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STUDIES ON THE REACTIVITIES OF THE SECONDARY HYDROXYL GROUPS IN 1,6-ANHYDRO-4′,6′-*O*-BENZYLIDENE-β-LACTOSE BY SELECTIVE BENZOYLATION*†

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ABSTRACT

Selective benzoylation of 1,6-anhydro-4′,6′-*O*-benzylidene-β-lactose (**1**), using 2.1 molar equivalents of benzoyl chloride in pyridine at −20°, yielded five benzoates which were designated **2** to **6** in order of decreasing R_F value on t.l.c. After column chromatography on silica gel, compounds **2**–**6** were separated as the 2,2′,3,3′-tetrabenzoate (**2**, 3%), 2,3,3′-tribenzoate (**3**, 11%), 2,2′,3′-tribenzoate (**4**, 5%), 2,3′-dibenzoate (**5**, 30%), and 3′-benzoate (**6**, 22%), respectively. Selective benzoylation of **5**, using 1.1 molar equivalents of benzoyl chloride, afforded **2**, **3**, and **4** in yields of 15, 56, and 8%, respectively, together with 5% of **5**. Thus, the order of reactivities of the secondary hydroxyl groups in **1** is 3′>2>3>2′. Compounds **3**–**6** have potential value in the chemical modification of lactose or the synthesis of lactose-containing oligosaccharides.

INTRODUCTION

In studies of chemical modifications of reducing disaccharides, 1,6-anhydro derivatives of β-lactose, cellobiose, and maltose are useful starting materials[1–7]. 1,6-Anhydro-6-thio-β-lactose[1], 6-acetamido-6-deoxylactose[2], 6′-acetamido-6′-deoxy-α-lactose[3], and other derivatives modified at position 6 in lactose[4] were synthesized from 1,6-anhydro-β-lactose derivatives. 4′-Acetamido-4′-deoxy-α-lactose was also synthesized, together with 6′-acetamido-6′-deoxy-α-cellobiose, from 1,6-anhydro-β-cellobiose[5]. 1,6-Anhydro-6-thio derivatives of β-cellobiose[6] and maltose[7] have also been synthesized and contain a sulphur atom in the reducing moiety.

In the preceding paper[3], benzylidenation of 1,6-anhydro-β-lactose was reported to yield 1,6-anhydro-4′,6′-*O*-benzylidene-β-lactose (**1**). Compound **1** contains only unblocked secondary hydroxyl groups, of which those in the reducing moiety are *trans*-diaxial and those in the non-reducing moiety are *trans*-diequatorial. Therefore,

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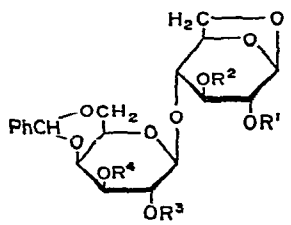
the reactions of **1** are of potential interest in relation to obtaining intermediates for the selective modification of particular secondary hydroxyl groups in lactose. We now report on the partial benzoylation of **1**.

RESULTS AND DISCUSSION

Benzoylation of **1** with 2.1 molar equivalents of benzoyl chloride in pyridine at −20° gave five products (t.l.c.) designated **2** to **6** in order of decreasing R_F value; **5** and **6** preponderated. Products **2**–**6** were isolated by column chromatography on silica gel.

Compound **2** was obtained in 3% yield, and was identified as 1,6-anhydro-2,2′,3,3′-tetra-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**2**) by comparison with an authentic sample.



1	R^1=R^2=R^3=R^4=H	7	R^1=R^2=R^4=Bz ; R^3=Ac
2	R^1=R^2=R^3=R^4=Bz	8	R^1=R^2=R^4=Bz ; R^3=Me
3	R^1=R^2=R^4=Bz ; R^3=H	9	R^1=R^3=R^4=Bz ; R^2=Ac
4	R^1=R^3=R^4=Bz ; R^2=H	10	R^1=R^3=R^4=Bz ; R^2=Me
5	R^1=R^4=Bz ; R^2=R^3=H	11	R^1=R^4=Bz ; R^2=R^3=Ac
6	R^1=R^2=R^3=H ; R^4=Bz	12	R^1=R^4=Bz ; R^2=R^3=Me
		13	R^1=R^2=R^3=Ac ; R^4=Bz
		14	R^1=R^2=R^3=Me ; R^4=Bz

Compound **3**, isolated in 11% yield, gave a crystalline acetate (**7**, 84%), in the ^{1}H-n.m.r. spectrum of which the signal for acetyl protons appeared at τ 8.05 as a singlet. From the ratio of acetyl to total protons, **7** was identified as an *O*-acetyl-tri-*O*-benzoyl derivative of **1**.

Methylation of **3** with diazomethane–boron trifluoride etherate, a reagent which does not cause acyl migration[8], yielded a crystalline tri-*O*-benzoyl-*O*-methyl derivative (**8**, 62%) of **1**, as indicated by n.m.r.-spectral and elemental analytical data. The location of the methyl group in **8** was determined as follows. Debenzoylation of **8** with methanolic sodium methoxide and debenzylidenation of the resulting syrup by palladium-catalysed hydrogenolysis afforded a syrupy product which, when hydrolyzed with dilute sulphuric acid, gave glucose and 2-*O*-methylgalactose, identified by p.c. Thus **3**, **7**, and **8** were assigned the structures 1,6-anhydro-2,3,3′-tri-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**3**), 2′-*O*-acetyl-1,6-anhydro-2,3,3′-tri-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**7**), and 1,6-anhydro-2,3,3′-tri-*O*-benzoyl-4′,6′-*O*-benzylidene-2′-*O*-methyl-β-lactose (**8**), respectively.

Eluted subsequent to **3** in column chromatography was a syrup which contained (t.l.c., benzene–ether) two components, R_F 0.45 (minor) and 0.38 (major) After further column chromatography, the major component (**4**, 5%) was obtained chromatographically homogeneous.

On acetylation, **4** afforded a crystalline acetate (**9**, 49%), and methylation as described above gave a chromatographically homogeneous, amorphous methyl ether (**10**), the low yield (36%) of which is attributed to the repeated chromatography necessary for purification.

After debenzoylation, debenzylidenation, and acid hydrolysis, the methyl group in **10** was shown to be located at C-3. Therefore, the following structures were assigned: 1,6-anhydro-2,2′,3′-tri-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**4**), 3-*O*-acetyl-1,6-anhydro-2,2′,3′-tri-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**9**), and 1,6-anhydro-2,2′,3′-tri-*O*-benzoyl-4′,6′-*O*-benzylidene-3-*O*-methyl-β-lactose (**10**).

Compound **5**, the major product (30%) in the selective benzoylation, yielded a crystalline diacetate (**11**, 91%) and an amorphous dimethyl ether (**12**, 68%). By using procedures similar to those described for **8** and **10**, the following structures were assigned: 1,6-anhydro-2,3′-di-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**5**), 2′,3-di-*O*-acetyl-1,6-anhydro-2,3′-di-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**11**), and 1,6-anhydro-2,3′-di-*O*-benzoyl-4′,6′-*O*-benzylidene-2′,3-di-*O*-methyl-β-lactose (**12**).

Compound **6** (22%, after rechromatography) was a hygroscopic, amorphous powder which yielded a crystalline triacetate (**13**, 64%) and a trimethyl ether (**14**, 54%). Using the procedures described above, the structures 1,6-anhydro-3′-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**6**), 2,2′,3-tri-*O*-acetyl-1,6-anhydro-3′-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**13**), and 1,6-anhydro-3′-*O*-benzoyl-4′,6′-*O*-benzylidene-2,2′,3-tri-*O*-methyl-β-lactose (**14**) were assigned.

The yields of **2**–**6** suggest that the reactivity of the hydroxyl groups in **1** is HO-3′>HO-2>HO-3 and HO-2′. The order of reactivity of HO-3 and HO-2′ was determined by selective benzoylation of **5** with 1.1 molar equivalents of benzoyl chloride. Column chromatography of the product mixture afforded **2**, **3**, and **4** in yields of 15, 56, and 8%, respectively, together with 5% of unreacted **5**. The greater yield of **3** than that of **4** indicates the reactivity sequence HO-3>HO-2′.

Thus, in **1**, HO-2′ has the lowest reactivity. Molecular models suggest that, because the conformation of the galactose moiety in **1** is fixed by the 1,3-dioxane ring, the bulky 1,6-anhydro-β-D-glucosidic residue strongly hinders HO-2′. Data[9] on the selective benzoylation of 1,6-anhydro-4′,6′-*O*-benzylidene-β-maltose suggest that HO-2′ is more reactive than in the lactose series.

There have been few reports on the reactivities of the secondary hydroxyl groups in lactose or its derivatives. Vazquez *et al.*[10] showed that selective benzoylation of lactose afforded the heptabenzoate having HO-3 unsubstituted. A study of the selective benzoylation of methyl β-lactoside[11] indicates the reactivity sequence 6′>3′>6>2>2′,4′>3 for the hydroxyl groups.

Compounds **3**–**6** are of potential value in the chemical modification of lactose and the synthesis of lactose-containing oligosaccharides.

EXPERIMENTAL

General. — Melting points are uncorrected. Solutions were concentrated *in vacuo* in a rotary evaporator at <40°. Optical rotations were measured in a 0.5-dm cell with a Yanagimoto OR-10 automatic polarimeter. I.r. spectra were recorded for Nujol mulls with a Jasco Model IR-S spectrophotometer. N.m.r. spectra were recorded at 100 MHz with a Jeol Model JNM-MH-100 spectrometer for solutions in $CDCl_3$ (internal Me_4Si). T.l.c. was performed on Silica Gel GF_{254} (Merck) activated at 110°, using *A*, 6:1 chloroform–acetone; *B*, 3:1 chloroform–acetone; *C*, 1:1 benzene–ether; and *D*, ether. Detection was effected with sulfuric acid or u.v. light. Column chromatography was performed on Wakogel C-200 (Wako Pure Chemical Industries Ltd., Osaka) (1 g of mixture per 20 g of adsorbent). Paper chromatography was performed on Toyo Filter Paper No. 50 (Toyo Roshi Kaisha, Ltd., Tokyo) by the ascending method using 6:4:3 1-butanol–pyridine–water[12], and detection with *A*, alkaline silver nitrate[13]; and *B*, aniline hydrogen phthalate[14].

1,6-Anhydro-4',6'-O-benzylidene-β-lactose (**1**). — A mixture of 1,6-anhydro-β-lactose (25 g, 77.2 mmol), powdered zinc chloride (25 g, 183.4 mmol), and freshly distilled benzaldehyde (250 ml, 2.46 mol) was shaken overnight at room temperature. After the addition of water (250 ml) and methanol (25 ml), the excess benzaldehyde was extracted with light petroleum (3 × 100 ml), and the organic layers were discarded. To the aqueous layer was added sodium carbonate (25 g, 235.8 mmol) portionwise with stirring. After 1 h, the mixture was filtered, the residue was washed with water, and the combined filtrate and washings were concentrated to dryness. The residue was extracted with dry acetone (8 × 200 ml), and the combined extracts were concentrated to dryness to give **1** as a hygroscopic, amorphous powder (25.8 g, 81%), $[\alpha]_D^{25}$ −64° (*c* 1.1, water).

Anal. Calc. for $C_{19}H_{24}O_{10}\cdot 0.5H_2O$: C, 54.16; H, 5.98. Found: C, 54.29; H, 5.88.

Compound **1** gave a tetra-acetate, m.p. 232–233° (from ethyl acetate), $[\alpha]_D^{26}$ +10° (*c* 1, chloroform), and a tetrabenzoate, m.p. 228–230°, $[\alpha]_D^{25}$ +113.5° (*c* 1.1, chloroform).

Selective benzoylation of 1,6-anhydro-4',6'-O-benzylidene-β-lactose (**1**). — To a chilled solution of **1** (4 g, 9.7 mmol) in dry pyridine (24 ml), benzoyl chloride (2.4 ml, 20.7 mmol) was added dropwise with stirring at −20°, and the stirring was continued, with the exclusion of moisture, for a further 1 h. The mixture was stored overnight at 5°, then treated with ice to decompose unreacted benzoyl chloride, and concentrated to dryness by repeated co-distillation with toluene. A solution of the residue in dichloromethane (200 ml) was washed with water (3 × 50 ml), dried (Na_2SO_4), and concentrated to dryness. The crystalline residue contained five components having R_F 0.98, 0.84, 0.40, 0.27 (major), and 0.05 (t.l.c., solvent *B*). Elution of the mixture from silica gel with dichloromethane, and 6:1, 3:1, and 1:1 chloroform–acetone gave the following products.

The component having R_F 0.98 crystallized from ethanol, and recrystallization

from ethanol–ethyl acetate gave a product (242 mg, 3%), m.p. 227–229°, $[\alpha]_D^{20}$ +110° (*c* 0.5, chloroform), which was indistinguishable (mixture m.p., i.r. spectrum, and t.l.c.) from 1,6-anhydro-2,2′,3,3′-tetra-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose[3] (**2**).

The component (774 mg, 11%) having R_F 0.84 was 1,6-anhydro-2,3,3′-tri-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**3**), which had m.p. 223–224° (from ethanol), $[\alpha]_D^{23}$ +68° (*c* 1.2, chloroform); R_F 0.53 (solvent *A*), 0.84 (solvent *B*), 0.55 (solvent *C*), and 0.75 (solvent *D*); ν_{max} 3535 cm^{-1} (OH).

Anal. Calc. for $C_{40}H_{36}O_{13}$: C, 66.29; H, 5.01. Found: C, 66.54; H, 5.29.

The component having R_F 0.40 was found to be a mixture of products, R_F 0.45 (minor) and 0.38 (major), on t.l.c. (solvent *C*, fourfold development). Elution of the mixture from silica gel with 3:1 benzene–ether gave 1,6-anhydro-2,2′,3′-tri-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**4**; 352 mg, 5%) as an amorphous powder, $[\alpha]_D^{22}$ +37° (*c* 0.7, chloroform); R_F 0.14 (solvent *A*), 0.40 (solvent *B*), 0.13 (solvent *C*), and 0.30 (solvent *D*); ν_{max} 3460 cm^{-1} (OH).

Anal. Calc. for $C_{40}H_{36}O_{13}$: C, 66.29; H, 5.01. Found: C, 66.28; H, 5.04.

Recrystallization of the component having R_F 0.27 gave 1,6-anhydro-2,3′-di-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**5**; 1.81 g, 30%), m.p. 243–245° (from methanol), $[\alpha]_D^{23}$ +61.5° (*c* 1, acetone); R_F 0.07 (solvent *A*), 0.27 (solvent *B*), 0.07 (solvent *C*), and 0.16 (solvent *D*); ν_{max} 3440 cm^{-1} (OH).

Anal. Calc. for $C_{33}H_{32}O_{12}$: C, 63.87; H, 5.20. Found: C, 63.58; H, 5.02.

The component having R_F 0.05 was a syrup which contained two products, R_F 0.46 (major) and 0.27 (minor) (t.l.c., 1:1 chloroform–acetone). Elution of the mixture from silica gel with 3:1 chloroform–acetone afforded, as the faster-moving product, 1,6-anhydro-3′-*O*-benzoyl-4′,6′-*O*-benzylidene-β-lactose (**6**; 1.1 g, 22%) as a hygroscopic, amorphous powder, $[\alpha]_D^{11}$ +19° (*c* 1.1, acetone); R_F 0.02 (solvent *A*), 0.05 (solvent *B*), and 0.02 (solvent *C*), and 0.03 (solvent *D*); ν_{max} 3100–3600 cm^{-1} (OH).

Anal. Calc. for $C_{26}H_{28}O_{11}\cdot H_2O$: C, 58.42; H, 5.66. Found: C, 58.61; H, 5.45.

2′-O-Acetyl-1,6-anhydro-2,3,3′-tri-O-benzoyl-4′,6′-O-benzylidene-β-lactose (**7**). — Compound **3** (200 mg) was conventionally acetylated with acetic anhydride (5 ml) and pyridine (5 ml) for 24 h at room temperature. Crystallization of the product from ethanol gave **7** (177 mg, 84%), m.p. 158–159°, $[\alpha]_D^{18}$ +79° (*c* 1.3, chloroform); R_F 0.76 (solvent *A*), 0.89 (solvent *B*), and 0.62 (solvent *C*). N.m.r. data: τ 8.05 (s, 3 H, OAc).

Anal. Calc. for $C_{42}H_{38}O_{14}$: C, 65.79; H, 5.00. Found: C, 65.51; H, 5.23.

1,6-Anhydro-2,3,3′-tri-O-benzoyl-4′,6′-O-benzylidene-2′-O-methyl-β-lactose (**8**). — To a solution of **3** (300 mg) in dry dichloromethane (5 ml) maintained at 0°, boron trifluoride etherate (2 drops) was added followed by a solution of diazomethane in dichloromethane until a faint yellow colour persisted. After 30 min at 0°, the mixture was stored overnight at room temperature, then filtered, and washed successively with 10% aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and concentrated. Recrystallization of the syrupy residue from ethanol gave **8** (190 mg, 62%),

m.p. 226–227°, $[\alpha]_D^{24}$ +75° (*c* 1.1, chloroform); R_F 0.74 (solvent *A*), 0.91 (solvent *B*), 0.70 (solvent *C*), and 0.82 (solvent *D*). N.m.r. data: τ 6.37 (s, 3 H, OMe).

Anal. Calc. for $C_{41}H_{38}O_{13}$: C, 66.66; H, 5.18. Found: C, 66.40; H, 4.92.

Identification of the component monosaccharides in **8**. — To a suspension of **8** (100 mg) in dry methanol (10 ml), methanolic sodium methoxide (0.5M, 0.2 ml) was added at room temperature and the mixture was stirred, with exclusion of moisture, for 3 h. Debenzoylation was monitored by t.l.c. Dry Amberlite IR-120 (H^+) resin was added, and the suspension was stirred for 30 min, then filtered, and concentrated to dryness. To a solution of the syrupy residue in methanol (10 ml), palladium catalyst [freshly prepared from palladium chloride[16] (100 mg)] was added and the mixture was hydrogenated with stirring at room temperature and atmospheric pressure; the theoretical amount of hydrogen was absorbed in 30 min. The mixture was filtered and concentrated, and a solution of the syrupy residue in 0.5M sulphuric acid (5 ml) was kept at ~95° for 2 h. The hydrolysate was neutralized with barium carbonate, filtered, and, after treatment with carbon, concentrated to a thin syrup, in which glucose and 2-*O*-methylgalactose[15] (R_{GLC} 1.35) were identified by p.c.

3-O-Acetyl-1,6-anhydro-2,2',3'-tri-O-benzoyl-4',6'-O-benzylidene-β-lactose (**9**). — Conventional acetylation of **4** (200 mg) with acetic anhydride (5 ml) and pyridine (5 ml) for 24 h at room temperature gave **9** (103 mg, 49%), m.p. 231–232°, $[\alpha]_D^{24}$ +84° (*c* 0.3, chloroform); R_F 0.64 (solvent *A*), 0.81 (solvent *B*), and 0.36 (solvent *C*). N.m.r. data: τ 7.90 (s, 3 H, OAc).

Anal. Calc. for $C_{42}H_{38}O_{14}$: C, 65.79; H, 5.00. Found: C, 65.86; H, 4.81.

1,6-Anhydro-2,2',3'-tri-O-benzoyl-4',6'-O-benzylidene-3-O-methyl-β-lactose (**10**). — To a chilled mixture of **4** (300 mg) in dry dichloromethane (10 ml) and boron trifluoride etherate (2 drops), a solution of diazomethane in dichloromethane was added at 0° until a faint yellow colour persisted. The mixture was processed, as described above for **8**, to afford syrupy **10** contaminated with a small proportion of by-products (t.l.c., solvent *B*). Elution of the product from silica gel, using 3:1 benzene–ether, afforded **10** (110 mg, 36%) as an amorphous powder, $[\alpha]_D^{17}$ +75.5° (*c* 1.3, chloroform); R_F 0.59 (solvent *A*), 0.81 (solvent *B*), 0.26 (solvent *C*), and 0.44 (solvent *D*). N.m.r. data: τ 6.54 (s, 3 H, OMe).

Anal. Calc. for $C_{41}H_{38}O_{13}$: C, 66.66; H, 5.18. Found: C, 66.62; H, 5.18.

Identification of the component monosaccharides in **10**. — Compound **10** (100 mg) was successively debenzoylated, debenzylidenated, and hydrolyzed with dilute sulphuric acid, as described above for **8**. The product contained galactose (R_{GLC} 0.89) and 3-*O*-methylglucose[17] (R_{GLC} 1.51), which were identified by p.c.

2',3-Di-O-acetyl-1,6-anhydro-2,3'-di-O-benzoyl-4',6'-O-benzylidene-β-lactose (**11**). — Conventional acetylation of **5** (200 mg) with acetic anhydride (5 ml) and pyridine (5 ml) gave **11** (206 mg, 91%), m.p. 236–237°, $[\alpha]_D^{22}$ +66° (*c* 1.2, chloroform); R_F 0.58 (solvent *A*), 0.72 (solvent *B*), and 0.24 (solvent *C*). N.m.r. data: τ 7.87 and 8.04 (2 s, 6 H, 2 AcO).

Anal. Calc. for $C_{37}H_{36}O_{14}$: C, 63.06; H, 5.15. Found: C, 62.84; H, 4.95.

1,6-Anhydro-2,3'-di-O-benzoyl-4',6'-O-benzylidene-2',3-di-O-methyl-β-lactose

(**12**). — To a chilled mixture of **5** (300 mg) in dry dichloromethane (20 ml) and boron trifluoride etherate (2 drops), a solution of diazomethane in dichloromethane was added at 0° until a faint yellow colour persisted. The mixture was then processed, as described above for **8**, to afford syrupy **12** contaminated with a small proportion of a by-product (t.l.c., solvent *B*). Elution of the product from silica gel, using 6:1 chloroform–acetone, gave **12** (214 mg, 68%) as an amorphous powder, $[\alpha]_D^{22}$ +59° (*c* 1, chloroform); R_F 0.50 (solvent *A*), 0.77 (solvent *B*), 0.26 (solvent *C*), and 0.49 (solvent *D*). N.m.r. data: τ 6.38 and 6.48 (2 s, 6 H, 2 MeO).

Anal. Calc. for $C_{35}H_{36}O_{12}$: C, 64.81; H, 5.59. Found: C, 64.82; H, 5.36.

Identification of the component monosaccharides in **12**. — Compound **12** (100 mg), when treated as described above for **8**, gave 2-*O*-methylgalactose (R_{GLC} 1.35) and 3-*O*-methylglucose (R_{GLC} 1.51), which were identified by p.c.

2,2',3-Tri-O-acetyl-1,6-anhydro-3'-O-benzoyl-4',6'-O-benzylidene-β-lactose (**13**). — Conventional acetylation of **6** (200 mg) with acetic anhydride (5 ml) and pyridine (5 ml) gave **13** (160 mg, 64%), m.p. 180–181°, $[\alpha]_D^{23}$ +53° (*c* 0.6, chloroform); R_F 0.50 (solvent *A*), 0.67 (solvent *B*), and 0.22 (solvent *C*). N.m.r. data: τ 7.85, 7.88, and 8.03 (3 s, 9 H, 3 AcO).

Anal. Calc. for $C_{32}H_{34}O_{14}$: C, 59.81; H, 5.33. Found: C, 59.67; H, 5.43.

1,6-Anhydro-3'-O-benzoyl-4',6'-O-benzylidene-2,2',3-tri-O-methyl-β-lactose (**14**). — To a chilled mixture of **6** (500 mg) in dichloromethane (20 ml) and boron trifluoride etherate (2 drops), a solution of diazomethane in dichloromethane was added at 0° until a faint yellow colour persisted. The mixture was processed, as described above for **8**, to afford syrupy **14** contaminated with a small proportion of by-product (t.l.c., solvent *B*). Elution of the product from silica gel, using 10:1 chloroform–acetone, gave **14** (290 mg, 54%) as an amorphous powder, $[\alpha]_D^{21}$ +20° (*c* 0.9, chloroform); R_F 0.42 (solvent *A*), 0.69 (solvent *B*), 0.25 (solvent *C*), and 0.40 (solvent *D*). N.m.r. data: τ 6.38, 6.52, and 6.54 (3 s, 9 H, 3 MeO).

Anal. Calc. for $C_{29}H_{34}O_{11}$: C, 62.36; H, 6.14. Found: C, 62.13; H, 6.04.

Identification of the component monosaccharides in **14**. — Treatment of **14** (100 mg), as described above for **8**, gave 2-*O*-methylgalactose (R_{GLC} 1.35) and 2,3-di-*O*-methylglucose[18] (R_{GLC} 1.88), which were identified by p.c.

Selective benzoylation of **5**. — To a chilled solution of **5** (1 g, 1.61 mmol) in dry pyridine (6 ml), benzoyl chloride (0.2 ml, 1.72 mmol) was added dropwise with stirring at −20°. Stirring was continued, with the exclusion of moisture, for a further 1 h. The mixture was stored overnight at 5° and then treated as described above for the selective benzoylation of **1**. Elution of the product mixture from silica gel afforded **2** (203 mg, 15%), **3** (648 mg, 56%), and **4** (97 mg, 8%), together with unreacted **5** (50 mg, 5%).

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