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REACTION OF SUGAR DERIVATIVES WITH DIBROMOMETHYL METHYL ETHER: FORMATION OF BROMODEOXY COMPOUNDS

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ABSTRACT

Treatment of methyl 4-*O*-benzoyl-2,3-*O*-isopropylidene-α-L-rhamnopyranoside and methyl 5-*O*-benzoyl-2,3-*O*-isopropylidene-α-D-lyxofuranoside with dibromomethyl methyl ether gave 2-bromo-2-deoxy-3-*O*-formylglycosyl bromides in good yields. Methyl 4,6-di-*O*-benzoyl-2,3-*O*-isopropylidene-α-D-mannopyranoside yielded a 6-bromo-6-deoxy-2-*O*-formylidose derivative *via* acyloxonium-ion rearrangements. Methyl 5-*O*-benzoyl-2,3-*O*-isopropylidene-β-D-ribofuranoside gave mainly a 2-bromo-2-deoxy derivative, but a small proportion of a 5-bromo-5-deoxy derivative could also be isolated. The glycosyl bromides were converted into the corresponding methyl glycosides. The *O*-formyl groups could be removed selectively.

INTRODUCTION

In previous papers of this series, the preparation of 2-bromo-2-deoxy sugars by treatment of acylated pyranoses[1] or furanoses[2] with dibromomethyl methyl ether (DBE) and zinc bromide was described. Since DBE is a mild reagent for generating glycosyl bromides[3], it was of interest to investigate its effect on carbohydrates protected with acetal groups, for example, isopropylidene derivatives.

RESULTS AND DISCUSSION

Treatment of methyl 4-*O*-benzoyl-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**1**) with DBE gave a 2-bromo-2-deoxy-L-quinovose derivative (**3**) containing a formyl group in the 3 position. The reaction probably proceeded *via* a glycosyl bromide, followed by cleavage of the isopropylidene group, formylation[4], and subsequent formation of a formoxonium ion (**2**). The ion **2** was probably attacked at C-2 by bromine from C-1, in a reaction similar to that described for the acylated derivatives[1], to give 4-*O*-benzoyl-2-bromo-2,6-dideoxy-3-*O*-formyl-α-L-glucopyranosyl bromide (**3**). Subsequent treatment with methanol and silver carbonate yielded the crystalline

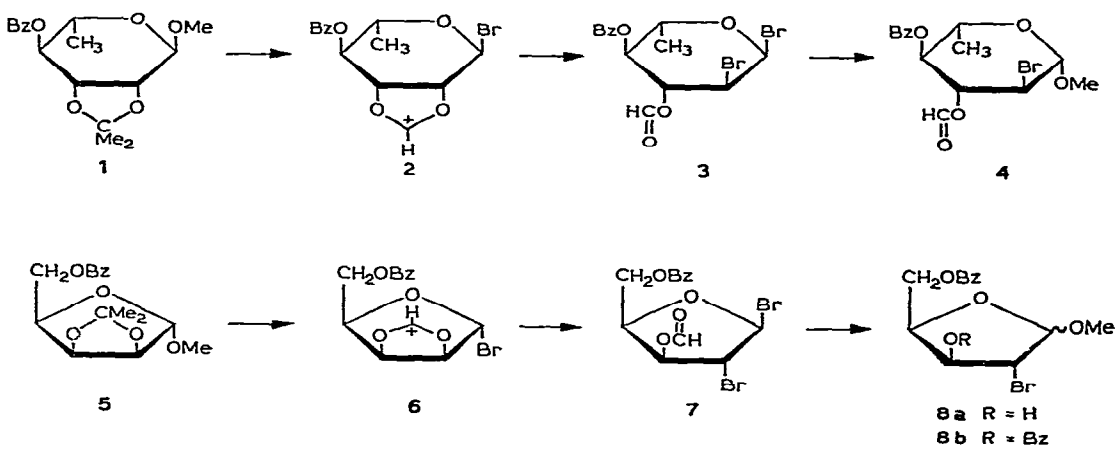
methyl glycoside **4**. Similarly, the reaction of methyl 5-*O*-benzoyl-2,3-*O*-isopropylidene-α-D-lyxofuranoside (**5**) with DBE gave 5-*O*-benzoyl-2-bromo-2-deoxy-3-*O*-formyl-β-D-xylofuranosyl bromide (**7**), presumably *via* the formoxonium ion **6**. Treatment of **7** with methanol in the absence of an acid acceptor gave a mixture of the anomeric 3-hydroxy-glycosides (**8a**), characterized as the known[2] dibenzoates (**8b**).

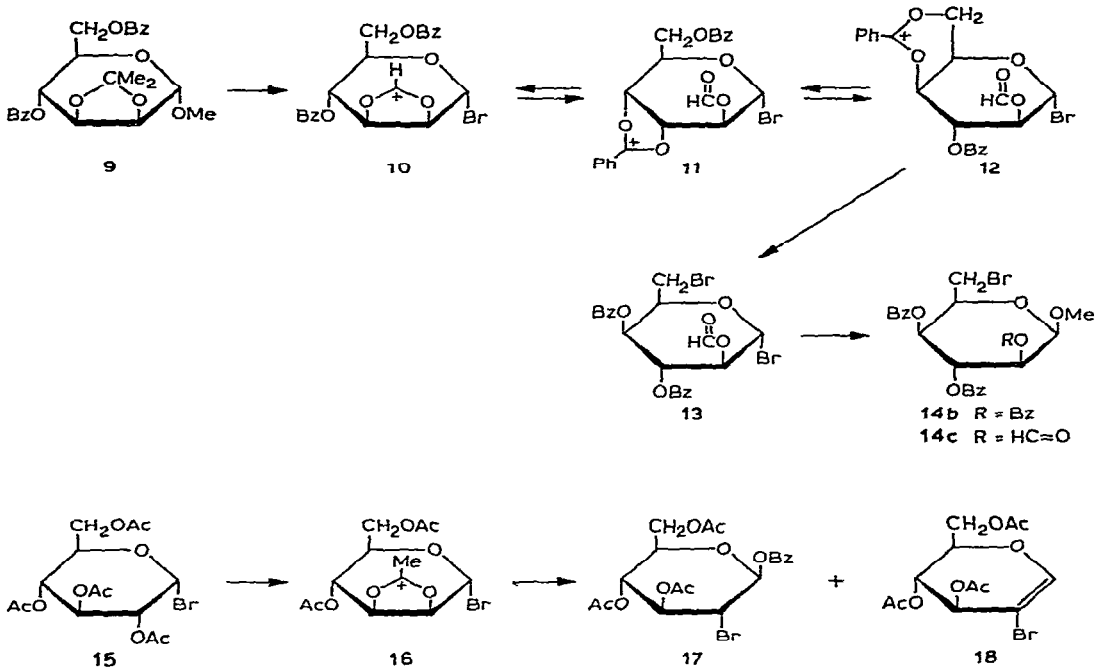
Treatment of methyl 4,6-di-*O*-benzoyl-2,3-*O*-isopropylidene-α-D-mannopyranoside (**9**) with DBE proceeded in a different manner. The compound isolated in 60% yield after reaction of the initial product with methanol and silver carbonate was methyl 3,4-di-*O*-benzoyl-6-bromo-6-deoxy-2-*O*-formyl-β-D-idopyranoside (**14c**), which was characterized by p.m.r. and ^{13}C-n.m.r. spectroscopy. Removal of the 2-*O*-formyl group with methanol and acid, followed by benzoylation, gave the crystalline tribenzoate (**14b**).

In all previously studied reactions of acylated pyranose or furanose derivatives with DBE, bromine was introduced at C-2 *via* a 2,3-oxonium ion. In the reaction of **9** with DBE, a 2,3-formoxonium ion (**10**) is probably formed, presumably in equilibrium with a 3,4-benzoxonium (**11**) and a 4,6-benzoxonium ion (**12**). Since benzoxonium ions are presumably more stable than formoxonium ions, it is not surprising that bromine reacts with the more abundant benzoxonium ion at the primary carbon (C-6). An analogous series of equilibria has been described by Paulsen *et al.*[5,6] for reactions of acylated sugar derivatives with antimony pentachloride.

When tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**15**) was treated with DBE, followed by silver benzoate, the only products isolated were the 2-bromo-2-deoxy-glucose derivatives **17** and **18**. By analogy with the corresponding xylose derivative[1], this reaction probably took place *via* a 2,3-acetoxonium ion having the *manno* configuration (**16**). This ion could be involved in equilibria of acetoxonium ions similar to **10**, **11**, and **12**. However, no 6-bromo-6-deoxyidose derivatives were detected.

Treatment of the dibromo compound **13** with methanol and silver carbonate gave exclusively the β-glycoside **14c**, indicating that the formyloxy group did not participate in the glycosidation reaction. Similar results have been reported in the

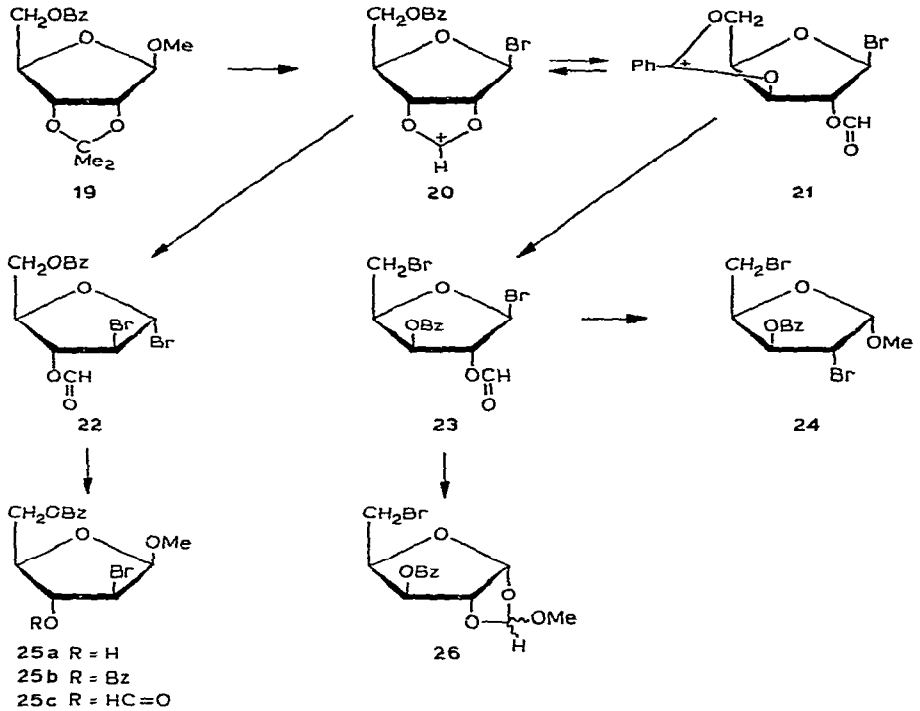




reaction of acetobromoidose with methanol and silver carbonate[7,8]. N.m.r. spectroscopy of the product mixture obtained from the reaction of acetobromoidose with methanol and silver carbonate revealed[9] its contents of β-glycoside (60%), α-glycoside (3%), and ortho ester (27%). A similar reaction of acetobromoaltrose gave[9] β-glycoside (29%), α-glycoside (2%), and ortho ester (69%). Thus, it is difficult to form α-glycosides of ido- or altro-pyranose derivatives, even though neighbouring-group participation from the acetoxy substituent at C-2 would be expected to favour the formation of such products.

Treatment of methyl 5-*O*-benzoyl-2,3-*O*-isopropylidene-β-D-ribofuranoside (**19**) with DBE, followed by treatment with methanol, gave a mixture of products derivable from the oxonium ions **20** and **21**. The main product, isolated in 45% yield, was the 2-bromo-2-deoxy 3-formate **25c**, characterized through the crystalline 3-hydroxy compound (**25a**) and the known[2] dibenzoate (**25b**). If only 2.2 equivalents of DBE were used in the reaction, 10% of the 5-bromo-5-deoxy 1,2-orthoformate **26** was isolated. When the reaction was carried out with a large excess of DBE, the ortho ester was further converted into the 2,5-dibromo derivative (**24**). This reaction is analogous to that described previously for acylated furanose derivatives[2].

Thus, treatment of carbohydrate derivatives protected with an isopropylidene group offers a convenient method for the preparation of bromodeoxy sugars having formate protecting-groups. These compounds may serve as valuable intermediates in the synthesis of more-complex carbohydrate derivatives, since the formyl group can be easily and selectively removed.



EXPERIMENTAL

General. — Dibromomethyl methyl ether (DBE) was prepared by the method of Gross *et al.*[10]. Optical rotations were measured on a Perkin–Elmer 141 instrument. ^{1}H- and ^{13}C-n.m.r. spectra were recorded with Bruker HX-90E, WH-90, HX-270, and WH-270 instruments. Melting points are uncorrected. P.l.c. was performed on 1-mm layers of silica gel (Merck PF_{254}). Elemental analyses were carried out by Novo Microanalytical Laboratory.

Reactions with DBE. — (*a*) *Methyl 4-O-benzoyl-2,3-O-isopropylidene-α-*L*-rhamnopyranoside* (**1**). To a solution of **1** (1.02 g) in chloroform (10 ml) were added zinc bromide (145 mg) and DBE (1 ml), and the mixture was stirred overnight at room temperature. Dichloromethane (50 ml) was then added and the solution was washed twice with 4M hydrochloric acid, dried ($MgSO_4$), and concentrated. The syrupy residue consisted of crude 4-*O*-benzoyl-2-bromo-2,6-dideoxy-3-*O*-formyl-α-L-glucopyranosyl bromide (3). ^{1}H-N.m.r. data ($CDCl_3$): δ 6.46 ($J_{1,2}$ 3.5 Hz, H-1), 4.22 ($J_{2,3}$ 10.5 Hz, H-2), 5.85 ($J_{3,4}$ 9.0 Hz, H-3), 5.19 ($J_{4,5}$ 9.0 Hz, H-4), 4.42 ($J_{5,6}$ 6.0 Hz, H-5), 1.50 (H-6), and 8.08 (*H*CO). ^{13}C-N.m.r. data ($CDCl_3$): 89.4 (C-1), 48.8 (C-2), 71.3, 71.4 (C-3,5), 73.8 (C-4), 17.1 (C-6), and 159.2 p.p.m. (HCO).

The syrup was stirred with methanol (10 ml), ether (10 ml), and silver carbonate (2 g) for 2 h at room temperature. Filtration through carbon and concentration gave crude methyl 4-*O*-benzoyl-2-bromo-2,6-dideoxy-3-*O*-formyl-β-L-glucopyranoside (**4**, 1.2 g). Crystallisation from ether–pentane gave material (360 mg, 30%) having m.p.

165–170°. P.l.c. (ether–pentane, 1:1) of the material in the mother liquor gave more **4** (142 mg, 12%), m.p. 170–174°. Recrystallisation from ether–pentane gave pure **4**, m.p. 175–177°, $[\alpha]_D^{20}$ +23° (*c* 1.8, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 4.69 ($J_{1,2}$ 7.8 Hz, H-1), 3.87 ($J_{2,3}$ 10.5 Hz, H-2), 5.58 ($J_{3,4}$ 9.5 Hz, H-3), 5.05 ($J_{4,5}$ 9.5 Hz, H-4), 3.76 ($J_{5,6}$ 6.0 Hz, H-5), 1.33 (H-6), 8.02 (*H*CO), and 3.52 (OMe). ^{13}C-N.m.r. data ($CDCl_3$): 103.2 (C-1), 49.5 (C-2), 74.0 (C-3), 74.3 (C-4), 70.6 (C-5), 17.4 (C-6), 159.4 (HCO), and 57.5 p.p.m. (OMe).

Anal. Calc. for $C_{15}H_{17}BrO_6$: C, 48.27; H, 4.59; Br, 21.41. Found: C, 48.21; H, 4.55; Br, 21.26.

(*b*) *Methyl 5-*O*-benzoyl-2,3-*O*-isopropylidene-α-*D*-lyxofuranoside* (**5**). To a solution of **5** (1 g) in chloroform (15 ml) were added zinc bromide (200 mg) and DBE (3 ml), and the mixture was stirred at room temperature for 48 h. After 24 h, more DBE (2 ml) was added. Work-up as described in (*a*) gave the crude, syrupy **7** (1.3 g, 98%). ^{1}H-N.m.r. data ($CDCl_3$): δ 6.60 ($J_{1,2}$ ~0 Hz, H-1), 4.84 ($J_{2,3}$ ~0 Hz, H-2), 5.73 ($J_{3,4}$ 5.5 Hz, H-3), 5.11 (H-4), 4.4–4.8 (H-5,5'), and 8.11 (*H*CO). ^{13}C-N.m.r. data ($CDCl_3$): 88.8 (C-1), 53.3 (C-2), 76.3 (C-3), 81.2 (C-4), 61.9 (C-5), and 159.2 p.p.m. (HCO).

Treatment of crude **7** with methanol (10 ml) at room temperature for 6 h, followed by neutralisation with pyridine (2 ml) and concentration, gave **8a** (1.0 g, αβ-ratio 1:2). ^{1}H-N.m.r. data ($CDCl_3$) for β-**8a**: δ 5.16 ($J_{1,2}$ ~0 Hz, H-1), 4.18 ($J_{2,3}$ ~0 Hz, H-2), and 4.3–4.8 (H-3,4,5,5'). ^{13}C-N.m.r. data ($CDCl_3$): 109.7 (C-1), 52.2 (C-2), 77.5 (C-3), 80.1 (C-4), 64.2 (C-5), and 55.6 (OMe). ^{1}H-N.m.r. data ($CDCl_3$) for α-**8a**: δ 5.02 ($J_{1,2}$ 4.0 Hz, H-1) and 4.3–4.8 (H-2,3,4,5,5'). ^{13}C-N.m.r. data ($CDCl_3$): 101.9 (C-1), 53.5 (C-2), 76.1 (C-3), 77.2 (C-4), 63.7 (C-5), and 55.9 p.p.m. (OMe).

Benzoylation of **8a** gave the known[2] dibenzoates **8b**, which were separated by p.l.c. (ether–pentane, 1:2). The fastest-moving fraction (520 mg, 42%) was β-**8b**, $[\alpha]_D^{20}$ −1.3° (*c* 5, chloroform); lit.[2], m.p. 66–67°, $[\alpha]_D$ −4.8°. The ^{1}H-n.m.r. data ($CDCl_3$) were identical with those published[2]. The slower-running fraction (260 mg, 21%) was syrupy α-**8b**, $[\alpha]_D^{20}$ +157° (*c* 1.6, chloroform); lit.[2], $[\alpha]_D$ +163.1°. The ^{1}H-n.m.r. data ($CDCl_3$) were identical with those published[2].

(*c*) *Methyl 4,6-di-*O*-benzoyl-2,3-*O*-isopropylidene-α-*D*-mannopyranoside* (**9**). To a solution of **9** (1 g) in chloroform (15 ml) were added zinc bromide (200 mg) and DBE (1 ml), and the mixture was stirred at room temperature for 20 h. Work-up as described in (*a*) and treatment of the resulting bromide with methanol (10 ml) and silver carbonate (1 g) gave the crude product (1.01 g). Purification by p.l.c. (ethyl acetate–hexane, 1:2) gave, as the main fraction, **14c** (637 mg, 57%). Crystallisation from ether–pentane gave material with m.p. 105–107°, $[\alpha]_D^{20}$ +47° (*c* 1.7, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.00 ($J_{1,2}$ 1.8 Hz, H-1), 5.33 ($J_{2,3}$ 4, $J_{2,4}$ 0.6 Hz, H-2), 5.63 ($J_{3,4}$ 4 Hz, H-3), 5.45 ($J_{4,5}$ 2.4 Hz, H-4), 4.47 ($J_{5,6}$ 4.8, $J_{5,6'}$ 7.2 Hz, H-5), 3.6–3.8 (H-6,6'), and 8.10 (HCO). ^{13}C-N.m.r. data ($CDCl_3$): 99.3 ($J_{C\text{-}1,H\text{-}1}$ 160 Hz, C-1), 68.2, 67.6, 66.8 (C-2,3,4), 74.8 (C-5), 30.0 (C-6), 57.8 (OMe), and 159.7 p.p.m. (HCO).

Anal. Calc. for $C_{22}H_{21}BrO_8$: C, 53.56; H, 4.29; Br, 16.20. Found: C, 53.27; H, 4.24; Br, 16.55.

Treatment of **14c** (0.2 g) with boiling methanol (10 ml) containing 2 drops of conc. HCl for 30 min, followed by work-up, gave **14a** as a syrup which, when conventionally treated with benzoyl chloride–pyridine, gave methyl 2,3,4-tri-*O*-benzoyl 6-bromo-6-deoxy-β-D-idopyranoside (**14b**), m.p. 211–213°, $[\alpha]_D^{20}$ −22° (*c* 1.3, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.05 ($J_{1,2}$ 1.5 Hz, H-1), 5.38 ($J_{2,3}$ 3.7, $J_{2,4}$ 0.7 Hz, H-2), 5.78 ($J_{3,4}$ 4 Hz, H-3), 5.42 ($J_{4,5}$ 3 Hz, H-4), 4.49 ($J_{5,6}$ 7, $J_{5,6'}$ 5.6 Hz, H-5), 3.76 ($J_{6,6'}$ 11 Hz, H-6), 3.64 (H-6'), and 3.64 (OMe). ^{13}C-N.m.r. data ($CDCl_3$): 99.6 (C-1), 68.1, 67.7, 67.7 (C-2,3,4), 74.9 (C-5), 29.7 (C-6), and 57.4 p.p.m. (OMe).

Anal. Calc. for $C_{28}H_{25}BrO_8$: C, 59.06; H, 4.43; Br, 14.03. Found: C, 58.87; H, 4.37; Br, 14.53.

(*d*) *Tetra-*O*-acetyl-α-*D*-glucopyranosyl bromide* (**15**). To a solution of **15** (0.6 g) in chloroform (10 ml) were added zinc bromide (150 mg) and DBE (2 ml), and the solution was stirred at room temperature for 20 h. Work-up as described in (*a*) gave the crude product. P.m.r. data showed that the main product was tri-*O*-acetyl-2-bromo-2-deoxy-α-D-glucopyranosyl bromide[12]. Treatment of the bromide with silver benzoate (2 g) in acetonitrile (20 ml) for 20 h, followed by work-up, gave a product (0.6 g) that was separated into two fractions by p.l.c. (ether–pentane, 2:1). The fastest-moving fraction (21 mg, 4%) was syrupy **18**. The next fraction (150 mg, 22%) was **17**, m.p. 152–153°. The ^{1}H-n.m.r. data for the two compounds were identical with those published[12].

(*e*) *Methyl 5-*O*-benzoyl-2,3-*O*-isopropylidene-β-*D*-ribofuranoside* (**19**). To a solution of **19** (764 mg) in chloroform (10 ml) were added zinc bromide (150 mg) and DBE (1.75 ml, 2.2 equiv.), and the mixture was stirred at room temperature for 20 h. Work-up as described in (*a*) gave crude, syrupy **22**. ^{1}H-N.m.r. data ($CDCl_3$): δ 6.64 ($J_{1,2}$ ~0 Hz, H-1), 4.79 ($J_{2,3}$ ~0 Hz, H-2), 5.50 ($J_{3,4}$ 3.5 Hz, H-3), 5.50 ($J_{3,4}$ 3.5 Hz, H-3), 4.5–5.0 (H-4,5,5'), and 8.09 (*H*CO). ^{13}C-N.m.r. data ($CDCl_3$): 90.1 (C-1), 54.0 (C-2), 79.0 (C-3), 84.6 (C-4), 63.2 (C-5), and 159.6 p.p.m. (HCO).

Treatment of **22** with methanol and silver carbonate, followed by work-up as described in (*a*), gave the crude glycoside (1.1 g), which was subjected to p.l.c. (ethyl acetate–hexane, 1:1). The fastest-moving fraction (100 mg, 10%) was syrupy **26** (epimer ratio, 2:1). ^{1}H-N.m.r. data ($CDCl_3$) of the major compound: δ 6.12 ($J_{1,2}$ 4 Hz, H-1), 4.75 ($J_{2,3}$ ~0 Hz, H-2), 5.66 ($J_{3,4}$ 3.2 Hz, H-3), 5.04 ($J_{4,5} = J_{4,5'} = 7$ Hz, H-4), 3.4–3.7 (H-5,5'), 5.86 (orthoformate-H), and 3.44 (OMe). ^{13}C-N.m.r. data ($CDCl_3$): 104.3 (C-1), 79.7, 82.6 (C-2,4), 76.0 (C-3), 26.0 (C-5), 116.9 (orthoformate-C), and 55.6 p.p.m. (OMe). ^{1}H-N.m.r. data ($CDCl_3$) of the minor compound: δ 6.17 ($J_{1,2}$ 3.8 Hz, H-1), 4.83 ($J_{2,3}$ ~0 Hz, H-2), 5.62 ($J_{3,4}$ 3.2 Hz, H-3), 4.59 ($J_{4,5} = J_{4,5'} = 7$ Hz, H-4), 3.4–3.7 (H-5,5'), 6.06 (orthoformate-H), and 3.30 (OMe). ^{13}C-N.m.r. data ($CDCl_3$): 105.0 (C-1), 79.2, 84.6 (C-2,4), 75.7 (C-3), 26.7 (C-5), 118.2 (orthoformate-C), and 50.7 p.p.m. (OMe).

The next fraction was syrupy **25c** (450 mg, 45%). ^{1}H-N.m.r. data ($CDCl_3$): δ 4.97 ($J_{1,2}$ 4 Hz, H-1), 4.3 ($J_{2,3}$ 6, $J_{4,5}$ 4, $J_{4,5'}$ 7.2 Hz, H-2,4), 5.76 ($J_{3,4}$ 8 Hz, H-3), 4.47 ($J_{5,5'}$ 12 Hz, H-5), 4.68 (H-5'), 8.11 (*H*CO), and 3.41 (OMe). ^{13}C-N.m.r. data

$CDCl_3$): 102.7 (C-1), 48.0 (C-2), 78.4 (C-3), 79.7 (C-4), 65.3 (C-5), 55.7 (OMe), and 159.9 p.p.m. (HCO).

Treatment of **25c** (450 mg) with methanol (10 ml) containing 2 drops of conc. HCl at room temperature for 2 h gave, after work-up, **25a** (300 mg, 72%), m.p. 106–109°. Recrystallisation from ether–pentane gave material having m.p. 108–110°, $[\alpha]_D^{20}$ −82° (*c* 1.48, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 4.90 ($J_{1,2}$ 4.4 Hz, H-1), 4.11 ($J_{2,3}$ 9 Hz, H-2), 4.57 ($J_{3,4}$ 7 Hz, H-3), 4.19 ($J_{4,5}$ 4, $J_{4,5'}$ 5.3 Hz, H-4), 4.41 ($J_{5,5'}$ 12 Hz, H-5), 4.54 (H-5'), and 3.40 (OMe). ^{13}C-N.m.r. data ($CDCl_3$): 102.4 (C-1), 52.4 (C-2), 76.9 (C-3), 80.3 (C-4), 64.8 (C-5), and 55.4 p.p.m. (OMe).

Anal. Calc. for $C_{13}H_{15}BrO_5$: C, 47.15; H, 4.57; Br, 24.13. Found: C, 47.07; H, 4.52; Br, 24.00.

When the reaction was carried out with a large excess of DBE (5 ml), the 2-formate **23** was transformed into a 2,5-dibromo-2,5-dideoxy derivative isolated as the glycoside (**24**, 4%), together with **25c** (51%) and **25a** (11%), after p.l.c. (ethyl acetate–hexane, 1:1). ^{1}H-N.m.r. data for **24** ($CDCl_3$): δ 5.09 ($J_{1,2}$ 4.5 Hz, H-1), 4.41 ($J_{2,3}$ 5.5 Hz, H-2), 5.81 ($J_{3,4}$ 5.5 Hz, H-3), 4.71 ($J_{4,5} = J_{4,5'} = 5.8$ Hz, H-4), 3.3–3.6 (H-5,5'), and 3.51 (OMe). ^{13}C-N.m.r. data ($CDCl_3$): 101.8 (C-1), 49.0 (C-2), 76.1 (C-3), 79.1 (C-4), 29.0 (C-5), and 56.2 p.p.m. (OMe).

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