatic polarimeter. ^{1}H-N.m.r. spectra were measured with a Jeol MH-100 spectrometer, and ^{13}C-n.m.r. spectra with a Varian XL-100-15 F.T. spectrometer, for solutions in $CDCl_3$ (internal Me_4Si).

Benzyl exo- (**2**) *and* endo-*3,4-O-benzylidene-β-D-arabinopyranoside* (**3**). — (*a*) A mixture of 5 g of **1** and 5 g of freshly fused $ZnCl_2$ was shaken in 25 ml of benzaldehyde for 24 h, and then diluted with ice–water (200 g). The organic layer was steam-distilled in the presence of a small amount of $NaHCO_3$. The residue (4.05 g), which solidified upon cooling, was a 1:1 mixture of **2** and **3**. Two recrystallisations

from ethanol (70 ml) gave **2** (1.85 g, 27.2%), m.p. 144–145°, $[\alpha]_D$ −148° (*c* 0.75, chloroform), R_F 0.83 (benzene–methanol, 9:1), R_T 5.87 min [column (*a*)]. ^{1}H-N.m.r. data: δ 7.50–7.20 (m, 10 H, 2 Ph), 6.18 (s, 1 H, PhC*H*), 4.97 (d, 1 H, H-1), 4.66 (q, 2 H, PhCH_2), 4.43 (dd, 1 H, H-3), 4.15 (dd, 1 H, H-4), 3.96 (d, 2 H, H-5a,5e), 3.88 (dd, 1 H, H-2), and 2.66 (d, 1 H, HO-2). ^{13}C-N.m.r. data: δ 103.0 (Ph-*C*H), 97.2 (C-1), 70.0 (C-2), 77.0 (C-3), 73.2 (C-4), 60.1 (C-5), 68.2 (Ph-*C*H_2), and 139.3 [CH-*C*-(CH)$_5$].

Anal. Calc. for $C_{19}H_{20}O_5$: C, 69.49; H, 6.14. Found: C, 69.79; H, 6.21.

The mother liquor from the crystallisation of **2** was concentrated, and the residue was thrice recrystallised from cyclohexane (50 ml) to give **3** (1.79 g, 26.3%), m.p. 95–96°, $[\alpha]_D$ −171° (*c* 0.47, chloroform), R_F 0.66 (benzene–methanol, 9:1), R_T 5.27 min [column (*a*)]. ^{1}H-N.m.r. data: δ 7.60–7.10 (m, 10 H, 2 Ph), 5.84 (s, 1 H, PhC*H*), 4.89 (d, 1 H, H-1), 4.62 (q, 2 H, PhCH_2), 4.33 (dd, 1 H, H-3), 4.20 (dd, 1 H, H-4), 4.01 (d, 2 H, H-5a,5e), 3.84 (dd, 1 H, H-2), and 2.96 (d, 1 H, HO-2). ^{13}C-N.m.r. data: δ 103.9 (Ph-*C*H), 96.8 (C-1), 69.8 (C-2), 75.9 (C-3), 74.7 (C-4), 60.0 (C-5), 69.8 (Ph-*C*H_2), and 137.4 [CH-*C*-(CH)$_5$].

Anal. Calc. for $C_{19}H_{20}O_5$: C, 69.49; H, 6.14. Found: C, 69.01; H, 6.06.

(*b*) A mixture of 10 g of **1**, *N*,*N*-dimethylformamide (60 ml), α,α-dimethoxytoluene (10 g), and toluene-*p*-sulphonic acid (200 mg) was kept at 80° *in vacuo* in the equipment described by Evans[35]. After 5 h, the mixture was cooled, treated with 3:1 hexane–ether (100 ml), and then poured into ice–water (250 g). The product (10.2 g) solidified upon stirring. The isomeric ratio was 1:1, and crystallization from ethanol gave **2** (4.71 g, 34.6%), m.p. 144–145°.

Crystallisation (from cyclohexane) of the residue obtained from the mother liquor gave **3** (4.16 g, 30.6%), m.p. 97°.

*Benzyl 2-*O*-benzyl-*exo*-3,4-*O*-benzylidene-β-*D*-arabinopyranoside* (**4**). — A mixture of 1.80 g of **2**, 5 g of powdered KOH, and 20 ml of benzyl chloride was kept at 100° for 4 h. The cooled mixture was washed with water (2 × 100 ml), and benzyl chloride was removed from the organic phase by steam distillation. The oily residue was triturated with cold ethanol (50 ml) and recrystallised from ethanol (30 ml) to give **4** (1.82 g, 79%), m.p. 85–86°, $[\alpha]_D$ −103° (*c* 0.64, chloroform), R_F 0.86 (benzene–methanol, 95:5), R_T 4.04 min [column (*b*)]. ^{1}H-N.m.r. data: δ 7.50–7.20 (m, 15 H, 3 Ph), 6.02 (s, 1 H, PhC*H*), 4.94 (d, 1 H, H-1), 4.73 and 4.63 (2 q, 4 H, 2 PhCH_2), 4.68 (dd, 1 H, H-3), 4.16 (dd, 1 H, H-4), 3.95 (d, 2 H, H-5a,5e), and 3.69 (dd, 1 H, H-2).

Anal. Calc. for $C_{26}H_{26}O_5$: C, 74.62; H, 6.26. Found: C, 75.02; H, 6.17.

*Benzyl 2-*O*-benzyl-*endo*-3,4-*O*-benzylidene-β-*D*-arabinopyranoside* (**5**). — Compound **3** (2.1 g) was benzylated, as for **2**, to give **5** (2.16 g, 80.7%), m.p. 80–82° (from ethanol), $[\alpha]_D$ −164° (*c* 0.8, chloroform), R_F 0.82 (benzene–methanol, 95:5), R_T 3.84 min [column (*b*)]. ^{1}H-N.m.r. data: δ 7.55–7.20 (m, 15 H, 3 Ph), 5.89 (s, 1 H, PhC*H*), 4.84 (d, 1 H, H-1), 4.62 and 4.59 (2 q, 4 H, 2 PhCH_2), 4.52 (dd, 1 H, H-3), 4.25 (dd, 1 H, H-4), 4.04 (d, 2 H, H-5a,5e), and 3.58 (dd, 1 H, H-2).

Anal. Calc. for $C_{26}H_{26}O_5$: C, 74.62; H, 6.26. Found: C, 74.81; H, 6.18.

Benzyl 2,4-di-O-acetyl-3-O-benzyl-β-D-arabinopyranoside (**8**). — $LiAlH_4$ (1.50 g) was added in portions to a solution of 2.5 g of **2** in 200 ml of ether–dichloromethane (1:1). A solution of 4.50 g of $AlCl_3$ in 25 ml of ether was then added dropwise during 2 min. The mixture was boiled under reflux and stirred for 15 min, and then cooled, the excess reagent was decomposed with ethyl acetate (6 ml), and $Al(OH)_3$ was precipitated with water (14 ml). The ether–dichloromethane layer was decanted, the precipitate was extracted with ether (2 × 30 ml), and the combined organic layers were washed with water (2 × 50 ml), dried (Na_2SO_4), and concentrated. A portion (10 mg) of the syrupy, crude product (2.42 g) was treated conventionally with 0.5 ml of pyridine and 0.5 ml of acetic anhydride, and the product was subjected to g.l.c. [column (*c*)], which revealed two components having R_T 10.8 (70%) and 13.32 min (30%). The mixture (2.40 g) of **6** and **7** was oxidized with 1 g of $NaIO_4$ in 200 ml of 50% aqueous ethanol overnight at 4°. The mixture was concentrated to dryness, and the residue was conventionally acetylated with acetic anhydride (25 ml) in pyridine (25 ml) to give a product from which the substance R_T 13.32 was absent. Elution from Kieselgel G (100 g) with benzene–ether (5:1) gave **8** (1.89 g, 59.9%) as a syrup, $[\alpha]_D$ −159° (*c* 0.64, chloroform), R_F 0.50 (benzene–ether, 5:1). ^{1}H-N.m.r. data: δ 7.35–7.15 (m, 10 H, 2 Ph), 5.26–4.86 (m, 2 H, H-2,4), 4.98 (d, 1 H, H-1), 4.46 and 4.40 (2 q, 4 H, 2 PhCH_2), 4.00–3.46 (m, 3 H, H-3, 5a,5e), 2.04 (s, 3 H, AcO-2), and 1.96 (s, 3 H, AcO-4).

Anal. Calc. for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 65.92; H, 6.22.

Benzyl 3-O-benzyl-β-D-arabinopyranoside (**6**). — Compound **8** (0.5 g) was treated with 20 ml of methanol containing 0.1 ml of methanolic 0.1M sodium methoxide. After 16 h, the solution was neutralized with Amberlite IR-120(H^+) resin, and concentrated *in vacuo* to give **6** (0.36 g, 90.3%) as a syrup, $[\alpha]_D$ −112.5° (*c* 0.52, chloroform), R_F 0.34 (benzene–methanol, 9:1), R_T 3.83 min [column (*d*)].

Anal. Calc. for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 68.75; H, 6.58.

Benzyl 2,3-di-O-acetyl-4-O-benzyl-β-D-arabinopyranoside (**9**). — A solution of 2.5 g of **3** in 100 ml of ether–dichloromethane (1:1) was treated with a solution of 1.5 g of $LiAlH_4$ and 4.5 g of $AlCl_3$ in 25 ml of ether, as described in the hydrogenolysis of **2**. Work-up furnished 2.36 g of crude product, which was treated with acetic anhydride (25 ml) and pyridine (25 ml). T.l.c. (benzene–ether, 5:1) of the product revealed two components, R_F 0.62 (major) and 0.50. G.l.c. [column (*c*)] revealed components having R_T 13.41 (78%) and 10.88 min (22%).

The crude mixture of acetates (2.82 g) was eluted from Kieselgel G (120 g) with benzene–ether (5:1) to give, first, **9** (1.95 g, 61.8%), m.p. 66–68° (from ether–pentane, 3:1), $[\alpha]_D$ −198° (*c* 0.75, chloroform). ^{1}H-N.m.r. data: δ 7.40–7.20 (m, 10 H, 2 Ph), 5.22–5.08 (m, 2 H, H-2,3), 5.00 (d, 1 H, H-1), 4.48 and 4.44 (2 q, 4 H, 2 PhCH_2), 3.80 (m, 1 H, H-4), 3.75–3.56 (m, 2 H, H-5a,5e), and 2.01 (s, 6 H, 2 AcO).

Anal. Calc. for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.74; H, 6.18.

Benzyl 4-O-benzyl-β-D-arabinopyranoside (**7**). — Compound **9** (0.5 g) was deacetylated, as for **6**, to give **7** (0.31 g, 77.8%) as a foam, $[\alpha]_D$ −163° (*c* 0.45, chloroform), R_F 0.28 (benzene–methanol, 9:1), R_T 4.21 min [column (*d*)]. ^{1}H-

N.m.r. data: δ 7.40–7.22 (m, 10 H, 2 Ph), 4.86 (d, 1 H, H-1), 4.70–4.30 (2 q, 4 H, 2 PhCH_2), and 3.95–3.40 (m, 7 H, ring protons +2 HO).

Anal. Calc. for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71. Found: C, 69.00; H, 6.60.

Benzyl 2-O-benzyl-β-D-arabinopyranoside (**10**). — (*a*) A suspension of **4** (2 g) in 100 ml of 50% aqueous acetic acid was stirred at 80° for 4 h, and then concentrated *in vacuo*. Traces of acetic acid were removed from the syrupy residue by repeated evaporation of benzene therefrom. The residue was recrystallized from water (80 ml) to give **10** (1.08 g, 68.4%), m.p. 129–130°, $[\alpha]_D$ −189° (*c* 0.69, chloroform), R_F 0.25 (benzene–methanol, 9:1), R_T 3.71 min [column (d)]; lit.[38] for the L enantiomer, m.p. 130–131°, $[\alpha]_D$ +194° (*c* 0.75, chloroform).

(*b*) Compound **5** (0.5 g) was hydrolyzed in 25 ml of 50% acetic acid. Crystallization of the product from water gave **10** (0.20 g, 50.7%), m.p. 128–130°, $[\alpha]_D$ −188° (*c* 0.76, chloroform).

Benzyl 2,3-di-O-benzyl-β-D-arabinopyranoside (**11**). — A solution of **4** (1.02 g) in 50 ml of dichloromethane and 30 ml of ether was treated with a solution of 0.4 g of $LiAlH_4$ and 1.2 g of $AlCl_3$ in 20 ml of ether, as described for the hydrogenation of **2**. Work-up gave 0.96 g (93.7%) of a syrup which contained (t.l.c.; benzene–ether, 4:1) components having R_F 0.27 (major) and 0.35. G.l.c. [column (*a*)] revealed components having R_T 6.75 and 8.02 min, in the ratio 81.2:18.8. The components were separated on 20 g of Kieselgel G to give **11** (0.5 g, 48.8%), m.p. 58–60°, $[\alpha]_D$ −114° (*c* 0.37, chloroform).

Anal. Calc. for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71. Found: C, 74.02; H, 6.52.

Benzyl 2,4-di-O-benzyl-β-D-arabinopyranoside (**12**). — A solution of **5** (1 g) in 50 ml of dichloromethane and 30 ml of ether was treated with 0.4 g of $LiAlH_4$ and 1.2 g of $AlCl_3$ in 20 ml of ether, as described in the preparation of **11**. Work-up gave 0.98 g (98%) of a crude product which g.l.c. [column (*a*)] showed to contain two components having R_T 8.01 (84.4%) and 6.76 min (15.6%). Crystallization from cyclohexane gave the major product **12** (0.72 g, 72%), m.p. 79–80°, $[\alpha]_D$ −152° (*c* 0.74, chloroform), R_F 0.34 (benzene–ether, 4:1), R_T 8.01 min [column (*a*)].

Anal. Calc. for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71. Found: C, 74.42; H, 6.66.

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