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THE SYNTHESES OF 4,6-DIDEOXY-4,6-DIFLUORO- AND 4-DEOXY-4-FLUORO-α,α-TREHALOSE*

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ABSTRACT

Prolonged treatment of 2,3-di-*O*-benzyl-4,6-di-*O*-mesyl-α-D-glucopyranosyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside with tetrabutylammonium fluoride in acetonitrile gave the 4,6-difluoride (71% yield), from which 4,6-dideoxy-4,6-difluoro-α-D-galactopyranosyl α-D-glucopyranoside was prepared In a similar reaction with 2,3-di-*O*-benzyl-4,6-di-*O*-mesyl-α-D-galactopyranosyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside, two products were formed, as indicated by the ^{19}F-n m r spectrum of the reaction mixture, and tentatively identified as the required 4,6-difluoride and the 6-fluoro-4-ene Fluoride displacement of the mesyloxy group of 2,3-di-*O*-benzyl-4-*O*-mesyl-6-*O*-trityl-α-D-glucopyranosyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside readily gave the 4-fluoride which, on deprotection, gave 4-deoxy-4-fluoro-α-D-galactopyranosyl α-D-glucopyranoside

INTRODUCTION

Our interest in the synthesis of non-symmetrically substituted, deoxyfluoro analogues of trehalose as specific inhibitors of the trehalase group of enzymes has been outlined previously[1,2]. A method for their synthesis has been described[1], and the 6-fluoro analogue was found to act as a competitive inhibitor of the trehalase isolated from the greenbottle fly These studies have now been extended to the synthesis of 4,6-difluorides and 4-fluorides

RESULTS AND DISCUSSION

When 2,3-di-*O*-benzyl-4,6-di-*O*-mesyl-α-D-glucopyranosyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside[1] (**1**) was heated with tetrabutylammonium fluoride in acetonitrile for 4 days, it gave the syrupy 4,6-difluoride **5** in 71% yield Hydrogenolysis of **5** over palladium-on-charcoal under acidic conditions afforded

*Chemical Modification of Trehalose Part XXI For Part XX, see Ref 1

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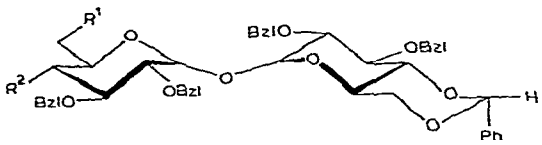
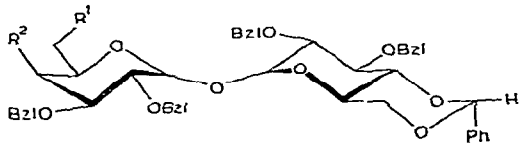
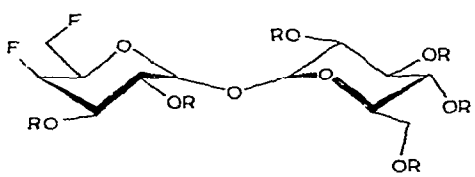


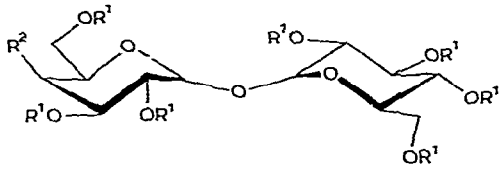
1 $R^1 = R^2 = OMs$
2 $R^1 = R^2 = F$
3 $R^1 = OTr, R^2 = OMs$
4 $R^1 = OTr\ R^2 = N_3$



5 $R^1 = R^2 = F$
6 $R^1 = R^2 = OBz$
7 $R^1 = R^2 = OMs$
8 $R^1 = OTr, R^2 = OMs$
9 $R^1 = OTr\ R^2$ F
10 $R^1 = OTr, R^2 = OBz$



11 R = H
12 R = Ac



13 $R^1 = H, R^2 = F$
14 $R^1 = Ac\ R^2 = F$
15 $R^1 = H, R^2 = OH$
16 $R^1 = Ac, R^2 = OAc$

TABLE I

^{19}F-NMR DATA[a] AT 56.4 MHz

	5[b]	9[c]	11[d]	12[b]	13[e]	14[b]
F-6	69.1 m[f]		67.9 (td)	70.1 (td)		
F-4	56.9 (dt)	57.0 (dt)	56.9 (dt)	59.1 (dt)	60.9 (dt)	59.1 m
$J_{F-6\ H-6a}$			~54	~54		
$J_{F-6\ H-6b}$			~54	~54		
$J_{F-6\ H-5}$			~14	~14		
$J_{F-4\ H-5}$	31	~31	~31	~31	30	
$J_{F-4\ H-4}$	51	~51	~53	~53	57	
$J_{F-4\ H-3}$	31	~31	~31	~31	30	

[a]First-order chemical shifts in p.p.m. to high field of external C_6F_6, coupling constants in Hz. [b]$CDCl_3$. [c]CH_2Cl_2. [d]$(CD_3)_2SO$. [e]D_2O. [f]Key: dt, doublet of triplets; m, second-order multiplet; td, triplet of doublets.

4,6-dideoxy-4,6-difluoro-α-D-galactopyranosyl α-D-glucopyranoside (**11**) in 38% yield, which was further characterized as its hexa-acetate **12**.

The ^{19}F-n.m.r. spectra of the 4,6-difluorides **5**, **11**, and **12** each showed two resonances separated by 11–12 p.p.m. (Table I). In each spectrum, F-6 resonated as a triplet of doublets with $J_{F-6\ H-6a} = J_{F-6\ H-6b} = 54$ Hz and $J_{F-6,H-5} \sim 14$ Hz, which were similar to the values reported[2] for the symmetrical 4,6,4′,6′-tetrafluoro analogues.

The resonances due to F-4 appeared at lower field as doublets of triplets, and the relatively large couplings (~31 Hz) between F-4 and H-3 and H-5 were indicative of an antiperiplanar relationship

Attempts were also made to synthesise the 4,6-dideoxy-4,6-difluorotrehalose derivative **2** from the appropriate galactosyl derivative **7** Difficulties in this type of synthesis by nucleophilic substitution were encountered[2] in the synthesis of 4,6,4',6'-tetradeoxy-4,6,4',6'-tetrafluoro-α,α-trehalose Elimination reactions are more competitive in the *galacto*-series, because of the antiperiplanar relationship between the 4-sulphonyloxy group and the two vicinal protons at the 3- and 5-positions A further complicating factor is the resistance of 6-sulphonyloxy groups of galactopyranosides to nucleophilic displacement, compared to the corresponding glucopyranosides[3] The appropriate 4,6-dimesylate **7** was prepared in 53% yield from the corresponding glucopyranoside **1** by treatment with sodium benzoate in hexamethylphosphoric triamide followed by debenzoylation and mesylation Treatment of **7** with tetrabutylammonium fluoride in boiling acetonitrile for 24 h gave two products, as indicated by t.l c The ^{19}F-n m.r. spectrum of the reaction mixture contained three ^{19}F-resonances at −34 5, −58 2, and −75 5 p p m relative to external hexafluorobenzene The resonances at −58 2 and −75 5 p p m were assigned to the F-4 and F-6 signals of the 4,6-difluoride **2** Inversion of configuration at C-4 was confirmed by the values of the coupling constants $J_{F\text{-}4\ H\text{-}5}$ (~2–3 Hz) and $J_{F\text{-}4\ H\text{-}3}$ (~13 Hz), which were in agreement with those found for 4-deoxy-4-fluoro-D-glucopyranosides[4] The F-6 resonance at −75 4 p p m was the expected triplet of doublets $J_{F\text{-}6,H\text{-}6a} = J_{F\text{-}6\ H\text{-}6b} = 47$ Hz and $J_{F\text{-}6\ H\text{-}5} = 26$ Hz characteristic of 6-deoxy-6-fluoro-D-glucopyranosides[5] The resonance at −34 5 p p m appeared as a triplet ($J_{F\text{-}6\ H\text{-}6a} = J_{F\text{-}6\ H\text{-}6b} = 48$ Hz), which is consistent with the absence of a hydrogen atom at C-5, suggesting that the product was the 6-fluoro-4-ene

The reaction pathway may be rationalised by an initial fluoride displacement of the 6-mesyloxy group, followed by both displacement at C-4, with inversion of configuration, and elimination The two products could not be separated satisfactorily

The synthesis of 4-deoxy-4-fluoro-α-D-galactopyranosyl α-D-glucopyranoside (**13**) was conveniently achieved from the appropriate 4-sulphonate **3** Tritylation of 2,3-di-*O*-benzyl-α-D-glucopyranosyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside, followed directly by the addition of mesyl chloride to the reaction mixture, afforded the required 6-*O*-trityl-4-mesylate **3** in 66% yield In preliminary experiments, only poor yields of **3** were obtained. and subsequently it was shown that hydrolysis of the trityl group during column chromatography on silica gel was responsible, this was successfully circumvented by the incorporation of triethylamine (0 5% v/v) in the eluting solvent. When the 4-mesylate **3** was heated with tetrabutylammonium fluoride in acetonitrile for 2 days, it was converted into the 4-fluoro derivative **9** in 59% yield Deprotection of the latter product by catalytic hydrogenolysis under acidic conditions afforded, as an amorphous solid, 4-deoxy-4-fluoro-α-D-galactopyranosyl α-D-glucopyranoside (**13**) in 25% yield, which was characterised

as the crystalline hepta-acetate **14** The structures of **9** and **13** were confirmed by their ^{19}F-n m r spectra (Table I) In each case, a doublet of triplets was observed, in which the values (~30 Hz) of $J_{F\text{-}4,H\text{-}3}$ and $J_{F\text{-}4,H\text{-}5}$ were consistent with an anti-periplanar relationship between the fluorine substituent and the two vicinal hydrogen atoms[6].

4-Deoxy-4-fluorotrehalose was synthesised from the axial 4-sulphonate **8**, which was prepared from the 6-*O*-trityl-4-mesylate **3** by S_N2 displacement of the sulphonyloxy group by benzoate anion in hexamethylphosphoric triamide, to give the 4-benzoate **10** (87% yield), followed by debenzoylation and mesylation The ^{1}H-n m r spectrum of **8** was mainly second-order, except for the H-4 resonance which, typical of galactopyranosides[2 6], occurred as a broadened doublet ($J_{3,4}$ 3, $J_{4,5}$ ~1 Hz) downfield at τ 3.82

The reaction of the 4-mesylate **8** with tetrabutylammonium fluoride in acetonitrile afforded a single product which, since it did not exhibit a ^{19}F-n m r resonance, was assumed to be an unsaturated derivative, the product was not isolated This observation was not unexpected, in view of the difficulties reported[6] in the synthesis of 4,4′-dideoxy-4,4′-difluorotrehalose It is of interest that the related displacement of methyl 4-*O*-mesyl-2,3-di-*O*-methyl-6-*O*-trityl-α-D-galactopyranoside by fluoride was successful, and the 4-fluoroglucoside was obtained in 71% yield Furthermore, the possibility that steric effects emanating from the bulky triphenylmethyl group inhibit S_N2 displacement appear to be ruled out, since the 4-mesylate **8** readily underwent nucleophilic displacement with sodium azide in hexamethylphosphoric triamide, affording the 4-azide **4** in 50% yield

The 6-trityl-4-benzoate **10** was deprotected by treatment with sodium methoxide and immediately hydrogenolysed over palladium-on-charcoal, under acidic conditions, to give α-D-galactopyranosyl α-D-glucopyranoside[8 9] (**15**) in 26% overall yield The disaccharide was further characterised as its octa-acetate **16**

Previous studies[2] indicated that 6,6′-dideoxy-6,6′-difluoro-α,α-trehalose functioned as a reversible, competitive inhibitor of trehalase, and we have recently shown that 6-deoxy-6-fluoro-α-D-glucopyranosyl α-D-glucopyranoside is a competitive inhibitor having an affinity ~1 4 times greater than that of the natural substrate In an extension of these investigations, 4-deoxy-4-fluoro-α-D-galactopyranosyl α-D-glucopyranoside (**13**) and α-D-galactopyranosyl α-D-glucopyranoside (**15**) were assayed for activity against the trehalase isolated from the flight muscle of the green-bottle fly *Lucilia sericata*. Unfortunately, the 4,6-difluoride **11** could not be evaluated, because it interfered with the assay system The 4-fluoride **13** was metabolised by trehalase, but at a much lower rate than trehalose, and had about a thirty-fold lower affinity for the enzyme than trehalose It was similarly shown that α-D-galactopyranosyl α-D-glucopyranoside (**15**) had about a sixteen-fold lower affinity for the enzyme than trehalose

EXPERIMENTAL

For general methods, see Ref 1

2,3-Di-O-benzyl-4,6-dideoxy-4,6-difluoro-α-D-galactopyranosyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**5**) — The dimesylate[1] **1** (1 g, 1 06 mmol) was dissolved in a 50% w/v solution of tetrabutylammonium fluoride in acetonitrile (4 cm^3) and heated under reflux for 4 days, t l c (light petroleum–ethyl acetate, 3 1) then indicated the formation of one major product The excess of reagent was removed by passing the reaction mixture through a short column of silica gel, using acetonitrile as eluant Evaporation of the eluate afforded a dark-brown syrup, which was chromatographed on silica gel with light petroleum–ethyl acetate (5 1) The difluoride **5** (0 6 g, 71%) was obtained as a syrup, $[\alpha]_D$ +85° (*c* 1, chloroform) (Found· C, 71 35, H, 6 4 $C_{47}H_{48}F_2O_9$ calc C, 71 0, H, 6 05%) Mass spectrum *m/e* 447 (0 9%), 431 (3 2), 363 (2 0), 347 (0 9), 341 (1 9), 339 (2 8), 325 (0 8), 323 (0 8), 255 (4 0), 239 (1 3), 235 (2 0), 233 (4 5), 219 (1 6), 217 (2 8), and 181 (100, $PhC^+H\ CH_2Ph$)

4,6-Dideoxy-4,6-difluoro-α-D-galactopyranosyl α-D-glucopyranoside (**11**) — To a solution of the difluoride **5** (4 g, 5 04 mmol) in dichloromethane was added ethanol (50 cm^3) and conc hydrochloric acid (1 cm^3) The mixture was hydrogenated over palladium-on-charcoal at 50 p s i for 18 h, and t l c then indicated that the reaction was complete The solution was neutralised ($PbCO_3$), filtered, and evaporated with silica gel (3 g) The solid residue was loaded on to a column of silica gel and eluted with ethyl acetate–methanol (3 1), to afford the difluoro derivative **11** (0 69 g, 38%), m p 120–121 5° (from ethyl acetate–ethanol), $[\alpha]_D$ +197° (*c* 1, methanol) (Found· C, 39 5, H, 6 4 $C_{12}H_{20}F_2O_9$ H_2O calc C, 39 6, H, 6 0%) Water of hydration was indicated by the absorption band at 1650 cm^{-1} in the infrared spectrum Mass spectrum of the derived hexakis-*O*-trimethylsilyl derivative 451 (0 1%), 361 (4 0), 311 (1 3), 271 (1 8), 221 (1 0), 217 (19 9), 204 (35 5), and 73 (100, Me_3Si^+)

The hexa-acetate **12**, prepared in 58% yield in the usual way (acetic anhydride–pyridine), had m p 64–66° (from light petroleum–ether), $[\alpha]_D$ +180° (*c* 1, chloroform) (Found C, 47 9; H, 5 4 $C_{24}H_{32}F_2O_{15}$ calc C, 48 15, H, 5 35%) Mass spectrum *m/e* 331 (10 0%), 271 (0 7), 251 (22 9), 229 (1 0), 211 (0 9), 191 (63 1), 169 (44 7), 149 (31 6), and 43 (100, Ac^+)

4,6-Di-O-benzoyl-2,3-di-O-benzyl-α-D-galactopyranosyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**6**) — To a solution of the dimesylate **1** (5 g) in hexamethylphosphoric triamide (25 cm^3) was added sodium benzoate (2 g), and the mixture was heated at 130° for 16 h, t l c (light petroleum–ethyl acetate, 3 1) then indicated the reaction to be complete The solution was diluted with ethyl acetate, extracted with water (3 × 50 cm^3), dried ($MgSO_4$), and evaporated to dryness The resulting syrup crystallised from dichloromethane–ethanol to give the dibenzoate **6** (4 3 g, 81%), m p 157–158°, $[\alpha]_D$ +88° (*c* 1, chloroform) (Found C, 73 4, H, 6 0 $C_{61}H_{58}O_{13}$ calc C, 73 4, H, 5 8%) Mass spectrum *m/e* 567 (2 8%), 551 (17 8), 461 (8 7), 459 (3 0), 447 (4 5), 445 (3 0), 443 (2 5), 431 (3 0), 355 (4 5), 353 (6 2),

341 (4 5), 339 (6 2), 337 (3 1), 325 (2 5), 323 (3 1), 233 (8 0), 231 (8.9), 217 (3 0), and 181 (100%, PhCH⁻CHPh)

2,3-Di-O-benzyl-4,6-di-O-mesyl-α-D-galactopyranosyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**7**) — To a solution of the dibenzoate **6** (2 g, 2 mmol) in dichloromethane (40 cm^3) was added 0 5M methanolic sodium methoxide (25 cm^3). The mixture was then heated under reflux until t l c (light petroleum–ethyl acetate 2.1) indicated completion of reaction. The solution was passed through a short column of silica gel, to remove inorganic material, and eluted with ethyl acetate Evaporation of the neutral eluate gave a syrupy product, a solution of which in pyridine (15 cm^3) was cooled to −10° and treated with methanesulphonyl chloride (0.85 g, 7 5 mmol) After 16 h at 0°, the solution was diluted with chloroform (15 cm^3), from which pyridine was removed by extraction with M hydrochloric acid in the usual way. The dried ($MgSO_4$) organic phase was then evaporated to dryness and the residue was purified by chromatography on silica gel with light petroleum–ethyl acetate (1 3) The crystalline dimesylate **7** (1 g, 53%) had m p 119–120° (from ethanol–ether), $[\alpha]_D$ +96° (*c* 1, chloroform) (Found C, 61 8; H, 5 9 $C_{49}H_{54}O_{15}S_2$ calc C, 62 15, H, 5 7%)

2,3-Di-O-benzyl-4-O-mesyl-6-O-trityl-α-D-glucopyranosyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**3**) — To a solution of 2,3-di-*O*-benzyl-α-D-glucopyranosyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside[1] (10 g, 12 66 mmol) in pyridine (100 cm^3) was added chlorotriphenylmethane (8 g, 28 7 mmol) The mixture was heated under reflux for 24 h, and t l c (light petroleum–ethyl acetate, 3·1) then indicated the reaction to be complete The solution was cooled to −10° and treated with methanesulphonyl chloride (8 g, 70 mmol) After being kept at 0° for 18 h, the mixture was processed as described before Chromatographic fractionation of the product on silica gel, eluting initially with light petroleum–ethyl acetate (6 1) and then with light petroleum–ether acetate (2 1) [both containing triethylamine (0.5%)], afforded the crystalline mesylate **3** (9 3 g, 66%), m p 86–87° (methanol), $[\alpha]_D$ +77 5° (*c* 1, chloroform) (Found C, 72 2, H, 6 2 $C_{67}H_{66}O_{13}S$ calc · C. 72 4, H, 5 9%)

2,3-Di-O-benzyl-4-deoxy-4-fluoro-6-O-trityl-α-D-galactopyranosyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**9**) — The throughly dried mesylate **3** (1 g, 0 9 mmol) was dissolved in a 50% w/v solution of tetrabutylammonium fluoride in acetonitrile[1] (6 cm^3), and the solution was heated under reflux for 2 days, t l c (light petroleum–ethyl acetate, 3 1) then indicated that one major product had been formed, and the 4-fluoride **9** was obtained as a crystalline solid (0 55 g, 59%) by a series of steps similar to those already described for **5**, **9** had m p 177 5–179° (ethanol), $[\alpha]_D$ +50° (*c* 1, chloroform) (Found C, 76 7; H, 6 0 $C_{66}H_{63}FO_{10}$ calc : C, 76 6, H, 6 1%)

4-Deoxy-4-fluoro-α-D-galactopyranosyl α-D-glucopyranoside (**13**) — A solution of the 4-fluoride **9** (1 5 g, 1 45 mmol) in ethanol (100 cm^3) and ether (50 cm^3) was processed, as described for **11**, to afford **13** as an amorphous solid (0 13 g, 26%), $[\alpha]_D$ +172 6° (*c*, 0 5 methanol)

The hepta-acetate **14**, prepared in 45% yield from **13** in the usual way (acetic anhydride–pyridine), had m p 66–69°, $[\alpha]_D$ +168° (*c* 1, chloroform) (Found C, 49 2, H, 5 45 $C_{26}H_{35}FO_{17}$ calc C, 48 9, H, 5 5%) Mass spectrum *m/e* 331 (0 2%), 291 (0 4), 271 (0 1), 231 (1 9), 229 (0 1), 211 (0 1), 189 (0 1), 171 (0 1), 169 (2 0), and 43 (100, Ac^+)

4-O-Benzoyl-2,3-di-O-benzyl-6-O-trityl-α-D-galactopyranosyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**10**) — To a solution of the trityl mesylate **3** (1 g, 0 9 mmol) in hexamethylphosphoric triamide (5 cm^3) was added sodium benzoate (0 5 g, 3 5 mmol) The mixture was heated at 115° for 3 days, and t l c (light petroleum–ethyl acetate, 5 1) then showed the reaction to be complete The mixture was processed, as described above, to give the crystalline 4-benzoate **10** (0 85 g, 87%), m p 77–79° (from methanol), $[\alpha]_D$ +82° (*c* 1, chloroform) (Found C, 77 6, H, 6 3 $C_{73}H_{68}O_{12}$ calc C, 77 1, H, 6 0%)

2,3-Di-O-benzyl-4-O-mesyl-6-O-trityl-α-D-galactopyranosyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**8**) — To a solution of the 4-benzoate **10** (1 g, 0 88 mmol) in dichloromethane (20 cm^3) was added 0 05M methanolic sodium methoxide (20 cm^3), the mixture was then worked up as described above, and the product was mesylated to afford **8** (0 5 g, 51%). m p 208–209° (from ethanol), $[\alpha]_D$ +61° (*c* 1, chloroform) (Found C, 71 9, H, 6 3 $C_{67}H_{66}O_{13}S$ calc C, 72 45, H, 5 95%)

4-Azido-2,3-di-O-benzyl-4-deoxy-6-O-trityl-α-D-glucopyranosyl 2,3-di-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**4**) — The methanesulphonate **8** (0 5 g, 0 45 mmol) in hexamethylphosphoric triamide (5 cm^3) was heated with sodium azide (0 5 g, 7 7 mmol) at 90° for 24 h The solution was then processed in the usual way, to give the 4-azide **4** (0 24 g, 50%), m p 153–155° (from methanol), $[\alpha]_D$ +110° (*c* 1, chloroform) (Found C, 74 9, H, 6 3, N, 3 7 $C_{66}H_{63}N_3O_{10}$ calc C, 74 9, H, 5 95, N, 3 95%)

α-D-Galactopyranosyl α-D-glucopyranoside (**15**) — A solution of the 4-benzoate **10** (5 0 g, 4 5 mmol) in dichloromethane (25 cm^3) and 0 5M methanolic sodium methoxide (25 cm^3) was boiled under reflux until t l c (light petroleum–ethyl acetate, 3 1) indicated that no starting material remained The mixture was then allowed to percolate through a column of silica gel (100 g) which was then washed with ethyl acetate The syrupy product obtained upon evaporation of the solvent was dissolved in a mixture of ether (50 cm^3) and ethanol (150 cm^3), and acidified with conc hydrochloric acid (1 cm^3) Hydrogenation over palladium-on-charcoal at 55 p s i for 18 h gave a single product, as indicated by t l c (ethyl acetate–methanol, 2 1) The solution was neutralised ($PbCO_3$), filtered, and then evaporated *in vacuo* Chromatographic fractionation of the product on silica gel (ethyl acetate–methanol, 2 1) afforded α-D-galactopyranosyl α-D-glucopyranoside (**13**, 0 4 g, 26%) as an amorphous solid Mass spectrum of the derived octa-*O*-trimethylsilyl derivative *m/e* 451 (0 3%), 361 (35 5), 271 (4 5), 217 (20 4), 204 (7 1), and 73 (100%, $MeSi^+$)

The octa-acetate **16**, prepared (41%) in the usual way from **13**, had m p 110–112°, $[\alpha]_D$ +172° (*c* 1, chloroform), lit [9] $[\alpha]_D$ +196° (Found C, 49 5, H, 5 8

$C_{23}H_{38}O_{19}$ calc.· C, 49.6; H, 5.6%). Mass spectrum *m/e* 331 (34.7%), 271 (0 1), 211 (0.1), 169 (53 7), and 43 (100%, Ac^+)

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