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Papulacandins and chaetiacandin: a stereoselective route to their basic skeleton by a palladium-mediated arylation of 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-1-tributylstannyl-D-glucal*

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ABSTRACT

Palladium(0)-catalysed coupling of 1,5-anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-1-tributylstannyl-D-*arabino*-hex-1-enitol (**7**) with 3,5-dibenzyloxy-2-bromobenzyl alcohol gave 1,1^2-anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-1-(4,6-dibenzyloxy-2-hydroxymethylphenyl)-α-D-*arabino*-hexopyranose (**13**). The same reaction buffered by sodium carbonate provided 1,5-anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-1-(4,6-dibenzyloxy-2-hydroxymethylphenyl)-D-*arabino*-hex-1-enitol (**11**). Stereoselective oxidative spiroacetalisation of **11** provided 1,1^2-anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-1-(4,6-dibenzyloxy-2-hydroxymethyl-phenyl)-α-D-glucopyranose (**15**), the basic tricyclic structure of papulacandins. In a model study, **15** was converted in three steps into 1,1^2-anhydro-1-(4,6-dihydroxy-2-hydroxymethylphenyl)-3-*O*-octadecanoyl-α-D-glucopyranose (**24**), a structural analogue of papulacandin D. Morcover, stereoselective hydroboration–oxidation of **11** furnished 2-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-3,5-dibenzyloxy-1-hydroxymethylbenzene (**26**), the structural skeleton of the chaetiacandin **3**.

INTRODUCTION

Papulacandins A–C (**1**) and D (**2**)[2,3] and the chaetiacandin **3**[4,5] are closely related antifungal antibiotics isolated from strains of *Papularia sphaerosperma* and *Monochaetia dimorphospora*, respectively. Classical chemical and spectroscopic investigations led to the structures **1–3**, and the absolute configuration of the spirocentres in **1** and **2** was revealed by an X-ray crystallographic study of a di-*p*-bromobenzyl derivative. These compounds are both β-*C*-D-glucosyl derivatives of 1,3-dihydroxy-5-hydroxymethylbenzene, the oxygen at the benzylic position being attached at the anomeric carbon in the spirocyclic structure for **1** and **2**. Their common features are a 6-*O*-acyl-β-D-galactopyranosyl residue at O-4 and an acylation with an unusual C_{18} (papulacandins) or C_{14} (chaetiacandin) polyunsaturated fatty acid chain at O-3 of the glucosyl moiety.

The substances exhibit strong activities against yeasts, especially *Candida albicans*, that could be related to the inhibition of the (1→3)-β-D-glucan synthase in various

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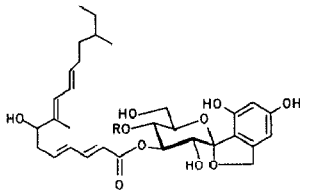
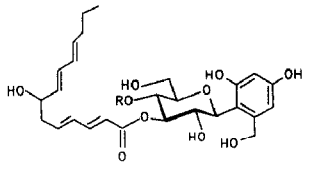


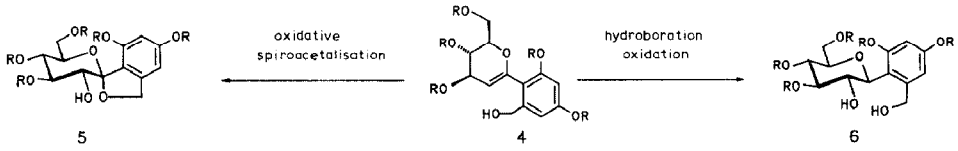
1 Papulacandin A,B,C, R = 6 – O – acyl – β – D – galactopyranosyl
2 Papulacandin D, R = H



3 Chaetiacandin, R = 6 – O – acyl – β – D – galactopyranosyl

organisms[7-10], as shown with papulacandin B, the major component of the antibiotic complex produced by *P. sphaerosperma*. Although essential for inhibiting fungal growth, the 6-*O*-acyl-β-D-galactosyl moiety in papulacandin B is not required for activity against glucan biosynthesis[2,10]. The long-chain acyl residue at O-3, however, is crucial for biological activity[10]. In this respect, the lipophilic *p*-octyloxybenzoyl side chain of cilogungin[11], a cyclopeptide antifungal antibiotic related to echinocandin B[12], is also essential for the *in vitro* inhibition of the (1→3)-β-D-glucan synthase of *Neurospora crassa* and *C. albicans*[13].

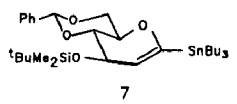
These substances have low acute toxicities[4,14], which has stimulated recent work on synthesis; this includes a total synthesis of a racemic spiroacetal unit, using a hetero Diels–Alder reaction as the key step[15] or coupling reactions of aryl nucleophiles with derivatives of methyl D-gluconate[16] or D-gluconolactone[17,18]. We have shown[19,20] that 1-tributylstannyl-D-glucals can be arylated efficiently with aryl bromides under palladium-(0) catalysis, providing the corresponding 1-aryl-D-glucals that could be transformed stereoselectively into various *C*-glucosylarenes. Thus, it was anticipated that the basic structural units of both papulacandins **1** and **2** and the chaetiacandin **3** could be synthesised from a suitable 1-aryl-D-glucal derivative **4** by either an oxidative spiroacetalisation (→**5**) or a hydroboration–oxidation (→**6**) sequence. Work on model substances[19,20] and studies of similar compounds[21-23] suggested that these reactions would occur from the desired α-face.



5 4 6

RESULTS AND DISCUSSION

1,5-Anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-1-tributylstannyl-D-*arabino*-hex-1-enitol (**7**) was obtained[20] in five steps from methyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[24]. The possibility of a regioselective β-D-galactosylation at O-4 and acylation at O-3 of the D-glucosyl residue justified the choice of the protecting groups in **7**. Furthermore, it was found that a silyl group instead of a benzyl group at O-3 enabled the preparation of **7** in higher yields[20] from the correspond-



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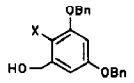
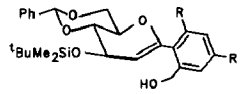
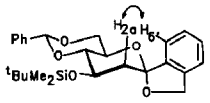


8 X = H
9 X = Br



10 R = H
11 R = OBn



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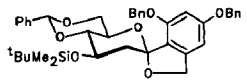

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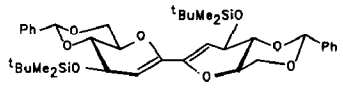

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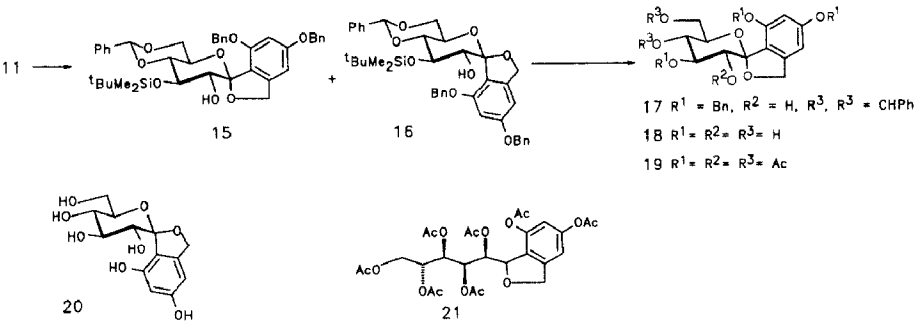
ing unsaturated sulphone. Regioselective bromination[26,27] of 3,4-dibenzyloxybenzyl alcohol[25] (**8**) by *N*-bromosuccinimide at reflux in carbon tetrachloride provided 3,5-dibenzyloxy-2-bromobenzyl alcohol[28] (**9**, 97%).

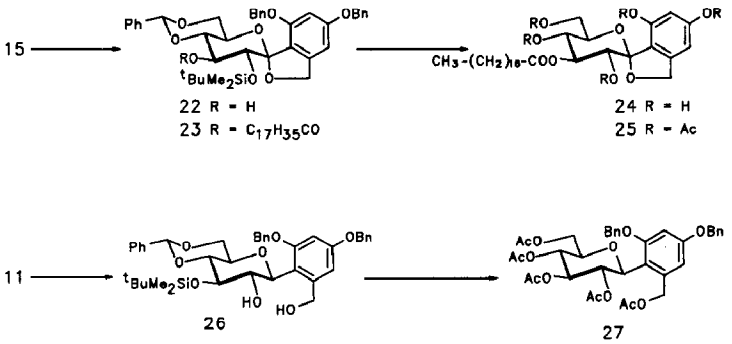
In a model study, tetrakis(triphenylphosphine)palladium(0)-catalysed (0.05 equiv.) coupling of **7** with *o*-bromobenzyl alcohol furnished, after several hours at reflux, a mixture of the 1-arylglycal **10** and the spiroacetal **12** which, upon prolonged heating, led to **12** as the only stereoisomer (73%) together with the dimer **14** (20%). This behaviour was not observed when a benzyl protecting group was used instead of the *tert*-butyldimethylsilyl group at O-3 of the stannane[19,20]. Likewise, coupling of **7** with **9** provided, after boiling under reflux for 12 h, 71% of the bicycloacetal **13** as a single isomer and 15% of the homocoupling product **14**. This one-step construction of a 2-deoxy analogue of the tricyclic skeleton of papulacandins may be explained by an acid-catalysed acetalisation of **11**, the initial product of the reaction, as in the conversion of **10** into **12**. Acidic species that catalyse the spiroacetalisation may be provided by slow degradation of the initially formed tributyltin bromide. When the Pd(0)-catalysed reaction was carried out in the presence of sodium carbonate, the expected glycals **10** and **11** were obtained (76 and 78%, respectively) together with the dimer **14**. The ^{1}H-n.m.r. spectra of the 1-aryl-D-glucals **10** and **11** and the dimer **14** showed the expected doublets at δ 4.92–5.51 p.p.m. ($J_{2,3}$ 2.0–2.5 Hz). The J values for **12** and **13** were similar for the tetrahydropyran ring ($J_{2ax,3}$, $J_{2eq,3}$, $J_{3,4}$, and $J_{4,5}$ values: 10.4, 5.9, 8.9, and 9.8 Hz for **12**, 11.0, 5.3, 8.9, and 9.9 Hz for **13**, respectively), suggesting the same equatorial (β) orientation of the 1-aryl bond in a $^4C_1$(D) conformation for each compound. Irradiation of the aromatic proton H-6 in **12** ($\delta \sim 7.2$) caused n.O.e. of the resonance of H-2*ax* but not that of H-2*eq*, a result which was compatible only with an *S* configuration at the spirocentre.

Treatment of glycal **11** with *m*-chloroperoxybenzoic acid in the presence of sodium hydrogencarbonate at low temperature provided 82% of a 6:1 mixture of the D-*gluco* isomers **15** and **16**. This stereoselective oxidative spiroacetalisation occurred without a detectable intermediate (*e.g.*, epoxide), which suggested that the intramolecular nucleophilic attack of the benzylic oxygen might be concerted with the oxygen transfer from *m*-chloroperoxybenzoic acid to the olefinic substrate in a peroxy acid–olefin transition structure[29,30]. In this respect, it is well known that treatment of glycals

with peroxy acids does not lead to 1,2-anhydro sugars, but rather to the corresponding *cis*- or *trans*-opened products by reaction with the solvent or the corresponding acid[31]. The favoured α-attack of a transient oxocarbonium ion at the anomeric centre explains the selective formation of isomer **15**. At this stage, the isomer **16** could not be converted, by any acid-catalysed isomerisation, into the spirocyclic isomer **15** having the configuration of the natural substances. However, after fluoride-promoted desilylation, catalytic hydrogenolysis, and acetylation, **15** and **16** each gave the same hexa-acetate **19**, identical with that obtained from the natural antibiotics[16]. Anomerisation of **16** in the course of its transformation into **18** occurred most probably during hydrogenolysis. However it was not possible, even using buffered reaction mixtures, to isolate the sensitive tetraol **20**. In the same deprotection sequence, hydrogenolysis in methanol–ethyl acetate in the presence of hydrochloric acid or prolonged hydrogenolysis on either **15** or **16** provided, after acetylation, the same reductively opened hepta-acetate **21** with undefined configuration at C-1. The D-*gluco* configuration of the isomers **15** and **16**, demonstrated by their chemical transformation into **19**, was also confirmed by the ^{1}H-n.m.r. data (C_6D_6). Thus, the J values for **15** ($J_{2,3}$ = $J_{3,4}$ = 9.0, $J_{4,5}$ 10 Hz) indicated H-2,3,4,5 to be axial and the conformation to be $^4C_1$(D). The highly strained isomer **16** gave similar data ($J_{2,3}$ 7.5, $J_{3,4}$ 8.5, and $J_{4,5}$ 9.8 Hz), which reflected the rigidity imposed by the benzylidene ring. The configuration at the spirocentres of **15** and **16** was indicated by the deshielding effect of the phenolic oxygen O-6 on H-2 in **15** (δ 4.87, *cf.* δ 4.28 for H-2 in **16**) and on H-3 in **16** (δ 4.79, *cf.* δ 4.32 for H-3 in **15**) due to the steric proximities. A similar effect was observed on H-2*ax* in the 2-deoxy analogue **13** of **15**, in which the quartets for H-2*ax* and H-2*eq* occurred at δ 3.33 and 2.55, respectively.



Regioselective 3-*O*-acylation of the tricyclic skeleton found in papulacandins was unexpectedly difficult by the application of a standard protection–deprotection sequence to **15**, due to a 3→2 silyl migration. The mixture could be forced towards the 2-*O*-silylated product **22** by treatment of an oxolane solution of **15** with sodium hydride at room temperature. Acylation of **22** with stearic acid in the presence of 1,3-dicyclohexylcarbodi-imide and 4-dimethylaminopyridine, followed by treatment with trifluoroacetic acid and hydrogenolysis, yielded the papulacandin D analogue **24**, characterised as the penta-acetate **25**.



The stereoselective hydration of the 1-arylglucal **11** would also provide an entry to the *C*-β-D-glucopyranosylarene moiety of the chaetiacandin. Hydroboration of **11** by the borane–oxolane complex followed by treatment with basic hydrogen peroxide gave 75% of 2-(4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-3,5-dibenzyloxy-1-hydroxymethylbenzene (**26**) as the only detectable isomer that represents the skeleton of the chaetiacandin **3**. Compund **26** was characterised as the penta-acetate **27**.

Compounds **26** and **27** gave ^{1}H-n.m.r. spectra which, under the usual conditions ($CDCl_3$ or C_6D_6 at 25°), could not be interpreted, due to hindered rotation around the C-1→C-aryl bond. The configurations at C-1,2 in **27** were revealed by a spectrum recorded in methyl sulfoxide-d_6 at 140°, which showed the coupling constants expected for the β-*gluco* configuration in the usual $^4C_1$ conformation ($J_{1,2}$, $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ values of 9.9, 8.9, 8.9, and 9.5 Hz, respectively)*.

EXPERIMENTAL

General methods. — Melting points were determined with a Büchi apparatus and are uncorrected. $[\alpha]_D$ Values were measured on solutions in $CHCl_3$ at 22 ± 2° with a Perkin–Elmer Model 141 polarimeter. ^{1}H-N.m.r. spectra (internal Me_4Si) were recorded with a Bruker AM-300 WB (300 MHz) spectrometer. Desorption c.i.(ammonia)-mass spectra were recorded with a Ribermag R-10-10 instrument. All solvents and reagents were purified and dried according to standard procedures[34]. Tetrakis(triphenylphosphine)palladium(0) was prepared as described in ref. 35. T.l.c. was performed on Silica Gel 60-F_{254} (Merck) with detection by quenching of fluorescence and by charring with H_2SO_4–EtOH (ratio 10:1). Products were purified by flash-column chromatography on Silica Gel 60 (Merck, 3–63 μm). Elemental analyses were performed by the Service Central de Micro-Analyse du Centre National de la Recherche Scientifique.

*1,5-Anhydro-4,6-O-benzylidene-3-O-*tert*-butyldimethylsilyl-2-deoxy-1-(2-hydroxymethylphenyl)*-D-arabino-*hex-1-enitol* (**10**). — To a stirred solution of **7**[20] (100 mg,

* While this work was being written[1], a similar investigation appeared in the literature[32,33].

0.15 mmol) in anhydrous toluene (2 mL) under Ar were added successively *o*-bromobenzyl alcohol (43 mg, 0.23 mmol, 1.5 equiv.), sodium carbonate (122 mg, 1.15 mmol), and $Pd(PPh_3)_4$ (17 mg, 15 μmol, 0.1 equiv.). The mixture was boiled under reflux overnight, then filtered through Celite, and the solvent was evaporated. Column chromatography (10:1 hexane–ethyl acetate containing 0.1% of triethylamine) of the residue gave dimer **14** (11 mg, 20%). Further elution provided **10** (53 mg, 76%) which, after crystallisation from ethyl ether–hexane, had m.p. 119°, $[\alpha]_D$ − 28° (*c* 1.0). ^{1}H-N.m.r. data ($CDCl_3$): δ 0.01 and 0.03 (2 s, 6 H, 2 Me), 0.91 (s, 9 H, ^{t}Bu), 3.90 (t, 1 H, $J_{5,6ax}$ = $J_{6ax,6eq}$ = 10.5 Hz, H-6*ax*), 3.94 (dd, 1 H, $J_{3,4}$ 7.5, $J_{4,5}$ 10.1 Hz, H-4), 4.13 (ddd, $J_{5,6eq}$ 5.0, Hz, H-5), 4.42 (dd, 1 H, H-6*eq*), 4.64–4.69 (m, 3 H, H-3 and OCH_2Ar), 4.97 (d, 1 H, $J_{2,3}$ 2.0 Hz, H-2), 5.65 (s, 1 H, C*H*Ph), and 7.27–7.58 (m, 9 H, aromatic).

Anal. Calc. for $C_{26}H_{34}O_5Si$: C, 68.69; H, 7.54. Found: C, 68.76; H, 7.28.

*1,5-Anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-1-(4,6-dibenzyloxy-2-hydroxymethylphenyl)-*D*-arabino-hex-1-enitol* (**11**) *and 1,1'bis(1,5-anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-*D*-arabino-hex-1-enitol)* (**14**). — Reaction of **7** (500 mg, 0.77 mmol) in anhydrous toluene (10 mL) with 3,5-dibenzyloxy-2-bromobenzyl alcohol[28] (**9**; 384 mg, 0.96 mmol, 1.2 equiv.), sodium carbonate (612 mg), and $Pd(PPh_3)_4$ (45 mg, 38 μmol, 0.05 equiv.) at reflux temperature for 4 h, as described for **10**, gave, after column chromatography (20:1 toluene–ethyl acetate containing 0.1% of triethylamine), **14** (44 mg, 16%), m.p. 206–208° (from ether–hexane), $[\alpha]_D$ − 43° (*c* 1.1). ^{1}H-N.m.r. data (C_6D_6): δ 0.14 and 0.18 (2 s, 12 H, 4 Me), 1.05 (s, 18 H, 2 ^{t}Bu), 3.42 (dd, 2 H, $J_{5,6ax}$ 9.5, $J_{6ax,6eq}$ 10.5 Hz, 2 H-6*ax*), 3.75 (dd, 2 H, $J_{3,4}$ 7.0, $J_{4,5}$ 9.5 Hz, 2 H-4), 3.81 (dt, 2 H, $J_{5,6eq}$ 5.0 Hz, 2 H-5), 4.11 (dd, 2 H, 2 H-6*eq*), 4.65 (dd, 2 H, $J_{2,3}$ 2.1 Hz, 2 H-3), 5.23 (s, 2 H, 2 C*H*Ph), 5.51 (d, 2 H, 2 H-2), and 7.10–7.62 (m, 10 H, 2 Ph). Mass spectrum: *m/z* 563 (M^+ − ^{t}BuMe$_2$SiO, 100%), 695 (M^+ + 1, 69).

Anal. Calc. for $C_{38}H_{54}O_8Si_2$: C, 65.67; H, 7.83. Found: C, 65.49; H, 8.11.

Further elution provided **11** (397 mg, 78%), m.p. 98–99° (from pentane), $[\alpha]_D$ − 11° (*c* 1.2). ^{1}H-N.m.r. data (C_6D_6): δ 0.10 and 0.18 (2 s, 6 H, 2 Me), 1.01 (s, 9 H, ^{t}Bu), 3.55 (dd, 1 H, $J_{5,6ax}$ 9.5, $J_{6ax,6eq}$ 10.5 Hz, H-6*ax*), 3.97 (dd, 1 H, $J_{3,4}$ 7.1, $J_{4,5}$ 10.0 Hz, H-4), 4.05 (ddd, 1 H, $J_{5,6eq}$ 5.0 Hz, H-5), 4.17 (dd, 1 H, H-6*eq*), 4.69 (s, 4 H, OCH_2Ph), 4.70 (dd, 1 H, $J_{2,3}$ 2.5 Hz, H-3), 4.77 (s, 2 H, CH_2OH), 4.99 (d, 1 H, H-2), 5.32 (s, 1 H, C*H*Ph), 6.50 and 6.88 (2 d, 2 H, *J* 2.5 Hz, H-3,5), and 7.0–7.7 (m, 15 H, 3 Ph). Mass spectrum: *m/z* 535 (M^+ − ^{t}BuMe$_2$SiO, 24%), 667 (M^+ + 1, 100).

Anal. Calc. for $C_{40}H_{46}O_7Si$: C, 72.04; H, 6.95. Found: C, 72.20; H, 6.89.

*1,1^2-Anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-1-(2-hydroxymethylphenyl)-α-*D*-arabino-hexopyranose* (**12**). — Reaction of **7** (100 mg, 0.15 mmol) in toluene (2 mL) with *o*-bromobenzyl alcohol (43 mg, 0.23 mmol, 1.5 equiv.) and $Pd(PPh_3)_4$ (17 mg, 15 μmol, 0.1 equiv.) at reflux temperature for 24 h provided, after column chromatography (15:1 hexane–ethyl acetate containing 0.1% of triethylamine), **14** (10 mg, 20%) and **12** (52 mg, 73%) isolated as a colourless syrup, $[\alpha]_D$ + 1.5° (*c* 0.9). ^{1}H-N.m.r. data (C_6D_6): δ 0.12 and 0.18 (2 s, 6 H, 2 Me), 1.0 (s, 9 H, ^{t}Bu), 2.37 (dd, 1 H, $J_{2eq,3}$ 5.9, $J_{2eq,2ax}$ 13.0 Hz, H-2*eq*), 2.45 (dd, 1 H, $J_{2ax,3}$ 10.4 Hz, H-2*ax*), 3.58 (dd, 1 H, $J_{5,6ax}$ 10.2, $J_{6ax,6eq}$ 10.5 Hz, H-6*ax*), 3.64 (dd, 1 H, $J_{3,4}$ 8.9, $J_{4,5}$ 9.8 Hz, H-4), 4.20 (dd, 1 H, $J_{5,6eq}$

5.0 Hz, H-6*eq*), 4.35 (ddd, 1 H, H-5), 4.63 (ddd, 1 H, H-3), 4.68 and 4.86 (2 d, 2 H, *J* 13 Hz, OCH_2Ar), 5.47 (s, 1 H, C*H*Ph), and 6.76–7.71 (m, 9 H, aromatic H).

Anal. Calc. for $C_{26}H_{34}O_5Si$: C, 68.69; H, 7.54. Found: C, 68.91; H, 7.47.

*1,1²-Anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-1-(4,6-dibenzyloxy-2-hydroxymethylphenyl)-*α-D-arabino*-hexopyranose* (**13**). — Reaction of **7** (383 mg, 0.59 mmol) in toluene (10 mL) with **9** (282 mg, 0.70 mmol, 1.2 equiv.) and $Pd(PPh_3)_4$ (69 mg, 59 μmol, 0.1 equiv.) at reflux temperature for 24 h provided, after column chromatography (dichloromethane containing 0.1% of triethylamine), **13** (288 mg, 72%), m.p. 141–142° (from ethyl acetate–hexane), $[\alpha]_D$ −2.5° (*c*, 1.0). ^{1}H-N.m.r. data (C_6D_6): δ 0.14 and 0.19 (2 s, 6 H, 2 Me), 1.03 (s, 9 H, ^{t}Bu), 2.55 (dd, 1 H, $J_{2eq,3}$ 5.3, $J_{2eq,2ax}$ 13.1 Hz, H-2*eq*), 3.33 (dd, 1 H, $J_{2ax,3}$ 11.0 Hz, H-2*ax*), 3.66 (t, 1 H, $J_{5,6ax}$ = $J_{6ax,6eq}$ = 10.5 Hz, H-6*ax*), 3.77 (dd, 1 H, $J_{3,4}$ 8.9, $J_{4,5}$ 9.9 Hz, H-4), 4.27 (dd, 1 H, $J_{5,6eq}$ 5.0 Hz, H-6*eq*), 4.42 (ddd, 1 H, H-5), 4.67 and 4.69 (2 s, 4 H, 2 CH_2Ph), 4.72 (d, 1 H, *J* 12.5 Hz, OC*H*Ar), 4.73 (m, 1 H, H-3), 4.90 (d, 1 H, *J* 12.5 Hz, OC*H*Ar), 5.38 (s, 1 H, C*H*Ph), 6.09 (d, 1 H, *J* 2.0 Hz, H-5), 6.46 (d, 1 H, *J* 2.0 Hz, H-3), and 7.03–7.70 (m, 15 H, 3 Ph).

Anal. Calc. for $C_{40}H_{46}O_7Si$: C, 72.04; H, 6.95. Found: C, 72.27; H, 6.97.

*1,1²-Anhydro-4,6-*O*-benzylidene-3-*O*-tert-butyldimethylsilyl-1-(4,6-dibenzyloxy-2-hydroxymethylphenyl)-α-* (**15**) and *-β-D-glucopyranose* (**16**). — To a solution of **11** (380 mg, 0.57 mmol) in anhydrous dichloromethane (6 mL) in the presence of sodium hydrogencarbonate (359 mg, 4.27 mmol) under Ar at −78° was added 85% *m*-chloroperoxybenzoic acid (109 mg, 0.85 mmol, 1.5 equiv.). The mixture was stirred for 5 h, then diluted with dichloromethane. The organic layer was washed with aqueous 15% sodium hydrogensulfite, saturated aqueous sodium hydrogencarbonate, and water, dried (Na_2SO_4), and filtered, and the solvent was evaporated. Column chromatography (6:1 hexane–ethyl acetate) of the residue gave **15** (251 mg, 70%), m.p. 132–133° (from ether–hexane), $[\alpha]_D$ +9.5° (*c* 1.7). ^{1}H-N.m.r. data (C_6D_6): δ 0.24 and 0.29 (2 s, 6 H, 2 Me), 1.08 (s, 9 H, ^{t}Bu), 1.85 (bs, 1 H, OH), 3.59 (dd, 1 H, $J_{5,6ax}$ 10.0, $J_{6ax,6eq}$ 11.0 Hz, H-6*ax*), 3.70 (dd, 1 H, $J_{3,4}$ 9.0, $J_{4,5}$ 10.0 Hz, H-4), 4.26 (dd, 1 H, $J_{5,6eq}$ 5.0 Hz, H-6*eq*), 4.32 (t, 1 H, $J_{2,3}$ 9.0 Hz, H-3), 4.33 (dt, 1 H, H-5), 4.66 (s, 4 H, 2 CH_2Ph), 4.67 and 4.87 (2 d, 2 H, *J* 13.0 Hz, OCH_2Ar), 4.87 (bd, 1 H, H-2), 5.28 (s, 1 H, C*H*Ph), 6.09 (d, 1 H, *J* 2.0 Hz, H-5), 6.44 (d, 1 H, *J* 2.0 Hz, H-3), and 7.00–7.70 (m, 15 H, 3 Ph). Mass spectrum: *m/z* 683 (M^+ + 1, 100%).

Anal. Calc. for $C_{40}H_{46}O_8Si$: C, 70.35; H, 6.79. Found: C, 70.64; H, 6.98.

Further elution provided **16** (45 mg, 11.5%), isolated as a colourless syrup, $[\alpha]_D$ +25° (*c* 1.2). ^{1}H-N.m.r. data (C_6D_6): δ 0.08 and 0.12 (2 s, 6 H, 2 Me), 1.07 (s, 9 H, ^{t}Bu), 2.30 (d, 1 H, $J_{2,OH}$ 3.9 Hz, OH), 3.57 (dd, 1 H, $J_{5,6ax}$ 10.0, $J_{6ax,6eq}$ 10.5 Hz, H-6*ax*), 3.81 (dd, 1 H, $J_{3,4}$ 8.5, $J_{4,5}$ 9.8 Hz, H-4), 4.17 (dd, 1 H, $J_{5,6eq}$ 5.0 Hz, H-6*eq*), 4.28 (dd, 1 H, $J_{2,3}$ 7.5 Hz, H-2), 4.41 (ddd, H-5), 4.60 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 4.65 (d, 1 H, *J* 13.0 Hz, OC*H*Ar), 4.71 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 4.79 (dd, 1 H, H-3), 5.07 (d, 1 H, *J* 13.0 Hz, OC*H*Ar), 5.33 (s, 1 H, C*H*Ph), 6.10 (d, 1 H, *J* 2.0 Hz, H-3), 6.44 (d, 1 H, *J* 2.0 Hz, H-5), and 6.90–7.70 (m, 15 H, 3 Ph). Mass spectrum: *m/z* 683 (M^+ + 1, 100%), 700 (M^+ + 18, 22).

Anal. Calc. for $C_{40}H_{46}O_8Si$: C, 70.35; H, 6.79. Found: C, 70.42; H, 6.84.

*1,2²-Anhydro-4,6-O-benzylidene-1-(4,6-dibenzyloxy-2-hydroxymethylphenyl)-α-*D*-glucopyranose* (**17**). — To a stirred solution of **15** (30 mg, 44 μmol) in dry oxolane (2 mL) was added tetrabutylammonium fluoride (23 mg, 88 μmol, 2 equiv.) at 0° under Ar. The mixture was stirred at room temperature for 4 h, the solvent was evaporated, and a solution of the residue in dichloromethane was washed with saturated aqueous ammonium chloride and water, dried (Na_2SO_4), and filtered, and the solvent was evaporated. Column chromatography (1:1 hexane–ethyl acetate) of the residue gave **17** (22 mg, 85%), m.p. 91–95° (from ether–hexane), $[\alpha]_D$ + 27° (*c* 1.5). ^{1}H-N.m.r. data (C_6D_6 with one drop of D_2O): δ 3.58 (t, 1 H, $J_{5,6ax}$ = $J_{6ax,6eq}$ = 10 Hz, H-6*ax*), 3.73 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4), 4.24 (dd, 1 H, $J_{5,6eq}$ 5.0 Hz, H-6*eq*), 4.28 (t, $J_{2,3}$ 9.5 Hz, H-3), 4.34 (ddd, 1 H, H-5), 4.64–4.75 (m, 4 H, 2 CH_2Ph), 4.80 (d, 1 H, *J* 13.0 Hz, OC*H*Ar), 4.84 (d, 1 H, H-2), 4.91 (d, 1 H, *J* 12.2 Hz, OC*H*Ar), 5.32 (s, 1 H, C*H*Ph), 6.07 and 6.43 (2 d, 2 H, *J* 1.5 Hz, H-3,5), and 7.03–7.66 (m, 15 H, 3 Ph). Mass spectrum: *m/z* 569 (M^+ + 1, 47%).

Anal. Calc. for $C_{34}H_{32}O_8 \cdot 0.5H_2O$: C, 70.70; H, 5.76. Found: C, 70.90; H, 5.68.

*2,3,4,6-Tetra-O-acetyl-1,1²-anhydro-1-(4,6-diacetoxy-2-hydroxymethylphenyl)-α-*D*-glucopyranose* (**19**). — (*a*) *From* **15**. As described above, treatment of **15** (30 mg, 44 μmol) gave crude **17**, a solution of which in ethyl acetate–methanol (2:1, 4 mL) was stirred under H_2 in the presence of 10% Pd/C (~ 5 mg) for the appropriate time (usually several hours) at room temperature. The mixture was filtered through Celite, the insoluble material was washed several times with methanol, and the combined filtrate and washings were concentrated to give crude **18** which was treated with pyridine–acetic anhydride (4:1, 3 mL) at room temperature. After 12 h, ice was added, the mixture was extracted with ether, the extract was washed with saturated aqueous potassium hydrogensulfate, aqueous 20% sodium hydrogencarbonate, and water, then dried (Na_2SO_4), and the solvent was evaporated. Column chromatography (20:1 dichloromethane–acetone) of the residue provided **19** (20 mg, 80%), m.p. 197° (from light petroleum–hexane), $[\alpha]_D$ −9° (*c* 1.1); lit.[23] m.p. 199°, $[\alpha]_D$ −7.5°. ^{1}H-N.m.r. data ($CDCl_3$): δ 1.79, 2.01, 2.05, 2.06, 2.28, and 2.40 (6 s, 18 H, 6 OAc), 4.02 (m, 1 H, H-6a), 4.24–4.33 (m, 2 H, H-5,6b), 5.16 and 5.22 (2 d, 2 H, *J* 14 Hz, OCH_2Ar), 5.25 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ = 10.0 Hz, H-4), 5.59 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-3), 5.70 (d, 1 H, H-2), 6.92 and 7.00 (2 d, 2 H, *J* 1.8 Hz, Ph). Mass spectrum: *m/z* 570 (M^+ + 18, 100%).

Anal. Calc. for $C_{25}H_{28}O_{14}$: C, 54.35; H, 5.11. Found: C, 54.33; H, 5.12.

(*b*) *From* **16**. Treatment of **16** (43 mg, 64 μmol), under the conditions described above, gave, after chromatography, **19** (24 mg, 69%).

*2,3,4,5,6-Penta-O-acetyl-1,1²-anhydro-1-(4,6-diacetoxy-2-hydroxymethylphenyl)-*D*-glucitol* (**21**). — A solution of **15** (27 mg, 40 μmol) in methanol–ethyl acetate–M hydrochloric acid (4:4:1, 2.25 mL) was stirred in the presence of 10% Pd/C (~ 5 mg) under H_2 (3 atm.) for 2 h. The mixture was filtered through Celite, the insoluble material was washed several times with methanol, the combined filtrate and washings were neutralised with Dowex 1 (HO^-) resin and filtered, and the solvent was evaporated. Acetylation of the residue overnight with pyridine–acetic anhydride (2:1, 3 mL) and the usual work-up gave, after column chromatography (1:1 hexane–ethyl acetate), **21**

(14 mg, 60%), isolated as a colourless syrup, $[\alpha]_D$ −8° (*c* 1.0). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.68, 2.02, 2.06, 2.11, 2.21, 2.27, and 2.31 (7 s, 21 H, 7 OAc), 4.16 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.25 (dd, 1 H, $J_{5,6b}$ 2.9 Hz, H-6b), 5.07 (m, 1 H, *J* 12.4 Hz, OC*H*Ar), 5.16 (ddd, 1 H, $J_{4,5}$ 8.7 Hz, H-5), 5.22 (m, 1 H, *J* 12.4 Hz, OC*H*Ar), 5.38 (dd, 1 H, $J_{1,2}$ 1.9, $J_{2,3}$ 9.0 Hz, H-2), 5.53 (dd, 1 H, $J_{3,4}$ 2.1, H-4), ~5.54 (m, 1 H, H-1), 5.73 (dd, 1 H, H-3), 6.85 and 6.93 (2 m, 2 H, Ph). Mass spectrum: *m/z* 614 (M^+ + 18, 100%).

*1,1^2-Anhydro-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-(4,6-dibenzyloxy-2-hydroxymethylphenyl)-*α*-*D*-glucopyranose* (**22**). — To a solution of **15** (270 mg, 0.39 mmol) in anhydrous oxolane (5 mL) under Ar was added sodium hydride (24 mg of a 60% suspension in oil, 0.59 mmol, 1.5 equiv.) at 0°. After stirring at room temperature for 1 h, the mixture was cooled to 0° and 2-methyl-2-propanol was added. The mixture was concentrated, then diluted with dichloromethane. The organic phase was washed with saturated aqueous ammonium chloride and water, then dried (Na_2SO_4), and the solvent was evaporated. Column chromatography (6:1 hexane–ethyl acetate) of the residue gave, first, **22** (129 mg), isolated as a colourless syrup, and **15** (125 mg). Repetition of the treatment on the recovered **15** gave **22** (59 mg; total yield, 70%) and **15** (55 mg, 20%). Compound **22** had $[\alpha]_D$ −18° (*c* 1.3). ^{1}H-N.m.r. data (C_6D_6): δ −0.04 (s, 3 H, Me), 0.26 (s, 3 H, Me), 0.83 (s, 9 H, ^{t}Bu), 2.05 (bs, 1 H, OH), 3.61 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.4 Hz, H-4), 3.64 (t, 1 H, $J_{5,6ax} = J_{6ax,6eq}$ = 10.4 Hz, H-6*ax*), 4.28 (bt, $J_{2,3} = J_{3,4}$ = 9.4 Hz, H-3), 4.29 (dd, 1 H, $J_{5,6eq}$ 5.0 Hz, H-6*eq*), 4.45 (ddd, 1 H, H-5), 4.70 (s, 2 H, CH_2Ph), 4.71 and 4.77 (2 d, 2 H, *J* 11.3 Hz, CH_2Ph), 4.73 (d, 1 H, H-2), 4.99 and 5.04 (2 d, 2 H, *J* 12.3 Hz, OCH_2Ar), 5.35 (s, 1 H, C*H*Ph), 6.10 and 6.48 (2 d, 2 H, *J* 2.0 Hz, H-3,5), and 7.10–7.60 (m, 15 H, 3 Ph).

Anal. Calc. for $C_{40}H_{46}O_8Si$: C, 70.35; H, 6.79. Found: 70.40; H, 6.83.

*1,1^2-Anhydro-4,6-*O*-benzylidene-2-*O*-tert-butyldimethylsilyl-1-(4,6-dibenzyloxy-2-hydroxymethylphenyl)-3-*O*-octadecanoyl-*α*-*D*-glucopyranose* (**23**). — To a solution of **22** (100 mg, 0.15 mmol) in anhydrous dichloromethane (3 mL) under Ar were added 4-dimethylaminopyridine (18 mg, 19 μmol, 0.13 equiv.), stearic acid (58 mg, 0.23 mmol, 1.5 equiv.), and 1,3-dicyclohexylcarbodi-imide (48 mg, 0.23 mmol, 1.5 equiv.). The mixture was stirred overnight at room temperature, then filtered, and diluted with dichloromethane, and the organic phase was washed with iced 0.1M hydrochloric acid, saturated aqueous sodium hydrogencarbonate, and water, dried (Na_2SO_4), and concentrated to dryness. Column chromatography (6:1 hexane–ethyl acetate) of the residue provided **23** (101 mg, 73%), isolated as a colourless syrup, $[\alpha]_D$ −27° (*c* 3.1). ^{1}H-N.m.r. data (C_6D_6): δ −0.24 (s, 3 H, Me), 0.16 (s, 3 H, Me), 0.84 (s, 9 H, ^{t}Bu), ~0.9–1.9 (m, 33 H), 2.32–2.44 (m, 2 H, CH_2CO), 3.67 (t, 1 H, $J_{5,6ax} = J_{6ax,6eq}$ = 10.5 Hz, H-6*ax*), 3.82 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H-4), 4.26 (dd, 1 H, $J_{5,6eq}$ 5.0 Hz, H-6*eq*), 4.57 (ddd, 1 H, H-5), 4.71 (s, 2 H, CH_2Ph), 4.74 and 4.79 (2 d, 2 H, *J* 11.5 Hz, CH_2Ph), 4.93 (d, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 4.94 and 5.01 (2 d, 2 H, *J* 12.7 Hz, OCH_2Ar), 5.45 (s, 1 H, C*H*Ph), 6.09 (d, 1 H, *J* 1.8 Hz, H-3 or H-5), 6.22 (t, 1 H, H-3), 6.48 (d, 1 H, *J* 1.8 Hz, H-3 or H-5), and 7.05–7.20 (m, 15 H, 3 Ph). Mass spectrum: *m/z* 949 (M^+ + 1, 100%).

Anal. Calc. for $C_{58}H_{80}O_9Si$: C, 73.54; H, 8.51. Found: C, 73.21; H, 8.62.

*2,4,6-Tri-*O*-acetyl-1,1^2-anhydro-1-(4,6-diacetoxy-2-hydroxymethylphenyl)-3-*O*-*

octadecanoyl-α-D-glucopyranose (**25**). — A solution of **23** (40 mg, 42 μmol) in trifluoroacetic acid–water (10:1, 0.15 mL) was stirred at room temperature for 1 h. Water was added (0.02 mL) and the solution was concentrated. Toluene was evaporated several times from the residue, a solution of which in ethyl acetate–methanol (1:1, 1 mL) was treated by 10% Pd/C (~ 5 mg) under H_2 for 1 h. Work-up and acetylation, as described for the preparation of **19**, gave, after column chromatography (5:2 hexane–ethyl acetate), **25** (20 mg, 61%), isolated as a colourless syrup, $[\alpha]_D$ − 9° (*c* 0.5). ^{1}H-N.m.r. data (C_6D_6): δ 0.91 (t, 3 H, *J* 6.8 Hz, CH_3CH_2, ~ 1.1–1.4 (m, 30 H, CH_2), 1.48, 1.64, 1.69, 1.78, and 1.92 (5 s, 15 H, 5 OAc), 2.25 (t, 2 H, *J* 7.5 Hz, CH_2CO), 4.01 (dd, 1 H, $J_{5,6a}$ 2.2, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.36 (ddd, 1 H, $J_{5,6b}$ 4.0, $J_{4,5}$ 10.0 Hz, H-5), 4.48 (dd, 1 H, H-6b), 4.70 and 4.79 (2 d, 2 H, *J* 13.1 Hz, OCH_2Ar), 5.68 (t, 1 H, $J_{3,4}$ ~ 10.0 Hz, H-4), 6.11 (t, 1 H, $J_{2,3}$ ~ 10.0 Hz, H-3), 6.20 (d, 1 H, H-2), 6.52 and 7.11 (2 d, *J* 2.0 Hz, H-3,5). Mass spectrum: *m/z* 794 (M^+ + 18, 100%).

Anal. Calc. for $C_{41}H_{60}O_{14}$: C, 63.39; H, 7.78. Found: C, 63.71; H, 7.96.

2-(4,6-O-Benzylidene-3-O-tert-butyldimethylsilyl-β-D-glucopyranosyl)-3,5-dibenzyloxy-1-hydroxymethylbenzene (**26**). — To a stirred solution of **11** (75 mg, 0.11 mmol) in anhydrous oxolane (1 mL) at 0° under Ar was added borane–oxolane complex (M in oxolane, 0.45 mL, 0.45 mmol, 4.0 equiv.). The mixture was stirred at room temperature for 5 h, and 3M sodium hydroxide (4.0 equiv.), 10M hydrogen peroxide (12.0 equiv.), and ethanol (0.2 mL) were added at 0°. Stirring was continued at room temperature overnight. The mixture was concentrated and then diluted with dichloromethane, the organic phase was washed with aqueous 20% sodium hydrogensulfite, saturated aqueous ammonium chloride, and water, then dried (Na_2SO_4), and the solvent was evaporated. Column chromatography (3:1 hexane–ethyl acetate) of the residue gave **26** (58 mg, 75%), isolated as a colourless syrup, $[\alpha]_D$ − 15° (*c* 0.6). The ^{1}H-n.m.r. spectrum was unassignable at 25°. Mass spectrum: *m/z* 529 (M^+ − 155, 100%), 685 (M^+ + 1, 33), 702 (M^+ + 18, 87).

Anal. Calc. for $C_{40}H_{48}O_8Si$: C, 70.15; H, 7.06. Found: C, 70.03; H, 6.96.

1-Acetoxymethyl-3,5-dibenzyloxy-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)benzene (**27**). — A solution of **26** (40 mg, 58 μmol) in methanol–M hydrochloric acid (4:1, 2.5 mL) was stirred overnight at room temperature, then neutralised with Dowex 1 (HO^-) resin, filtered, and concentrated. Toluene was evaporated several times from the residue which was then acetylated as described for the preparation of **19**. Column chromatography of the product gave **27** (27 mg, 67%), isolated as a colourless syrup, $[\alpha]_D$ − 23° (*c* 1.7). ^{1}H-N.m.r. data [$(CD_3)_2SO$, 140°]: δ 1.66, 1.89, 1.91, 1.97, and 2.05 (5 s, 15 H, 5 OAc), 3.88 (ddd, $J_{5,6a}$ 3.7, $J_{5,6b}$ 4.3, $J_{4,5}$ 9.9 Hz, H-5), 4.08 (m, 2 H, H-6a,6b), 4.96 (dd, 1 H, $J_{3,4}$ 8.9 Hz, H-4), 5.02 (d, 1 H, $J_{1,2}$ 9.9 Hz, H-1), 5.02–5.22 (m, 6 H, CH_2Ph), 5.24 (t, 1 H, $J_{2,3}$ 8.9 Hz, H-3), 5.57 (dd, 1 H, 9.9 Hz, H-2), 6.63 and 6.71 (2 d, 2 H, *J* 2.3 Hz, H-4,6), and 7.26–7.52 (m, 10 H, 2 Ph). Mass spectrum: *m/z* 710 (M^+ + 18, 100%).

Anal. Calc. for $C_{37}H_{40}O_{13}$; C, 64.15; H, 5.88. Found: C, 64.07; H, 5.88.

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