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Note

Synthesis of the H-disaccharide (2-*O*-α-L-fucopyranosyl-D-galactose) *via* the trichloroacetimidate method*

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Many L-fucose-containing glycoconjugates have important biological functions in solution and on cell surfaces, including growth regulation, receptor function, cell–cell interactions, and antigenicity[2–8]. All glycoconjugates studied, thus far, contain α-L-fucose at non-reducing positions linked (1→2) to Gal, (1→3) to Glc, or (1→3), (1→4), or (1→6) to GlcNAc. Di- and oligo-saccharides with these linkages have been the targets of synthesis[9].

The successful application[10–12] of the trichloroacetimidate method to α-manno-, α-gluco-, and α-galacto-pyranosylation encouraged an investigation of α-fucosylation[13]. The target molecule was the title H-disaccharide, syntheses of which by other routes have been described[14–19].

Treatment of L-fucose with acidic ion-exchange resin in boiling methanol afforded crystalline methyl α-L-fucopyranoside[20] (**1**, 80–90% after recycling). Benzylation (→**2**) of **1** followed by hydrolysis then gave known[21] 2,3,4-tri-*O*-benzyl-L-fucopyranose (**3**). It was not possible to obtain the β-trichloroacetimidate as the kinetic product when **3** was treated with trichloroacetonitrile in dichloromethane with potassium carbonate as the catalyst. This finding contrasts with the results obtained with the corresponding glucose and galactose derivatives[10] and may be due to the lower acidity of HO-1 in the 6-deoxyhexose system. However, **3** was readily transformed into the crystalline α-trichloroacetimidate **4** by reaction with trichloroacetonitrile in dichloromethane at room temperature with sodium hydride as the catalyst.

Treatment of 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactose[22] (**5**) with **4** and trimethylsilyl triflate (TMSOTf)[23] as the catalyst in ether at room temperature gave 91% of a 9:1 α,β-mixture from which the crystalline α-glycoside **6α** was isolated. In agreement with previous results[10–12], the TMSOTf catalyst gives mainly the thermodynamically more-stable product. Catalysis with *tert*-butyldimethylsilyl

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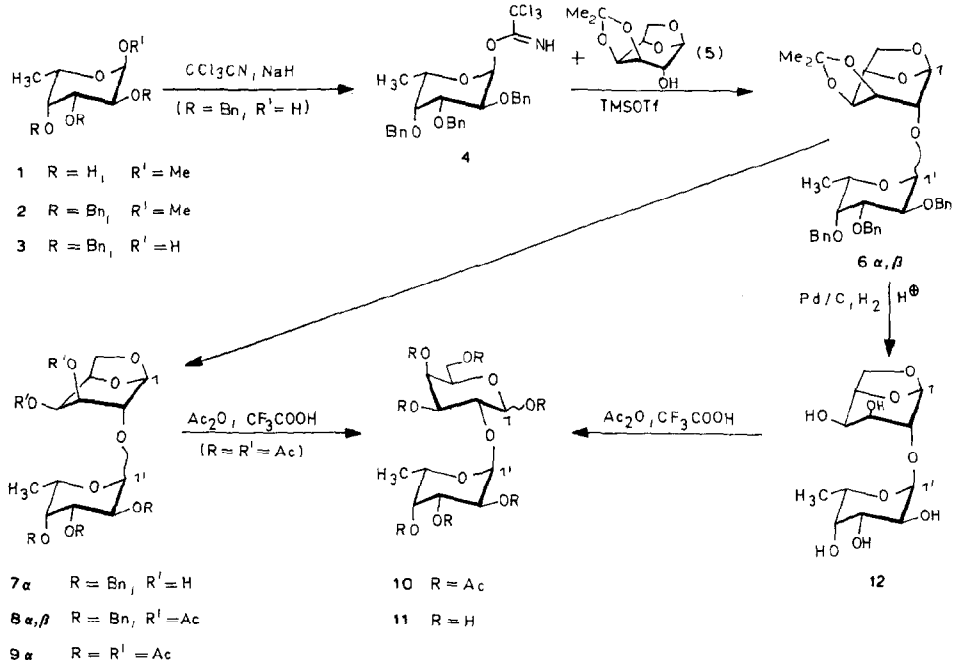

triflate[10] gave similar results. The glycosides **6α** and **6β** were characterised by n.m.r. techniques (^{1}H and ^{13}C, COSY and spin decoupling).

Treatment of **6α** with methanolic hydrochloric acid removed the isopropylidene group and afforded compound **7α** in better yields than when trifluoroacetic acid was used. Treatment of **7α** with acetic acid–acetic anhydride–trifluoroacetic acid acetylated the hydroxyl group (→**8α**) but did not cleave the 1,6-anhydro ring of the galactose unit. Similarly, **6α,β** gave **8α,β** which were characterised by n.m.r. methods.

Application of the boron trifluoride etherate–acetic anhydride method[24] to **8α** did not affect the 1,6-anhydro ring, but cleaved the glycosidic linkage probably due to the benzyl groups in the fucose unit. Therefore, **8α** was debenzylated by hydrogenolysis and acetylation then gave **9α**. Treatment of **9α** with acetic anhydride–trifluoroacetic acid cleaved the 1,6-anhydro ring to give known[16] **10α,β**. Zemplén deacetylation of **10** afforded the H-disaccharide, which had ^{1}H-n.m.r. and optical rotation data identical with those reported[14,16–18,25].

The results described led to the conclusion that, during opening of the 1,6-anhydro ring, the fucosyl glycoside bond will be less affected in an *O*-unprotected compound because *O*-acetylation of the fucose will take place during the reaction process. The required *O*-unprotected compound **12** could be obtained directly from **6α** by hydrogenolysis under acidic conditions, and treatment of **12** with acetic anhydride–trifluoroacetic acid gave a quantitative yield of **10**. Deacetylation then completed a high-yielding synthesis of the H-disaccharide **11**.

EXPERIMENTAL

General methods. — Melting points are uncorrected. ^{1}H- and ^{13}C-n.m.r. spectra (internal Me_4Si) were recorded with Bruker WM 250 Cryospec and Jeol JNM-GX 400 instruments. R_F values refer to t.l.c. on silica gel (Merck). Column chromatography was carried out on silica gel (Merck 70–230 mesh ASTM and 230–400 mesh ASTM for flash chromatography under normal pressure, and Merck LiChroprep Si 60, 40–60 μm, for medium-pressure operation). Light petroleum refers to the fraction b.p. 35–60°. Optical rotations were determined with a Perkin–Elmer 241 MC polarimeter. The glycoside synthesis was performed under dry nitrogen with molecular sieves (4 Å).

Methyl α-L-fucopyranoside (**1**). — Compound **1** was prepared[20] from L-fucose and the yield was increased to 80–90% (lit. 44%) by re-equilibrating the material in the mother liquors 3–4 times.

O-(2,3,4-Tri-O-benzyl-α-L-fucopyranosyl)trichloroacetimidate (**4**). — To a solution of **3**[21] (1.26 g, 2.9 mmol) in dry dichloromethane (20 mL) was added potassium carbonate (1.53 g) and trichloroacetonitrile (1.6 mL). The suspension was stirred vigorously for 6.5 h with the exclusion of moisture. Sodium hydride (75 mg) was added, and the mixture was stirred for 5 h, then filtered through Celite, washed with water, and concentrated under reduced pressure. The residue crystallised from dry ether–light petroleum (1:1, 50 mL) to give **4** (0.84 g, 50%), m.p. 88–90°, $[\alpha]_{589}^{20}$ −60° $[\alpha]_{578}^{20}$ −61.5° (*c* 1, chloroform); R_F 0.70 (1:1 ether–light petroleum); ν_{max}^{KBr} 3340 (N–H), 1670 cm^{-1} (C=N). N.m.r. data ($CDCl_3$): ^{1}H (250 MHz), δ 8.50 (s, 1 H, NH), 7.38–7.22 (m, 15 H, 3 Ph), 6.50 (d, 1 H, $J_{1,2}$ 3.66 Hz, H-1), 5.03–4.65 (m, 6 H, 3 PhCH_2), 4.24 (dd, 1 H, $J_{1,2}$ 3.66, $J_{2,3}$ 10.07 Hz, H-2), 4.09 (q, 1 H, J_{5,CH_3} 6.41, $J_{4,5}$ <1 Hz, H-5), 4.02 (dd, 1 H, $J_{2,3}$ 10.07, $J_{3,4}$ 2.14 Hz, H-3), 3.70 (d, 1 H, $J_{3,4}$ 2.14, $J_{4,5}$ <1 Hz, H-4), and 1.16 (d, 3 H, J_{5,CH_3} 6.41 Hz, CH_3); ^{13}C (62.97 MHz), δ 160.85 (C=N), 94.88 (C-1), 91.17 (CCl_3), and 16.62 (CH_3). The mother liquor contained more **4**, which was isolated as an oil (~20%).

Anal. Calc. for $C_{29}H_{30}Cl_3NO_5$ (578.91): C, 60.16; H, 5.22; Cl, 18.37; N, 2.42. Found: C, 59.94; H, 5.25; Cl, 18.26; N, 2.31.

1,6-Anhydro-3,4-O-isopropylidene-2-O-(2,3,4-tri-O-benzyl-α- and -β-L-fucopyranosyl)-β-D-galactopyranose (**6α** *and* **6β**). — To a solution of **5**[22] (70 mg, 0.35 mmol) and **4** (297 mg, 0.51 mmol) in dry ether (20 mL) at room temperature was added trimethylsilyl triflate (0.15 mmol), and the mixture was stirred for 5 h. T.l.c. (1:1 light petroleum–ether) then revealed one major product. Sodium hydrogencarbonate (1 g) was added, and the mixture was stirred for 15 min, then filtered, and extracted with ether. The extract was washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated to dryness. Column chromatography (1:1 light petroleum–ether) or flash chromatography (2:1 light petroleum–ether) of the residue yielded **6α** (175 mg, 82%), m.p. 103–104° (from light petroleum–ether), $[\alpha]_{589}^{22}$ −7.7°, $[\alpha]_{578}^{22}$ −8.2° (*c* 1, chloroform); R_F 0.42 (1:1 light petroleum–ether). N.m.r. data ($CDCl_3$): ^{1}H (400 MHz, and 2D-COSY), δ 7.47–7.19 (m, 15 H, 3 Ph),

5.43 (s, 1 H, H-1), 4.98–4.61 (m, 7 H, 3 PhCH_2, and including, at δ 4.91, H-1′, d, $J_{1',2'}$ 3.67 Hz), 4.47–4.40 (m, 2 H, $J_{3,4}$ 6.96, $J_{5,6}$ 5.62 Hz, H-4,6), 4.24 (d, 1 H, $J_{3,4}$ 6.96 Hz, H-3), 4.08 (d, 1 H, $J_{5,6}$ 7.33, $J_{6,6}$ <1 Hz, H-6), 4.04 (dd, 1 H, $J_{1',2'}$ 3.67, $J_{2',3'}$ 10.25 Hz, H-2′), 3.98 (q, 1 H, J_{5',CH_3} 6.59 Hz, H-5′), 3.94 (dd, 1 H, $J_{2',3'}$ 10.25, $J_{3',4'}$ 2.20 Hz, H-3′), 3.71 (s, 1 H, H-2), 3.68 (d, 1 H, $J_{3',4'}$ 2.20, $J_{4',5'}$ <1 Hz, H-4′), 3.53 (dd, 1 H, $J_{5,6}$ 5.62, $J_{5,6}$ 7.33, $J_{4,5}$ <1 Hz, H-5), 1.51 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), and 1.12 (d, 3 H, J_{5',CH_3} 6.59 Hz, CH_3); ^{13}C (99.98 MHz), δ 108.46 (acetal-C), 100.41 (C-1), 99.13 (C-1′), 25.76 (CCH_3), 24.34 (CCH_3), and 16.59 (fucose CH_3).

Eluted second was **6β** (19 mg, 9%), isolated as a colourless oil, $[\alpha]_{589}^{25}$ −93.5°, $[\alpha]_{578}^{25}$ −96.5° (*c* 1, chloroform); R_F 0.38. N.m.r. data: ^1H, δ 7.40–7.26 (m, 15 H, 3 Ph), 5.46 (s, 1 H, H-1), 5.00–4.70 (m, 6 H, 3 PhCH_2), 4.54–4.41 (m, 4 H, H-3,4,6, and including, at δ 4.45, H-1′, d, $J_{1',2'}$ 7.69 Hz), 4.10 (d, 1 H, $J_{5,6}$ 7.33, $J_{6,6}$ <1 Hz, H-6), 3.84 (s, 1 H, H-2), 3.81 (dd, 1 H, $J_{1',2'}$ 7.69, $J_{2',3'}$ 9.64 Hz, H-2′), 3.59 (dd, 1 H, $J_{5,6}$ 5.37, $J_{5,6}$ 7.33, $J_{4,5}$ <1 Hz, H-5), 3.55 (d, 1 H, $J_{3',4'}$ 2.69, $J_{4',5'}$ <1 Hz, H-4′), 3.50 (dd, 1 H, $J_{2',3'}$ 9.64, $J_{3',4'}$ 2.69 Hz, H-3′), 3.44 (q, 1 H, J_{5',CH_3} 6.72 Hz, H-5′), 1.52 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), and 1.14 (d, 3 H, J_{5',CH_3} 6.72 Hz, CH_3); ^{13}C, δ 108.26 (acetal-C), 104.53 (C-1′), 99.87 (C-1), 25.79 (CCH_3), 24.42 (CCH_3), and 16.76 (fucose CH_3).

Anal. Calc. for $C_{36}H_{42}O_9$ (618.7): C, 69.88; H, 6.84. Found: for **6α**, C, 69.60; H, 6.89; for **6β**, C, 69.52; H, 6.79.

When *tert*-butyldimethylsilyl triflate was used as a catalyst[10], similar results were obtained.

1,6-Anhydro-2-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-β-D-galactopyranose (**7α**). — (*a*) To a solution of **6α** (80 mg, 0.13 mmol) in dichloromethane (3 mL) at room temperature was added trifluoroacetic acid (60%, 0.5 mL). The mixture was stirred overnight, when the reaction was still incomplete (t.l.c.). More trifluoroacetic acid (60%, 0.5 mL) was added, the mixture was boiled under reflux for 1 h, and the organic phase was washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated to dryness. Column chromatography (1:1 light petroleum–ethyl acetate) of the residue yielded **7α** (45–52 mg, 60–69%; yield not optimised), isolated as a colourless oil, $[\alpha]_{589}^{22}$ −53.5°, $[\alpha]_{578}^{22}$ −55.5° (*c* 1, chloroform); R_F 0.24 (1:1 light petroleum–ethyl acetate). N.m.r. data ($CDCl_3$): ^1H (250 MHz), δ 7.42–7.26 (m, 15 H, 3 Ph), 5.45 (s, 1 H, H-1), 5.00–4.58 (m, 7 H, 3 PhCH_2, and including, at δ 4.86, H-1′, d, $J_{1',2'}$ 3.66 Hz), 4.40 (dd, 1 H, $J_{5,6}$ 4.23, $J_{4,5}$ <1 Hz, H-5), 4.18 (d, 1 H, $J_{5,6}$ 7.94 Hz, H-6), 4.06–3.88 (m, 5 H), 3.69 (d, 1 H, $J_{3',4'}$ 1.53, $J_{4',5'}$ <1 Hz, H-4′), 3.62–3.57 (m, 2 H), 3.00 (d, 1 H, $J_{H,OH}$ 8.24 Hz, OH, exchangeable by CD_3OD), 2.67 (d, 1 H, $J_{H,OH}$ 7.32 Hz, OH, exchangeable by CD_3OD), and 1.10 (d, 3 H, J_{5',CH_3} 6.41 Hz, CH_3); ^{13}C (99.98 MHz), δ 100.91 (C-1), 98.97 (C-1′), and 16.55 (fucose CH_3).

Anal. Calc. for $C_{33}H_{38}O_9$ (578.63): C, 68.49; H, 6.62. Found: C, 68.04; H, 6.63.

(*b*) Compound **6α** (219 mg, 0.35 mmol) was treated with M hydrochloric acid (0.5 mL) in methanol (2.5 mL) at 40° overnight to give, after work-up, **7α** (174 mg, 85%), m.p. 49–50° (from light petroleum–ether).

3,4-Di-O-acetyl-1,6-anhydro-2-O-(2,3,4-tri-O-benzyl-α- and -β-L-fucopyranosyl)-β-D-galactopyranose (**8α** *and* **8β**). — To a solution of **6α,β** (5.1 g, 8.24 mmol) in dichloromethane (100 mL) at room temperature was added trifluoroacetic acid (60%, 13.5 mL). The mixture was boiled under reflux for 19 h, then washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated to dryness. Column chromatography (as for **7α**) of the residue gave **7α,β** (1.8 g, 3.11 mmol), which was stirred with dry pyridine (40 mL) and dry acetic anhydride (20 mL) overnight at room temperature. The mixture was concentrated and the remaining pyridine was removed by repeated evaporation of toluene from the oily residue. Flash chromatography (2:1 or 1:1 light petroleum–ethyl acetate) then yielded amorphous **8α** (1.67 g, 81%), $[\alpha]_{589}^{22}$ −43°, $[\alpha]_{578}^{22}$ −44.5° (*c* 1, chloroform); R_F 0.72 (1:1 light petroleum–ethyl acetate). N.m.r. data ($CDCl_3$): ^1H (400 MHz and 2D-COSY), δ 7.41–7.22 (m, 15 H, 3 Ph), 5.42 (s, 1 H, H-1), 5.30 (dd, 1 H, $J_{2,3}$ 1.22, $J_{3,4}$ 4.86 Hz, H-3), 5.27 (dd, 1 H, $J_{3,4}$ 4.86, $J_{4,5}$ <1 Hz, H-4), 4.99–4.62 (m, 7 H, 3 PhCH_2, and including, at δ 4.94, H-1′, d, $J_{1',2'}$ 3.67 Hz), 4.47 (dd, 1 H, $J_{5,6}$ 3.91, $J_{4,5}$ <1 Hz, H-5), 4.31 (d, 1 H, $J_{5,6}$ 7.57 Hz, H-6), 4.02 (dd, 1 H, $J_{1',2'}$ 3.67, $J_{2',3'}$ 10.13 Hz, H-2′), 3.98 (q, 1 H, J_{5',CH_3} 6.35 Hz, H-5′), 3.94 (dd, 1 H, $J_{2',3'}$ 10.13, $J_{3',4'}$ 2.69 Hz, H-3′), 3.70–3.67 (m, H-4′,6), 3.57 (s, 1 H, H-2), 2.12 (s, 3 H, CH_3), 2.05 (s, 3 H, CH_3), and 1.10 (d, 3 H, J_{5',CH_3} 6.35 Hz, CH_3); ^{13}C (62.97 MHz), δ 169.67 (>C=O), 169.15 (>C=O), 100.33 (C-1), 98.44 (C-1′), 20.98 (CH_3, acetyl), 20.73 (CH_3, acetyl), and 16.54 (CH_3, fucose).

Eluted second was amorphous **8β** (0.13 g, 6%), $[\alpha]_{589}^{22}$ +4.5°, $[\alpha]_{578}^{22}$ +5° (*c* 1, chloroform); R_F 0.60. N.m.r. data ($CDCl_3$): ^1H, δ 7.39–7.25 (m, 15 H, 3 Ph), 5.62 (dd, 1 H, $J_{2,3}$ 1.46, $J_{3,4}$ 4.94 Hz, H-3), 5.41 (s, 1 H, H-1), 5.31 (dd, 1 H, $J_{3,4}$ 4.94, $J_{4,5}$ <1 Hz, H-4), 4.99–4.69 (m, 6 H, 3 PhCH_2), 4.48 (dd, 1 H, $J_{5,6}$ 4.23, $J_{4,5}$ <1 Hz, H-5), 4.42 (d, 1 H, $J_{1',2'}$ 7.81 Hz, H-1′), 4.30 (d, 1 H, $J_{5,6}$ 7.32 Hz, H-6), 3.84 (dd, 1 H, $J_{1',2'}$ 7.81, $J_{2',3'}$ 9.77 Hz, H-2′), 3.71–3.68 (m, 2 H, H-2,6), 3.54 (d, 1 H, $J_{3',4'}$ 2.74, $J_{4',5'}$ <1 Hz, H-4′), 3.49 (dd, 1 H, $J_{2',3'}$ 9.77, $J_{3',4'}$ 2.74 Hz, H-3′), 3.46 (q, 1 H, J_{5',CH_3} 6.35 Hz, H-5′), 2.09 (s, 3 H, CH_3), 2.02 (s, 3 H, CH_3), and 1.17 (d, 3 H, J_{5',CH_3} 6.35 Hz, CH_3); ^{13}C (99.98 MHz), δ 169.59 (>C=O), 169.11 (>C=O), 104.65 (C-1′), 100.12 (C-1), 20.90 (CH_3, acetyl), 20.66 (CH_3, acetyl), and 16.75 (CH_3, fucose).

Anal. Calc. for $C_{37}H_{42}O_{11}$ (662.71): C, 67.05; H, 6.39. Found: for **8α**, C, 66.94; H, 6.34; for **8β**, C, 66.83; H, 6.34.

3,4-Di-O-acetyl-1,6-anhydro-2-O-(2,3,4-tri-O-acetyl-α-L-fucopyranosyl)-β-D-galactopyranose (**9α**). — To a solution of **8α** (965 mg, 1.46 mmol) in dry ethyl acetate (20 mL) and dry methanol (20 mL) was added 10% Pd/C (250 mg). After 2 h of hydrogenation, the mixture was filtered and concentrated to dryness. The debenzylated compound, R_F 0.79 (1:1 chloroform–methanol), was stirred with dry pyridine (25 mL) and dry acetic anhydride (10 mL) overnight at room temperature. Solvents were evaporated, the remaining pyridine was removed by repeated evaporation of toluene from the residue, and **9α** (662 mg, 88% from **8α**) was obtained as colourless needles from ethanol; m.p. 172–173°, $[\alpha]_{589}^{22}$ −119° $[\alpha]_{578}^{22}$ −123°

(*c* 1, chloroform); R_F 0.67 (1:2 light petroleum–ethyl acetate). N.m.r. data ($CDCl_3$): ^1H (250 MHz), δ 5.43 (s, 1 H, H-1), 5.36–5.08 (m, 6 H, including, at δ 5.25, H-1′, d, $J_{1',2'}$ 3.66 Hz), 4.47 (dd, 1 H, $J_{5,6}$ 4.12 Hz, $J_{4,5}$ <1 Hz, H-5), 4.34–4.26 (m, 2 H, including, at δ 4.32, H-6, d, $J_{5,6}$ 7.63 Hz), 3.73 (dd, 1 H, H-6), 3.62 (s, 1 H, H-2), 2.16 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3), 2.05 (s, 3 H, CH_3), 1.99 (s, 3 H, CH_3), and 1.14 (d, 3 H, J_{5',CH_3} 6.41 Hz, CH_3); ^{13}C (62.97 MHz), δ 170.56 (>C=O), 170.48 (>C=O), 169.97 (>C=O), 169.72 (>C=O), 169.11 (>C=O), 100.15 (C-1), 96.74 (C-1′), 20.90–20.70 (5 CH_3, acetyl), and 15.88 (CH_3, fucose).

Anal. Calc. for $C_{22}H_{30}O_{14}$ (518.46): C, 50.96; H, 5.83. Found: C, 51.17; H, 5.82.

*1,3,4,6-Tetra-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-acetyl-α-*L*-fucopyranosyl)-α,β-*D*-galactopyranose* (**10**). — (*a*) *From* **9α**. To a solution of **9α** (402 mg, 0.78 mmol) in dry acetic anhydride (10 mL) was added, dropwise, 1:1 trifluoroacetic acid–acetic anhydride (6 mL). The mixture was stirred at 4° and then concentrated. Column chromatography (1:2 light petroleum–ethyl acetate) of the residue yielded **10** (460 mg, 96%), m.p. 83–85° (from ether), $[\alpha]_{589}^{22}$ −35.5°, $[\alpha]_{578}^{22}$ −36.5° (*c* 1, chloroform); R_F 0.73 (1:2 light petroleum–ethyl acetate). ^1H-N.m.r. data (250 MHz, $CDCl_3$): δ 6.35 (d, $J_{1,2}$ 3.97 Hz, H-1α), 5.64 (d, $J_{1,2}$ 8.24 Hz, H-1β), 5.43–4.94 (m, 6 H), 4.34–4.03 (m, 5 H), 2.23–1.98 (several s, 21 H, 7 CH_3), and 1.15 (d, 3 H, J_{5',CH_3} 6.41 Hz, CH_3).

Anal. Calc. for $C_{26}H_{36}O_{17}$ (620.55): C, 50.32; H, 5.85. Found: C, 50.44; H, 5.83.

(*b*) *From* **12**. To a solution of **12** (140 mg, 0.45 mmol) in dry acetic anhydride (7 mL) and glacial acetic acid (15 mL) was added trifluoroacetic acid (1 mL) within 5 min. The mixture was stirred at room temperature. After 4 h, acetic anhydride (3 mL) and trifluoroacetic acid (0.7 mL) were added, and stirring at room temperature was continued for 14 h. T.l.c. then indicated the complete disappearance of **12**. The product (267 mg, 95%) was isolated as in (*a*).

*2-*O*-α-L-Fucopyranosyl-D-galactose* (**11**). — To a solution of **10** (131 mg, 0.21 mmol) in dry methanol (5 mL) were added 5 drops of methanolic M NaOMe. The mixture was stirred at 4°, then neutralised with acidic ion-exchange (H^+) resin, filtered, and concentrated. Flash chromatography (1:2 chloroform–methanol) of the residue yielded amorphous **11** (68 mg, 99%), $[\alpha]_D^{22}$ −56° (*c* 1.2, water); lit.[18] $[\alpha]_D$ −56° (water); R_F 0.48 (1:2 chloroform–methanol). The ^1H-n.m.r. data were in good agreement with those reported[14,16–18,25].

Anal. Calc. for $C_{12}H_{22}O_{10}$ (326.3): C, 44.17; H, 6.80. Found: C, 43.90; H, 6.71.

*1,6-Anhydro-2-*O*-α-L-fucopyranosyl-β-D-galactopyranose* (**12**). — To a solution of **6α** (873 mg, 1.41 mmol) in dry ethyl acetate (20 mL) and methanol (20 mL) was added 10% Pd/C (250 mg) containing traces of $PdCl_2$. After hydrogenation for 2 days, the mixture was filtered and concentrated *in vacuo*. Column chromatography (2:1 chloroform–methanol) of the oily residue yielded **12** (342 mg, 79%),

m.p. 88–92° (from chloroform–methanol 2:1), $[\alpha]_{589}^{22}$ −120°, $[\alpha]_{578}^{22}$ −125° (*c* 0.5, methanol); R_F 0.37 (2:1 chloroform–methanol). ^{1}H-N.m.r. data [250 MHz, $(CD_3)_2SO$]: δ 5.26 (s, 1 H, H-1), 5.00 (d, 1 H, *J* 6.41 Hz, OH), 4.83 (s, 1 H, OH), 4.69 (s, 1 H, H-1), 4.61 (s, 1 H, OH), 4.50 (s, 1 H, OH), 4.25–3.38 (m, 10 H), 3.18 (d, 1 H, *J* 5.19 Hz, OH), 1.08 (d, 3 H, J_{5',CH_3} 6.41 Hz, CH_3).

Anal. Calc. for $C_{12}H_{20}O_9 \cdot H_2O$ (326.3): C, 44.17; H, 6.80. Found: C, 44.38; H, 6.83.

Also isolated was 1,6-anhydro-2-*O*-α-L-fucopyranosyl-3,4-*O*-isopropylidene-β-D-galactopyranose (83 mg, 17%), m.p. 79–81° (from chloroform–methanol, 7:1), $[\alpha]_{589}^{23}$ −149°, $[\alpha]_{578}^{23}$ −155° (*c* 0.5, chloroform); R_F 0.73 (2:1 chloroform–methanol). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 5.44 (s, 1 H, H-1), 5.03 (s, 1 H, H-1), 4.54–3.56 (m, 13 H), 1.52 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.26 (d, 3 H, J_{5',CH_3} 6.41 Hz, CH_3).

Anal. Calc. for $C_{15}H_{24}O_9 \cdot 0.75\ H_2O$ (361.85): C, 49.79; H, 7.10. Found: C, 49.69; H, 7.34.

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