C-Glycosylation of naphthols using glucosyl donors

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Abstract
Attempts to effect direct *C*-glycosylation of naphthols **6**, **7**, and **8** using glucosyl donors **9** and **10** were unsuccessful. *O*-Glycosides **11**, **12** and **15** were obtained under Mitsunobu conditions, however, these failed to undergo rearrangement to the *C*-glycosides **13**, **14** and **16,** respectively. Successful *C*glycosylation of naphthols **7** and **8** was realized using the more reactive 2-deoxyglucosyl acetate donor **18** with trimethylsilyl triflate and silver perchlorate as the Lewis acid promoters. Use of acetonitrile as solvent formed the *C*-glycosides **20** and **22** in preference to the corresponding *O*-glycosides **19** and **21**, respectively.

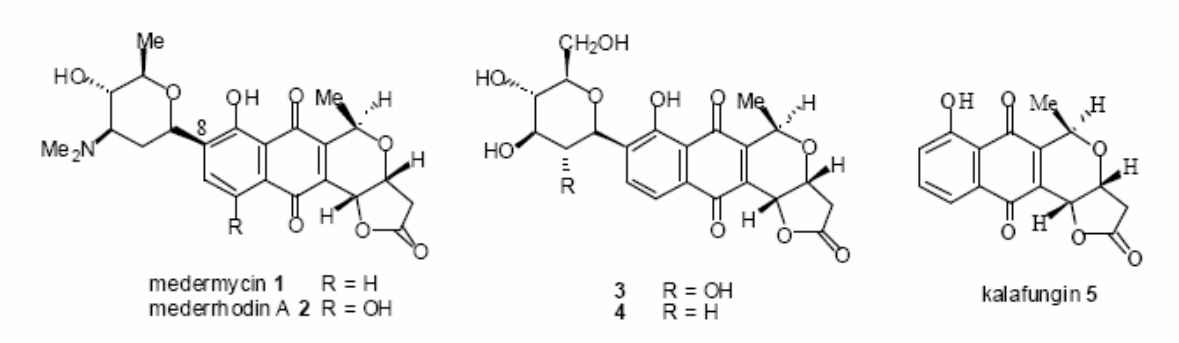
Keywords: Naphthols, *C*-glycosylation, glucosyl donors, 2-deoxyglucosyl donors, Lewis acids, pyranonaphthoquinone antibiotics

Introduction

The pyranonaphthoquinone family of antibiotics have attracted considerable synthetic interest[1] due to their proposed ability to act as bioreductive alkylating agents *via* quinone methide intermediates. Our approach to the synthesis of several of the simpler members of the pyranonaphthoquinone antibiotics has focused on the addition of a silyloxyfuran to a naphthoquinone followed by oxidative rearrangement of the resultant furonaphthofuran adduct.[2] Recently our attention has been directed towards the synthesis of some of the more complex pyranonaphthoquinone antibiotics which contain *C*-glycoside moieties as typified by medermycin **1**[3] and mederrhodin **2**.[4] To date only one lengthy synthesis of medermycin **1** has been reported[5] in which the pyranonaphthalene skeleton was assembled by addition of a *C*-glycosyl-sulfonylphthalide to an enone.

Given the significant biological activity exhibited by *C*glycosylpyranonaphthoquinone antibiotics such as medermycin **1**, we embarked on a flexible synthetic programme that would provide access to a range of *C*-glycosidic pyranonaphthoquinones for biological evaluation. Our initial attention focused on the synthesis of a glucosyl analogue of medermycin **3** and a 2-deoxyglucosyl analogue of medermycin **4** using a furofuran annulation – oxidative

rearrangement strategy as previously used for the synthesis of kalafungin **5** and related aglycones.[6,7]



Whilst the syntheses of aryl *C*-glycosides have been well documented,[8] the synthesis of *C*-glycosidic members of the pyranonaphthoquinone group of antibiotics has received little attention to date. Given that the naphthoquinone functionality is installed via oxidation of an oxygenated naphthalene precursor, a crucial step for the synthesis of glucosyl pyranonaphthoquinones **3** and **4** is a successful method to effect *C*-glycosylation of appropriate naphthol precursors. We therefore herein report our model studies on the *C*-glycosylation of naphthols **6**,**7** and **8** using glucosyl donors **9**,**10** and 2-deoxyglucosyl donors **17**,**18**.

Discussion

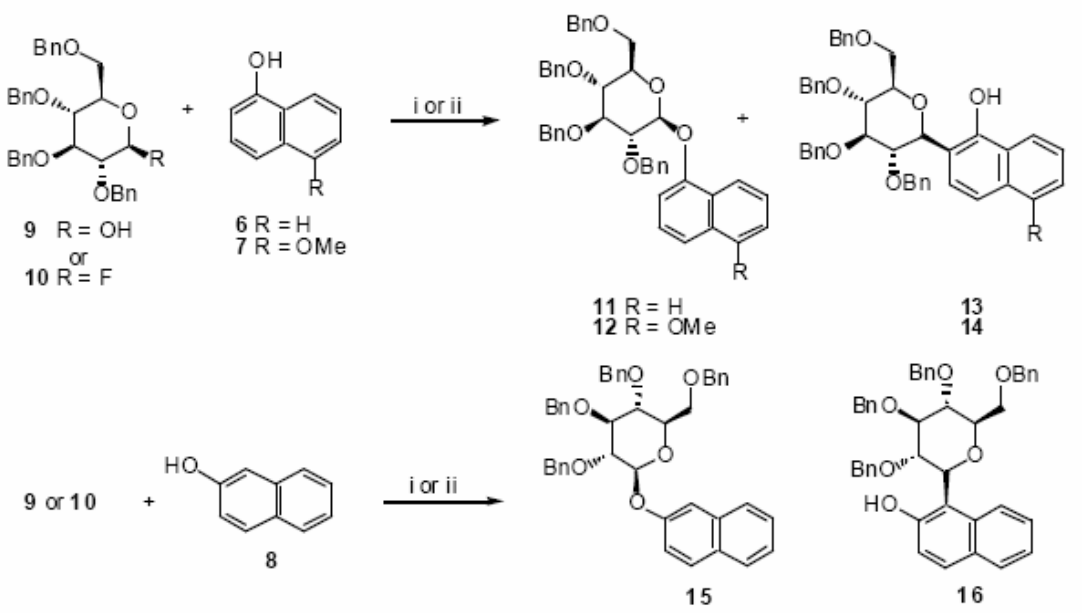
Our initial task was to establish conditions for effecting *C*-glycosylation of naphthols **6**,**7** and **8**. Pyranose **9** and glucosyl fluoride **10** were selected as the glucosyl donors as they are both readily available from D-glucose. Pyranose **9** was prepared from methyl-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside following the procedure of Glaudemans *et al.*[9] Pyranose **9** was then converted to glucosyl fluoride **10** using diethylaminosulfur trifluoride using the conditions reported by Posner and Haines[10] and later by Kovac *et al*.[11]

The acetate protected 2-deoxypyranoside **18** was prepared by acetylation of 2deoxyglucose following the procedure reported by Overend *et al.*[12] affording glycosyl acetate **18** (α:β, 10:1) in 73% yield. Alternatively, the procedure of Mioskowski *et al.*[13] required treatment of tri-*O*-acetyl-D-glucal with triphenylphosphine hydrobromide and acetic acid, affording the desired acetate **18** (α:β, 9:1) in 72% yield. The benzyl protected 2-deoxypyranoside **17** was also prepared from tri-*O*-benzyl-D-glucal according to the procedure of Mioskowski *et al*.[13] affording glycosyl acetate **17** (α:β, 9:1) in 86% yield. Attempts to prepare 2-deoxyglucosyl fluorides met with little success due to their apparent instability.[14]

A common method to effect *C*-glycosylation involves initial formation of an *O*-glycoside followed by effecting rearrangement to a *C*-glycoside. Suzuki *et al*.[15] favour the use of anomeric fluorides as the glycosyl donors with hafnocene dichloride and silver perclorate as the promoters to effect the *O*-to *C*–glycoside rearrangement. A mixture of glucosyl fluoride **10**, the appropriate

naphthol **6**, **7**, or **8** and 4Å molecular sieves in dry dichloromethane was cooled to -78 °C. The Lewis acid (hafnocene dichloride) and promoter (silver perchlorate) were then added. The solution was allowed to warm to -20 °C and stirred for 1 hour, however, the desired *C*-glycosides **13**, **14**, **16** were not observed (Scheme 1). Longer reaction times did not result in the formation of the desired product, even when the reaction was allowed to warm to room temperature. Use of an alternative Lewis acid, zirconocene dichloride, was also unsuccessful.

Disappointed by the lack of success in effecting *C*-glycosylation using Suzuki's methodology, attention turned to use of a two step procedure reported by Kometani *et al*.[16] for effecting *C*-glycosylation. This methodology involves the formation of an *O*-glycoside under Mitsunobu conditions followed by rearrangement to a β-*C*-glycoside after activation by boron trifluoride diethyletherate. Accordingly, a solution of glucopyranose **9** and the appropriate naphthol **6**, **7** or **8** in tetrahydrofuran at 0 °C was treated with diethyl azodicarboxylate and triphenylphospine to form the corresponding β-*O*-glycosides **11**, **12**, **15** in reasonable yields (Scheme 1).



Reagents and conditions: (i) **10**, Cp_2HfCl_2 (or Cp_2ZrCl_2), $AgClO_4$, CH_2Cl_2, MS4Å, -78 °C to -20 °C; (ii) **9**, DEAD, PPh_3, THF, 0 °C to r.t., 12 h., **11** (43%), **12** (63%); **15** (56%).

Scheme 1

O-Glycoside **11** was obtained as colourless needles in 43% yield. In the ^{1}H nmr spectrum the anomeric proton 1'-H resonated as a doublet at δ 5.23 with the coupling constant, *J*1',2' 7.7 Hz, confirming the β-stereochemistry about the glycosidic bond. In the ^{13}C nmr spectrum C-1' resonated downfield of the other glycosyl carbons at δ 101.5 consistent with formation of β-*O*-glycoside **11**. *O*-Glycoside **12** was isolated as tan platelets in 63% yield. In the ^{1}H nmr spectrum the anomeric proton, 1'-H, resonated as a doublet at δ 5.21, *J*1',2' 7.7 Hz and C-1' resonated at δ 101.6 in the ^{13}C nmr spectrum.

O-Glycoside **15** was obtained as colourless needles in 56% yield. In the ^{1}H nmr spectrum the anomeric proton 1'-H resonated as a doublet at δ 5.08, *J*1',2' 7.1 Hz and C1' resonated at δ 102.6 in the ^{13}C nmr spectrum. The synthesis of the *O*-glycoside **15** (α:β, 5:1) has recently been reported by Larsen and Andrews[17] with their data supporting the assignment of β-stereochemistry at the glycosidic linkage for our compound. For comparison, in the α-anomer 1'-H resonated as a doublet at δ 5.62 with coupling constant, $J_{1',2'}$ 3.5 Hz and C-1' resonated at δ 95.5 in the ^{13}C nmr spectrum.[17]

Treatment of the *O*-glycosides **11**, **12**, **15** in dichloromethane at room temperature with boron trifluoride diethyl etherate failed to effect rearrangement to the desired *C*-glycosides **13**, **14**, **16**. The glycosidic linkage was eventually cleaved instead, liberating the starting naphthols **6**, **7**, **8**. Given the lack of success at forming *C*-glycosides of the simple naphthols **6**, **7**, **8** when using glycosyl donors derived from D-glucose, it was decided to investigate the use of more reactive 2-deoxyglucosyl donors. It was felt that the bulky benzyloxy group at C2 might be preventing the *O*- to *C*-glycoside rearrangement from occurring.

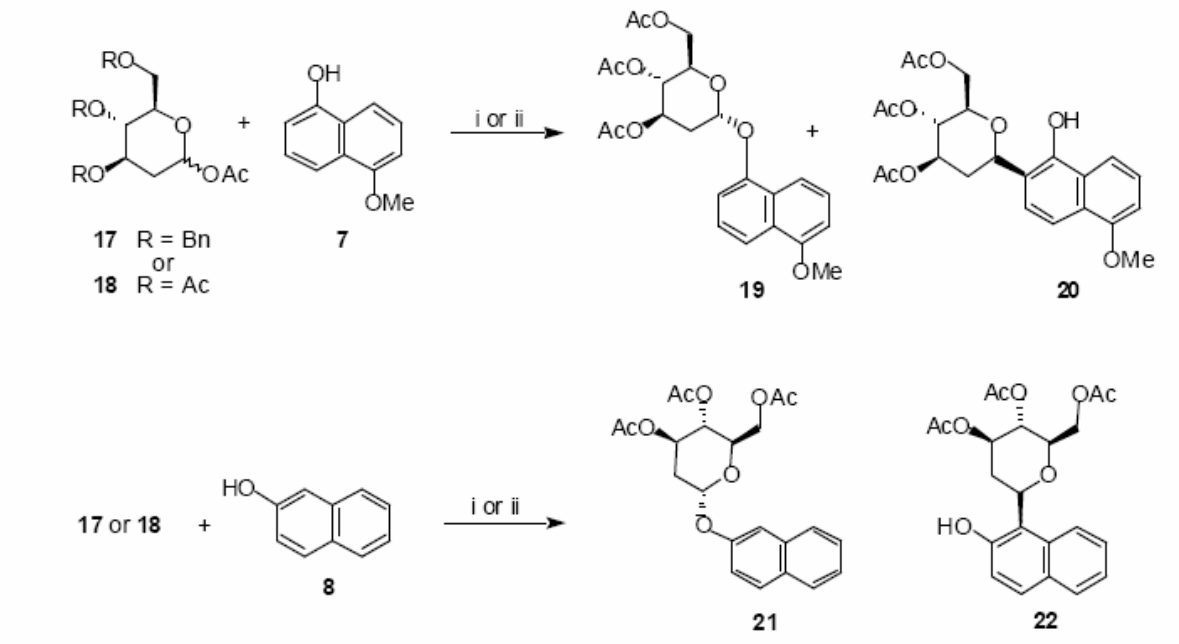
Given the difficulties experienced with the preparation and storage of the unstable 1-fluoro derivatives of 2-deoxysugars, our attention turned to the use of the more stable 1-*O*-acetyl-2-deoxyglucosyl donors **17** and **18**. 2-Deoxyglucosyl acetates **17** and **18** were reacted with naphthols **6**, **7** and **8** in dichloromethane using dicyclopentadienylhafnocenedichloride and silver perchlorate in the presence of 4Å molecular sieves (Scheme 2). In none of these reactions was *C*-glycoside formation observed.

It was next decided to investigate a different method for effecting *C*-glycosylation as reported by Toshima *et al*.[18] using trimethylsilyl triflate and silver perchlorate (1:1) as the Lewis acid promoters. Naphthols **7** and **8** were reacted with acetate protected 2deoxyglucosyl acetate **18** in dichloromethane at 0 °C using the trimethylsilyl triflatesilver perchlorate promoter system, the reaction then being warmed to room temperature over 1 h. For both naphthols **7** and **8** mixtures of the *O*-glycosides **19** and **21** and the desired β-*C*-glycosides **20** and **22** were obtained, even after prolonged stirring.

In contrast, using the more coordinating solvent, acetonitrile, β-*C*-glycosides **20** and **22** were formed exclusively, in yields of 82% and 97% respectively. A similar effect on changing the solvent to acetonitrile, when using boron trifluoride diethyletherate as the Lewis acid in analogous *C*-glycosylation reactions, has been reported by Larsen *et al.*[19] and by Allevi *et al*.[20]

The α-*O*-glycoside **19** was isolated in 34% yield and β-*C*-glycoside **20** was isolated in 29% yield from the reaction of naphthol **7** with 2-deoxylglucosyl donor **18** using dichloromethane as solvent with trimethylsilyl triflate and silver perchlorate as the promoters. The infra-red spectrum for α-*O*-glycoside **19** lacked a hydroxyl stretch and high resolution mass spectrometry confirmed the molecular formula as $C_{23}H_{26}O_9$. In the ^{1}H nmr spectrum the anomeric proton 1'-H resonated as a doublet at δ 5.85, with the coupling constant, $J_{1',2'}$ 2.5 Hz establishing the α-stereochemistry of the glycosidic bond. The anomeric carbon C-1' resonated at δ 95.3, characteristic of an *O*-glycoside.

High resolution mass spectrometry for β-*C*-glycoside **20** confirmed the molecular formula as $C_{23}H_{26}O_9$. A broad hydroxyl stretch in the infra-red spectrum supported the presence of a *C*-glycosylated naphthol. The ^{1}H nmr spectrum supported the proposed structure. The anomeric proton 1'-H resonated at δ 4.96 as a doublet of doublets with the coupling constants, $J_{1',2'}$ 10.1 and $J_{1',2'}$ 2.2 Hz, supporting formation of a β-*C*-glycoside. The hydroxyl proton resonated at δ 8.23 and the anomeric carbon, C-1', resonated at δ 76.6 in the ^{13}C nmr spectrum, providing further support for the *C*-glycoside structure.



Reagents and conditions: (i) **17** or **18**, Cp_2HfCl_2(or Cp_2ZrCl_2), $AgClO_4$, CH_2Cl_2, MS4Å, -78 °C to -20 °C ; (ii) **18**, Me_3SiOTf, $AgClO_4$, 0 °C to r.t., CH_2Cl_2,**19** (34%), **20** (29%%); CH_3 CN, **20** (82%); CH_2Cl_2, **21** (39%), **22** (31%); CH_3CN, **22** (97%).

Scheme 2

The α-*O*-glycoside **21** was isolated in 39% yield and the β-*C*-glycoside **22** in 31% yield from the reaction of naphthol **8** with 2-deoxyglucosyl acetate **18** using the trimethylsilyl triflate-silver perchlorate promoter system in dichloromethane. The anomeric proton 1'-H of the α-*O*-glycoside **21** resonated at δ 5.83 as a broad doublet, with the coupling constant, $J_{1',2'}$ 2.6 Hz establishing the α-stereochemistry at the anomeric position. The anomeric carbon C-1' resonated at δ 95.3 in the the ^{13}C nmr spectrum also consistent with formation of the α-*O*-glycoside **21**.

In the ^{1}H nmr spectrum of the β-*C*-glycoside **22**, the anomeric proton 1'-H resonated at δ 5.62 as a doublet of doublets, with the coupling constants, $J_{1',2'ax}$ 11.9 and $J_{1',2'eq}$ 2.1 Hz, allowing assignment of the β-stereochemistry of the *C*-glycoside bond. In the ^{13}C nmr spectrum, the anomeric carbon C-1' resonated at δ 76.6. During the course of this work compounds **21** and **22**

were synthesized by Larsen *et al*.[19] and the spectroscopic data obtained in the present work agreed well with their data.[19]

In conclusion, it was found that use of the more reactive 2-deoxyglucosyl donors rather than glucosyl donors was necessary to effect successful *C*-glycosylation of naphthols **6**, **7**, and **8**. The best conditions found for the *C*-glycosylation involved the use of trimethylsilyl triflate and silver perchlorate as the Lewis Acid promoters using acetonitrile as solvent. Having established an effective method for *C*-glycosylation of these model naphthols with 2-deoxyglycosyl donors, our attention can then focus on extension of this *C*-glycosylation to the use of a naphthol that has appropriate functionality for further elaboration to analogues of the *C*-glycosylpyranonaphthoquinone antibiotic medermycin **1**.

Experimental Section

General Procedures. Petroleum ether refers to the fraction with bp 40-60 ^{o}C and was redistilled before use. Dichloromethane and acetonitrile were distilled from calcium hydride immediately before use. Flash column chromatography was performed on Merck silica gel 60 (230-400 mesh) using the eluent specified under medium pressure. All reagents were purchased from commercial suppliers and were used without further purification. Melting points are uncorrected. Optical rotations were measured using a PolAAR 2001 polarimeter in various solvents at the temperature and concentration (g.100 mL^{-1}) indicated. Specific rotations are given in $10^{-1}deg.cm^2.g^{-1}$. Readings were taken using the 589.3 nm sodium line in a 0.5 dm cell. Infrared spectra were recorded using a Perkin Elmer 1600 Series FTIR spectrometer as a thin film on a single sodium chloride plate seated in the apparatus on a custom made perch. ^{1}H NMR spectra were recorded on a Bruker AC200B spectrometer (200.13 MHz) or a Bruker AM400 (400.12 MHz) spectrometer. Data is expressed as parts per million downfield shift from tetramethylsilane as an internal standard, and reported as a position (δH), relative integral, multiplicity (s = singlet, br.s = broad singlet, d = doublet, dd = double doublet, ddd = double double doublet, t = triplet, q = quartet or m = multiplet), coupling constant (*J* Hz) and assignment. ^{13}C NMR spectra were recorded on a Bruker AC200 (50.3 MHz) spectrometer at ambient temperatures with complete decoupling and were interpreted with the aid of DEPT 135 and DEPT 90 experiments. Elemental analyses were carried out by Dr R. G. Cunninghame and associates at the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. Low resolution mas spectra were recorded on a VG70-250S, a VG70-SD or an AEI model MS902 double focusing magnetic sector mass spectrometer operating with an ionisation potential of 70eV (EI, CI). High resolution mass spectra were recorded at nominal resolution of 5000 or 10000 as appropriate. Major fragments are given as percentages relative to the base peak and are assigned where possible. Ionisation methods employed were (i) electron impact (EI), (ii) chemical ionisation with ammonia as reagent gas (CI), (iii) fast atom bombardment (FAB), (iv) liquid secondary ion mass spectrometry (LSIMS) using a 4nitrobenzylalcohol (NBA) matrix.

2,3,4,6-Tetra-*O*-benzyl-a -D-glucopyranose (9). A mixture of acetic acid (120 mL) and methyl-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside[9] (6.0 g, 10.8 mmol) in hydrochloric acid (2 M, 48 mL) was heated at reflux for one day at 80 °C. Part of the product crystallized overnight and was removed by filtration. The filtrate was heated for another day then poured into water affording further product upon cooling. The crude product was recrystallized from methanol to give 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose **9** (1.0 g, 43%) as white needles, mp 147-148 °C; $[\alpha]D^{18}$ = +24.1° (c=5.01, $CHCl_3$) {lit.[21] mp 151-152 °C; $[\alpha]_D^{20}$ = +21.7 (c=2.19, $CHCl_3$)}.

2,3,4,6-Tetra-*O*-benzyl-*b*-D-glucopyranosyl fluoride (10). To a cold (-30 °C) solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose **9** (1.08 g, 2 mmol) in dry tetrahydrofuran (10 mL) was added diethylaminosulfur trifluoride (DAST) (0.3 mL, 2.4 mmol). The mixture was allowed to warm to room temperature and after 30 min. the reaction had proceeded to completion. After cooling to -20 °C, methanol (1 mL) was added and the mixture concentrated at reduced pressure. The residue was partitioned between dichloromethane (50 mL) and a 1:1 mixture of saturated aqueous solutions of sodium chloride and sodium bicarbonate (50 mL). The organic phase was dried and concentrated and the residue purified by flash chromatography using hexane-ethyl acetate (9:1) as eluent to give 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl fluoride **10** (α:β, 1:8) as a colourless oil (0.9 g, 83%). Recrystallization from isopropyl ether gave white needles, m.p. 43-44 °C; $[\alpha]_D^{18}$ = +31.0 (c=1.04, $CHCl_3$) {lit.[11] mp 48-48.5 °C, $[\alpha]_D^{22}$ = +38 (c=0.8, $CHCl_3$)}. The ^{1}H nmr data were in agreement with that reported in the literature.[11.]

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranoside (18). ***(i) Using 2-deoxyglucose.***[12] 2-Deoxy-D-glucose (1.5 g, 9.14 mmol) was suspended in dry pyridine (25 mL) at 0 °C and freshly distilled acetic anhydride (20 mL) was added. The reaction mixture was kept at 0 °C for 4 days, at the end of which time the starting material had completely dissolved. The solution was diluted with water and then extracted with chloroform. The combined extracts were washed with sulfuric acid (0.01 M, 3 x 50 mL), dilute sodium bicarbonate solution (50 mL) and water (50 mL). After drying (calcium chloride) the solvent was removed at reduced pressure and the residue was triturated with ethanol-diethyl ether (3:1). The resulting solid was recrystallized several times from ethanol to give 1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranoside **18** (2.21 g, 73%) (α:β, 10:1) as white needles, m.p. 92-93 °C; $[\alpha]_D^{18}$ = +10.9 (c=1.01, ethanol) {lit.[12] mp 91 °C; $[\alpha]_D^{20}$ = +12.3 (c=0.325, ethanol)}; n_{max} (film) cm^{-1} 1745 (C=O), 1376 (C-O); α-anomer: δH (200 MHz; $CDCl_3$) 1.87 (1H, ddd, J_{gem} 12.3, $J_{2ax,3}$ 11.3, $J_{2ax,1}$ 10.0 Hz, 2axH), 2.04, 2.05, 2.09, 2.12 (each 3H, s, 4 x $COCH_3$), 2.36 (1H, ddd, J_{gem} 12.3, $J_{2eq,3}$ 4.7, $J_{2eq,1}$ 2.3 Hz, 2_{eq}-H), 3.75 (1H, ddd, $J_{5,4}$ 9.4, $J_{5,6B}$ 4.7 and $J_{5,6A}$ 2.3 Hz, 5-H), 4.09 (1H, dd, J_{gem} 12.4, $J_{6A,5}$ 2.3 Hz, 6-HA), 4.32 (1H, dd, J_{gem} 12.4, $J_{6B,5}$ 4.7 Hz, 6-H_B), 4.97-5.14 (2H, m, 3-H, 4-H), 5.80 (1H, dd, $J_{1,2ax}$ 10.0 and $J_{1,2eq}$ 2.3 Hz, 1-H); δC (50 MHz; $CDCl_3$) 20.6, 20.7, 20.8, 20.9 (CH_3, 4 x $COCH_3$), 34.7 (CH_2, C-2), 61.9 (CH_2, C-6), 68.2, 70.1, 72.3 (CH, C-3, C-4, C-5), 91.0 (CH, C-1), 168.7, 169.7, 170.0, 170.6 (quat., 4 x $COCH_3$). β-anomer: δ_H (200 MHz; $CDCl_3$) 5.78 (1H, dd, $J_{1,2ax}$ 10.5 and $J_{1,2eq}$ 2.5 Hz, 1-H).

(ii) Using tri-O-acetyl-D-glucal.[13] Distilled glacial acetic acid (351 mL, 5.51 mol) was added to a stirred solution of tri-*O*-acetyl-D-glucal (1.002 g, 3.67 mmol) and triphenylphosphine hydrogen

bromide (63 mg, 0.184 mmol) in anhydrous dichloromethane (18 mL). The mixture was allowed to stir for 2 days at room temperature and the solvent removed at reduced pressure. The resultant oil was purified by flash chromatography using hexane-ethyl acetate (4:1) as eluent to give 1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranoside **18** as a mixture of anomers (α:β, 9:1) (879 mg, 72%). The spectroscopic data were in agreement with that reported in the literature. [13]

(2′,3′,4′,6′-Tetra-*O*-benzyl-b -D-glucopyranosyloxy)naphthalene (11). To a stirred solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose **10** (560 mg, 1.04 mmol) and 1-naphthol **6** (100 mg, 0.695 mmol) in dry tetrahydrofuran (3 mL) at 0 °C were added triphenylphosphine (272 mg, 1.04 mmol) and a solution of diethyl azodicarboxylate (DEAD) (181 mg, 1.04 mmol) in dry tetrahydrofuran (1 mL). The mixture was stirred at room temperature for 12 h by which time a more polar species was seen upon analysis by TLC. The solution was concentrated at reduced pressure and the product isolated by flash chromatography using hexane-ethyl acetate (9:1) then ethyl acetate as eluent to afford *(2',3',4',6'-tetra-O-benzyl-b-D-glucopyranosyloxy)naphthalene* **11** (304 mg, 43%). Recrystallization from ethanol gave white needles, mp 131.2-132.2 °C; $[\alpha]_D^{18}$ = -42.3 (c=1.06, $CHCl_3$); [Found (EI): M^+, 666.2979. $C_{44}H_{42}O_6$ requires M, 666.2981]; n_{max} (film) cm^{-1} 3029, 2904, 2869 (C-H), 1579, 1453 (C=C), 1398, 1358 (C-O), 1263, 1240; δH (400 MHz; $CDCl_3$) 3.65-3.85 (5H, m, 3'-H, 4'-H, 5'-H, 6'-H_A, 6'-H_B), 3.96 (1H, dd, $J_{2',3'}$ 8.7 and *J*2',1'7.7 Hz, 2'-H), 4.52, 4.60 (each 1H, d, J_{gem} 12.1 Hz, 2 x CHPh), 4.62, 4.87, 4.89, 4.94, 5.00, 5.17 (each 1H, d, J^{gem} 10.9 Hz, 6 x CHPh), 5.23 (1H, d, $J_{1',2'}$ 7.7 Hz, 1'-H), 7.14 (1H, d, $J_{2,3}$ 7.8 Hz, 2-H), 7.19-7.34 (20H, m, Ph-H), 7.36 (1H, dd, $J_{4,3}$ 8.3 and $J_{2,3}$ 7.8 Hz, 3-H), 7.43 (1H, ddd, $J_{7,8}$ 8.3, $J_{7,6}$ 8.1 and $J_{7,5}$ 1.3 Hz, 7-H), 7.49 (1H, ddd, $J_{6,7}$ 8.1, $J_{6,5}$ 7.7 and $J_{6,8}$ 1.3 Hz, 6-H), 7.55 (1H, d, $J_{4,3}$ 8.3 Hz, 4-H), 7.82 (1H, d, $J_{5,6}$ 7.7 Hz, 5-H), 8.30 (1H, d, $J_{8,7}$ 8.3 Hz, 8-H); δC (100 MHz; $CDCl_3$) 68.8 (CH2, C-6'), 73.5, 75.1 (CH2, 2 x CH_2Ph), 75.3 (CH, C-5'), 75.4, 75.8 (CH_2, 2 x CH_2Ph), 77.8, 82.2, 84.9 (CH, C-2', C-3', C-4'), 101.5 (CH, C-1'), 109.5 (CH, C-2), 122.1, 122.4, 125.5, 125.8, 126.3 (CH, C-3, C-4, C-5, C-6, C-7), 126.0 (quat., C-4a), 127.5-128.4 (CH, Ph, C-8), 134.6 (quat., C-8a), 138.0, 138.05, 138.1, 138.5 (quat., 4 x *ipso*-Ph), 152.9 (quat., C-1); *m/z* (EI) 666 (M^+, 1%), 522 (M-$C_{10}H_8O$, 4), 415 (3), 325 (3), 181 (15), 91 (C_7H_7, 100).

1-(2′,3′,4′,6′-Tetra-*O*-benzyl-b -D-glucopyranosyloxy)-5-methoxynaphthalene (12). To a stirred solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose **9** (280 mg, 0.52 mmol) and 5-methoxy-1-naphthol **7** (60 mg, 0.35 mmol) in dry tetrahydrofuran (1.5 mL) at 0 °C were added triphenylphosphine (136 mg, 0.52 mmol) and a solution of diethyl azodicarboxylate (90 mg, 0.52 mmol) in dry tetrahydrofuran (0.5 mL). The mixture was stirred at room temperature for 12 h. The solution was concentrated at reduced pressure and the product isolated by flash chromatography using hexane-ethyl acetate (4:1) as eluent to afford *1-(2',3',4',6'-tetra-O-benzyl-b-D-glucopyranosyloxy)-5-methoxynaphthalene* **12** (226 mg, 63%) as a brown solid that was recrystallized from ethanol to give tan platelets, mp 156-157 °C; $[\alpha]_D^{18}$ = -19.7 (c=1.78, $CHCl_3$); (Found: C, 77.25; H, 6.22. $C_{45}H_{44}O_7$ requires C, 77.55; H, 6.37%); n_{max} (film) cm^{-1} 3061, 3030, 2904, 2867 (C-H), 1630, 1600 (C=C), 1389, 1358 (C-O); δ_H (400 MHz; $CDCl_3$) 3.68-3.81 (4H, m, 4'-H, 5'-H, 6'-H_A, 6'-H_B), 3.82 (1H, dd, $J_{3',4'}$ 8.7 and $J_{3',2'}$ 8.3 Hz, 3'-H), 3.96 (1H, dd, $J_{2',3'}$ 8.3 and $J_{2',1'}$ 7.7 Hz, 2'-H), 4.00 (3H, s, OCH_3), 4.51, 4.59 (each 1H, d, J_{gem} 12.1 Hz, 2 x CHPh),

4.60, 4.86, 4.88, 4.92, 4.99, 5.17 (each 1H, d, J_{gem} 10.9 Hz, 6 x CHPh), 5.21 (1H, d, $J_{1',2'}$ 7.7 Hz, 1'-H), 6.84 (1H, d, $J_{2,3}$ 7.5 Hz, 2-H), 7.18-7.39 (23H, m, Ph-H, 3-H, 4-H, 7-H), 7.89 (1H, d, $J_{6,7}$ 8.4 Hz, 6-H), 7.97 (1H, d, $J_{8,7}$ 8.4 Hz, 8-H); δC (100 MHz; $CDCl_3$) 68.9 (CH_2, C-6'), 73.6, 75.0 (CH_2, 2 x CH_2Ph), 75.4 (CH, C-5'), 75.4, 75.8 (CH_2, 2 x CH_2Ph), 77.9, 82.3, 85.0 (CH, C-2', C-3', C-4'), 101.6 (CH, C-1'), 104.4, 114.5, 116.5, 125.1, 125.5, 127.5 (CH, C-2, C-3, C-4, C-6, C-7, C-8), 126.9, 127.1 (quat., C-4a, C-8a), 127.5-128.4 (CH, Ph), 138.2, 138.2, 138.2, 138.6 (quat., 4 x *ipso*-Ph), 152.9, 155.3 (quat., C-1, C-5); *m/z* (EI) 696 (M^+, 1%), 522 (M-$C_{10}H_8O$, 28), 325 (6), 181 (6), 91 (C_7H_7, 100).

2-(2′,3′,4′,6′-Tetra-*O*-benzyl-b -D-glucopyranosyloxy)naphthalene (15). To a stirred solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose **9** (560 mg, 1.04 mmol) and 2-naphthol **8** (100 mg, 0.695 mmol) in dry tetrahydrofuran (3 mL) at 0 °C were added triphenylphosphine (272 mg, 1.04 mmol) and a solution of diethyl azodicarboxylate (181 mg, 1.04 mmol) in dry tetrahydrofuran (1 mL). The mixture was stirred at room temperature for 12 h. The solution was concentrated at reduced pressure and the product purified by flash chromatography using hexane-ethyl acetate (4:1) then ethyl acetate as eluent to afford 2-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyloxy)naphthalene **15** (390 mg, 56%) which was recrystallized from ethanol to give colourless needles, mp 111.5-112.5 °C; $[\alpha]_D^{22}$ = -13.0 (c=1.08, $CHCl_3$); (Found: C, 79.25; H, 6.26. $C_{44}H_{42}O_6$ requires C, 79.24; H, 6.35%); n_{max} (film) cm^{-1} 3061, 3030, 2904, 2867 (C-H), 1630, 1600 (C=C), 1389, 1358 (C-O); δ_H (400 MHz; $CDCl_3$) 3.58-3.77 (6H, m, 2'-H, 3'-H, 4'-H, 5'-H, 6'-HA, 6'-H_B), 4.44-4.53 (3H, m, 3 x CHPh), 4.75-4.80 (3H, m, 3 x CHPh), 4.89, 5.01 (each 1H, d, J_{gem} 11.0 Hz, 2 x CHPh), 5.08 (1H, d, $J_{1',2'}$ 7.1 Hz, 1'-H), 7.13 (1H, dd, $J_{3,4}$ 7.7 and $J_{3,1}$ 2.0 Hz, 3-H), 7.16-7.34 (22H, m, Ph-H, 6-H, 7-H), 7.37 (1H, d, $J_{1,3}$ 2.0 Hz, 1H), 7.57 (1H, d, $J_{4,3}$ 7.7 Hz, 4-H), 7.69 (1H, d, $J_{8,7}$ 8.7 Hz, 8-H), 7.70 (1H, d, $J_{5,6}$ 7.7 Hz, 5-H); δC (100 MHz; $CDCl_3$) 69.8 (CH_2, C-6'), 74.3, 75.7, 75.8 (CH_2, 3 x CH_2Ph), 76.0 (CH, C-5'), 76.4 (CH_2, CH_2Ph), 78.5 (CH, C-2', C-3', C-4'), 102.6 (CH, C-1'), 112.3, 119.7, 125.0, 127.0, 128.2, 128.0, 130.1 (CH, C-1, C-3, C-4, C-5, C-6, C-7, C-8), 128.3-129.1 (CH, Ph), 130.7 (quat., C-4a), 135.1 (quat., C-8a), 138.8, 138.9, 139.0, 139.3 (quat., 4 x *ipso*-Ph), 155.9 (quat., C-2); *m/z* (EI) 666 (M^+, 2%), 522 (M-$C_{10}H_8O$, 4), 415 (1), 271 (1), 181 (8), 144 ($C_{10}H_8O$, 4), 115 (C_9H_7, 4), 91 (C_7H_7, 100).

2-(3′,4′,6′-Tri-*O*-acetyl-2′-deoxy-b -D-*arabino*-hexopyranosyl)-1-hydroxy-5-methoxynaphthalene 20 and 1-(3′,4′,5′-Tri-*O*-acetyl-2′-deoxy-a -D-*arabino*-hexopyranosyloxy)-5-methoxynaphthalene (19). Trimethylsilyl trifluoromethanesulfonate (5 μL, 0.023 mmol) was added dropwise to a mixture of 5methoxynaphthol 7 (39 mg, 0.23 mmol), 1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranoside 18 (38 mg, 0.114 mmol) and silver perchlorate (5 mg, 0.023 mmol) in dry dichloromethane (2 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature over 1 h then quenched with saturated aqueous sodium bicarbonate solution (2 mL). The mixture was extracted with diethyl ether (3 x 10 mL) and the extracts were washed with water (10 mL), brine (10 mL) then dried (magnesium sulfate). The solvent was removed at reduced pressure and the residue purified by flash chromatography using hexane-ethyl acetate (4:1) as eluent to give the α-*O-glycoside* 19 (17 mg, 34%) and the β-*C-glycoside* 20 (10 mg,

29%). Repeating the reaction on the same scale using dry acetonitrile (2 mL) as the solvent gave exclusively the β-*C-glycoside* 20 (28 mg, 82%) which was recrystallized from ethanol to give colourless needles, mp 140.3-140.9 °C; $[\alpha]_D^{19}$ = +80.0 (c=0.1, $CHCl_3$); [Found (FAB): M^+, 446.1572. $C_{23}H_{26}O_9$ requires M, 446.1577]; n_{max} (film) cm^{-1} 3469 (OH), 1746 (C=O, ester), 1230 (C-O); δ_H (200 MHz; $CDCl_3$) 2.04, 2.09, 2.18 (each 3H, s, 3 x $COCH_3$), 2.10 (1H, m, 2'$_{ax}$-H), 2.51 (1H, ddd, J_{gem} 13.9, $J_{2'eq,3'}$ 3.7 and $J_{2'eq,1'}$ 2.7 Hz, 2'$_{eq}$-H), 3.88 (1H, ddd, *J*5',4' 10.1, $J_{5',6'B}$ 4.4 and $J_{5',6'A}$ 2.3 Hz, 5'-H), 3.98 (3H, s, OCH_3), 4.22 (1H, dd, J_{gem} 12.3 and $J_{6'A,5'}$ 2.3 Hz, 6'-H_A), 4.35 (1H, dd, J_{gem} 12.3 and $J_{5',6'B}$ 4.4 Hz, 6'-H_B), 4.96 (1H, dd, $J_{1',2'ax}$ 10.1 and $J_{1',2'eq}$ 2.2 Hz, 1'-H), 5.20 (2H, m, 3'-H, 4'-H), 6.83 (1H, d, $J_{6,7}$ 7.5 Hz, 6-H), 7.02 (1H, d, $J_{3,4}$ 8.7 Hz, 3-H), 7.39 (1H, dd, $J_{7,8}$ 8.5 and $J_{7,6}$ 7.5 Hz, 7-H), 7.74 (1H, dd, *J*8,7 8.5 and $J_{8,6}$ 0.3 Hz, 8-H), 7.85 (1H, d, $J_{4,3}$ 8.7 Hz, 4-H), 8.23 (1H, s, OH); δC (50 MHz; $CDCl_3$) 20.7, 20.9, 21.0 (CH_3, 3 x $COCH_3$), 36.7 (CH_2, C-2'), 55.4 (CH_3, OCH_3), 63.3 (CH_2, C-6'), 68.4 (CH, C-5'), 69.4, 73.2, (CH, C-3', C-4'), 76.6 (CH, C-1'), 108.6 (quat., C-4a), 106.5, 108.7, 122.9, 124.9, 129.2 (CH, C-3, C-4, C-6, C-7, C-8), 126.2, 129.2 (quat., C-8a, C-2), 151.0, 152.5 (quat., C-1, C-5), 169.8, 170.2, 170.3 (quat., 3 x $COCH_3$); *m/z* (CI) 446 (M^+, 3%), 253 (1), 174 (100), 159 (9), 111 (25), 43 ($COCH_3$, 62).

The α-*O-glycoside* **19** was recrystallized from ethanol to give white needles, mp 128-131 °C; $[\alpha]_D^{20}$ = +119.0 (c=0.65, $CHCl_3$); [Found (FAB): M^+, 446.1572. $C_{23}H_{26}O_9$ requires M, 446.1577]; n_{max} (film) cm^{-1} 2958 (C-H), 1746 (C=O, ester), 1592 (C=C), 1229 (C-O); δ_H (400 MHz; $CDCl_3$) 2.02, 2.04, 2.09 (each 3H, s, 3 x $COCH_3$), 2.10 (1H, m, 2'$_{ax}$-H), 2.64 (1H, ddd, J_{gem} 13.1, $J_{2'eq,3'}$ 5.3 and $J_{2'eq,1'}$ 1.2 Hz, 2'$_{eq}$-H), 3.99 (1H, dd, J_{gem} 12.1 and $J_{6'A,5'}$ 2.1 Hz, 6'-H_A), 3.99 (3H, s, OCH_3), 4.09 (1H, ddd, $J_{5',4'}$ 10.1, $J_{5',6'B}$ 4.6 and $J_{5',6'A}$ 2.1 Hz, 5'-H), 4.30 (1H, dd, J_{gem} 12.1 and $J_{6'B,5'}$ 4.6 Hz, 6'-H_B), 5.16 (1H, dd, $J_{4',5'}$ 10.1 and $J_{4',3'}$ 9.5 Hz, 4'-H), 5.68 (1H, ddd, $J_{3',2'ax}$ 11.5, $J_{3',4'}$ 9.5 and $J_{3',2'eq}$ 5.4 Hz, 3'-H), 5.85 (1H, d, $J_{1',2'ax}$ 2.5 Hz, 1'-H), 6.85 (1H, d, $J_{6,7}$ 9.2 Hz, 6-H), 7.20 (1H, d, $J_{2,3}$ 7.5 Hz, 2-H), 7.34 (1H, dd, $J_{3,4}$ 8.4 and $J_{3,2}$ 7.5 Hz, 3-H), 7.42 (1H, dd, $J_{7,8}$ 8.5 and $J^{7,6}$ 7.7 Hz, 7-H), 7.84 (1H, d, $J_{8,7}$ 8.5 Hz, 8-H), 7.92 (1H, d, $J_{4,3}$ 8.4 Hz, 4-H); δC (100 MHz; $CDCl_3$) 20.6, 20.9, 20.9 (CH_3, 3 x $COCH_3$), 35.2 (CH_2, C-2'), 55.5 (CH_3, OCH_3), 61.9 (CH_2, C-6'), 68.7 (CH, C-5'), 68.9, 69.0 (CH, C-3', C-4'), 95.3 (CH, C-1'), 104.5, 108.9, 113.8, 116.0, 124.9, 125.7 (CH, C-2, C-3, C-4, C-6, C-7, C-8), 126.5, 126.6 (quat., C-8a, C-4a), 151.3, 155.2 (quat., C-1, C-5), 169.8, 170.2, 170.3 (quat., 3 x $COCH_3$); *m/z* (CI) 446 (M^+, 5%), 174 (100), 111 (28), 43 ($COCH_3$, 62).

1-(3′,4′,6′-Tri-*O*-acetyl-2′-deoxy-b -D-*arabino*-hexopyranosyl)-2-hydroxynaphthalene (22) and 2-(3′,4′,6′-Tri-*O*-acetyl-2′-deoxy-a -D-*arabino*-hexopyranosyloxy)naphthalene (21). Trimethylsilyl trifluoromethanesulfonate (5 μL, 0.023 mmol) was added dropwise to a mixture of 2-naphthol 8 (33 mg, 0.23 mmol), 1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-*arabino*-hexopyranoside 18 (38 mg, 0.114 mmol) and silver perchlorate (5 mg, 0.023 mmol) in dry dichloromethane (2 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature over 1 h then quenched with saturated aqueous sodium bicarbonate solution (2 mL). The mixture was extracted with diethyl ether (3 x 10 mL) and the combined extracts washed with water (10 mL) and brine (10 mL) then dried (magnesium sulfate). The solvent was removed at reduced pressure,

the residue purified by flash chromatography using hexane-ethyl acetate (4:1) as eluent to give the α-*O*-glycoside 21 (20 mg, 39%) and the β-*C*-glycoside 22 (16 mg, 31%). Repeating the reaction on the same scale but with dry acetonitrile (2 mL) as the solvent gave exclusively the β-*C*-glycoside 22 (49 mg, 97%) which was recrystallized from ethanol to give colourless needles, mp 127.5-128.0 °C (lit.[19] mp 128 °C); [Found (FAB): M^+, 416.1481. $C_{22}H_{24}O_8$ requires M, 416.1471]; n_{max} (film) cm^{-1} 3373 (br, OH), 3064, 2962 (C-H), 1747 (C=O, ester), 1622, 1600 (C=C), 1230 (C-O); δH (400 MHz; $CDCl_3$) 2.02 (3H, s, $COCH_3$), 2.09 (1H, m, 2'$_{ax}$-H), 2.11 (3H, s, $COCH_3$), 2.16 (3H, s, $COCH_3$), 2.50 (1H, ddd, J_{gem} 12.9, $J_{2'eq,3'}$ 3.7 and $J_{2'eq,1'}$ 2.7 Hz, 2'$_{eq}$-H), 3.93 (1H, ddd, $J_{5',4'}$ 9.7, $J_{5',6'B}$ 3.2 and $J_{5',6'A}$ 2.3 Hz, 5'-H), 4.20 (1H, dd, J_{gem} 12.5 and $J_{6'A,5'}$ 2.3 Hz, 6'-H_A), 4.22 (1H, dd, J_{gem} 12.5 and $J_{5',6'B}$ 3.2 Hz, 6'-H_B), 5.26-5.32 (2H, m, 3'-H, 4'-H), 5.62 (1H, dd, $J_{1',2'ax}$ 11.9 and $J_{1',2'eq}$ 2.1 Hz, 1'-H), 7.13 (1H, d, $J_{3,4}$ 8.9 Hz, 3-H), 7.33 (1H, ddd, $J_{7,8}$ 7.9, $J_{7,6}$ 7.1 and $J_{7,5}$ 1.0 Hz, H-7), 7.48 (1H, ddd, $J_{6,5}$ 8.6, $J_{6,7}$ 7.1 and $J_{6,8}$ 1.2 Hz, H-6), 7.66 (1H, br.d, $J_{5,6}$ 8.6 Hz, H-5), 7.71 (1H, d, $J_{4,3}$ 8.9 Hz, H-4), 7.76 (1H, br.d, $J_{8,7}$ 7.9 Hz, H-8), 8.48 (1H, s, OH); δC (100 MHz; $CDCl_3$) 20.67, 20.7, 20.9 (CH_3, 3 x $COCH_3$), 35.7 (CH_2, C-2'), 61.6 (CH_2, C-6'), 68.4, 71.4, 76.0, (CH, C-3', C-4', C-5'), 76.6 (CH, C-1'), 113.8 (quat., C-4a), 120.0, 120.4, 123.2, 127.1, 129.0, 130.3 (CH, C-3, C-4, C-5, C-6, C-7, C-8), 128.7, 130.5 (quat., C-8a, C-1), 153.6 (quat., C-2), 169.7, 170.3, 170.7 (quat., 3 x $COCH_3$); *m/z* (CI) 416 (M^+, 40%), 181 (100), 43 ($COCH_3$, 74). The spectroscopic data were in agreement with that reported in the literature.[19]

The α-*O*-glycoside **21** was recrystallized from ethanol to give colourless needles, mp 98.0-98.5 °C (lit.[19] mp 90 °C); [Found: C, 63.52; H, 5.87. $C_{22}H_{24}O_8$ requires C, 63.45; H, 5.81%]; *n*max (film) cm^{-1} 3066, 2955 (C-H), 1746 (C=O), 1629, 1600 (C=C), 1367, 1230 (C-O); δ_H (400 MHz; $CDCl_3$) 1.96, 2.05, 2.07 (each 3H, s, 3 x $COCH_3$), 2.10 (1H, m, 2'$_{ax}$-H), 2.54 (1H, ddd, J_{gem} 13.1, $J_{2'eq,3'}$ 5.4 and $J_{2'eq,1'}$ 1.2 Hz, 2'e_q-H), 3.99 (1H, dd, J_{gem} 12.1 and $J_{6'A,5'}$ 2.1 Hz, 6'-H_A), 4.10 (1H, ddd, $J_{5',4'}$ 10.1, $J_{5',6'B}$ 4.7 and $J_{5',6'A}$ 2.1 Hz, 5'-H), 4.32 (1H, dd, J_{gem} 12.1 and $J_{6'B,5'}$ 4.7 Hz, 6'-H_B), 5.12 (1H, dd, $J_{4',5'}$ 10.1 and $J_{4',3'}$ 9.5 Hz, 4'-H), 5.59 (1H, ddd, $J_{3',2'ax}$ 11.5, $J_{3',4'}$ 9.5 and $J_{3',2'eq}$ 5.4 Hz, 3'-H), 5.83 (1H, br.d, $J_{1',2'ax}$ 2.6 Hz, 1'-H), 7.24 (1H, dd, $J_{3,4}$ 9.2 and $J_{3,1}$ 1.9 Hz, 3-H), 7.35 (1H, dd, $J_{5,6}$ 6.9 and $J_{5,7}$ 1.3 Hz, 5-H), 7.41 (1H, d, $J_{1,3}$ 1.8 Hz, 1-H), 7.47 (1H, dd, $J_{8,7}$ 6.7 and $J_{8,6}$ 1.4 Hz, 8-H), 7.72-7.80 (3H, m, 4-H, 6-H, 7-H); δC (100 MHz; $CDCl_3$) 20.6, 20.7, 21.0 (CH_3, 3 x $COCH_3$), 35.1 (CH_2, C-2'), 62.0 (CH_2, C-6'), 68.6, 68.9, 69.1 (CH, C-3', C-4', C-5'), 95.3 (CH, C-1'), 110.4, 118.7, 124.3, 126.5, 127.1, 127.6, 129.5 (CH, C-1, C-3, C-4, C-5, C-6, C-7, C-8), 129.5, 134.26 (quat., C-8a, C-4a), 153.8 (quat., C-2), 169.9, 170.3, 170.6 (quat., 3 x $COCH_3$); *m/z* (CI) 416 (M^+, 1%), 356 (2), 273 (M-$C_{10}H_7O$, 1), 213 (18), 144 ($C_{10}H_8O$, 100), 111 (47), 43 ($COCH_3$, 80). The spectroscopic data were in agreement with that reported in the literature.[19]

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