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# Synthesis of bergenin-type *C*-glucosylarenes*

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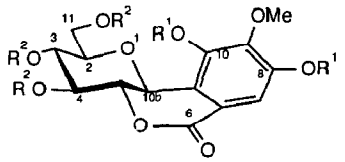
ABSTRACT

Reaction of 1,2,3-trimethoxybenzene with 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl trifluoroacetate (**5**) in the presence of $BF_3 \cdot OEt_2$ afforded the 4-β-*C*-glycosylarene **6**. Hydrogenolysis of **6**, then *O*-methoxycarbonylation, and bromination gave 1-bromo-2,3,4-trimethoxy-5-(2,3,4,6-tetra-*O*-methoxycarbonyl-β-D-glucopyranosyl)benzene (**9**). Bromine/lithium exchange of **9** and then reaction with diphenyl disulfide furnished 2,3,4-trimethoxy-1-phenylthio-5-(2,3,4,6-tetra-*O*-methoxycarbonyl-β-D-glucopyranosyl)benzene (**14**), oxidation of which afforded the phenylsulfinyl derivative **15**. Ortho-lithiation of **15** and then reaction with methyl chloroformate gave 2,3,4-trimethoxy-6-methoxycarbonyl-1-phenylsulfinyl-5-(2,3,4,6-tetra-*O*-methoxycarbonyl-β-D-glucopyranosyl)benzene (**17**). Removal of the phenylsulfinyl group from **15** with Raney nickel and then lactonisation with sodium methoxide provided 8,10-di-*O*-methylbergenin (**2**). The 3,4,11-triacetate (**4**) of **2** had physical data that accorded with those for the natural compound.

## INTRODUCTION

Bergenin (**1**) and the corresponding 8,10-di-*O*-methyl derivative **2**, isolated from various sources, exhibit interesting physiological properties[1,2]. The structure was assigned unequivocally by an X-ray analysis of 3,4,8,10,11-penta-*O*-acetylbergenin[2] (**3**), which was obtained by a low-yielding procedure[3]. The need for a versatile synthesis for this class of *C*-glycosylarene prompted the elaboration of an approach based on the formation of *C*-glycosyl bonds *via* electrophilic aromatic substitution and subsequent modification of the aryl group using aryl carbanion chemistry[4]. The execution of this strategy is now reported in the synthesis of 8,10-di-*O*-methylbergenin[1] (**2**) and its 3,4,11-triacetate[1] **4**.




**1** $R^1 = R^2 = H$
**2** $R^1 = Me$, $R^2 = H$
**3** $R^1 = R^2 = Ac$
**4** $R^1 = Me$, $R^2 = Ac$

* Aryl *C*-glycosides, Part 4. For Part 3, see ref. 2.
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RESULTS AND DISCUSSION

The tricyclic system of bergenin (**1**) involves D-glucopyranosyl and 4-*O*-methylgalloyl moieties linked by a $\beta$-*C*-glycosyl bond and a $\delta$-lactone bridge. Accordingly, electrophilic 2-substitution of an *O*-protected gallate with a glucopyranosyl donor should lead to a straightforward synthesis of this compound. However, attempts to perform this decisive reaction with various glucopyranosyl donors and 3,4,5-tri-*O*-methylgallate gave undesired products[4]. Therefore, in order to increase the nucleophilicity of the aromatic ring, the non-carboxylated compound 1,2,3-trimethoxybenzene was selected and its electrophilic substitution with a 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl donor was investigated.

Following the procedure of Allevi *et al.*[5], the $\beta$-glucosyl trifluoroacetate **5** was prepared *in situ* from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose and trifluoroacetic anhydride. Reaction of **5** in the presence of $BF_3 \cdot OEt_2$ with 1,2,3-trimethoxybenzene then afforded the 4-$\beta$-*C*-glucosylarene **6**. Hydrogenolysis of **6** removed the benzyl groups to yield **7**, *O*-methoxycarbonylation of which with methyl chloroformate in pyridine and 4-dimethylaminopyridine gave **8**, the structure of which was confirmed by the $^1$H-n.m.r. data (see Experimental).

Attempted electrophilic carboxylation of **6** and H-5/lithium exchange reactions gave unsatisfactory results. However, treatment of **8** with bromine afforded a single product in high yield which, as expected from the rules for electrophilic substitution of benzene derivatives, was the 1-bromo derivative **9**. The structure of **9** was deduced readily from the following reactions. Bromine/lithium exchange on **9** at $-100°$ with butyl-lithium generated the *C*-lithiated species **10**, which reacted with methyl chloroformate to give the methyl ester derivative **11** in good yield. For elucidation of the structure of **11**, the methoxycarbonyl groups were removed with methanolic sodium methoxide to give **12**; the formation of the lactone **2** under these trans-esterification conditions was not observed. Treatment of **12** with acetic anhydride in pyridine gave the tetra-acetate **13**. Thus, the bromination of **8** had occurred at position **6** since **13** was an "isobergenin"-type compound (see Table I for the $^1$H-n.m.r. data).

The next stage involved the introduction of a readily removable group at C-5 of the aromatic ring, which would facilitate 6-lithiation. On the basis of earlier findings[6,7],

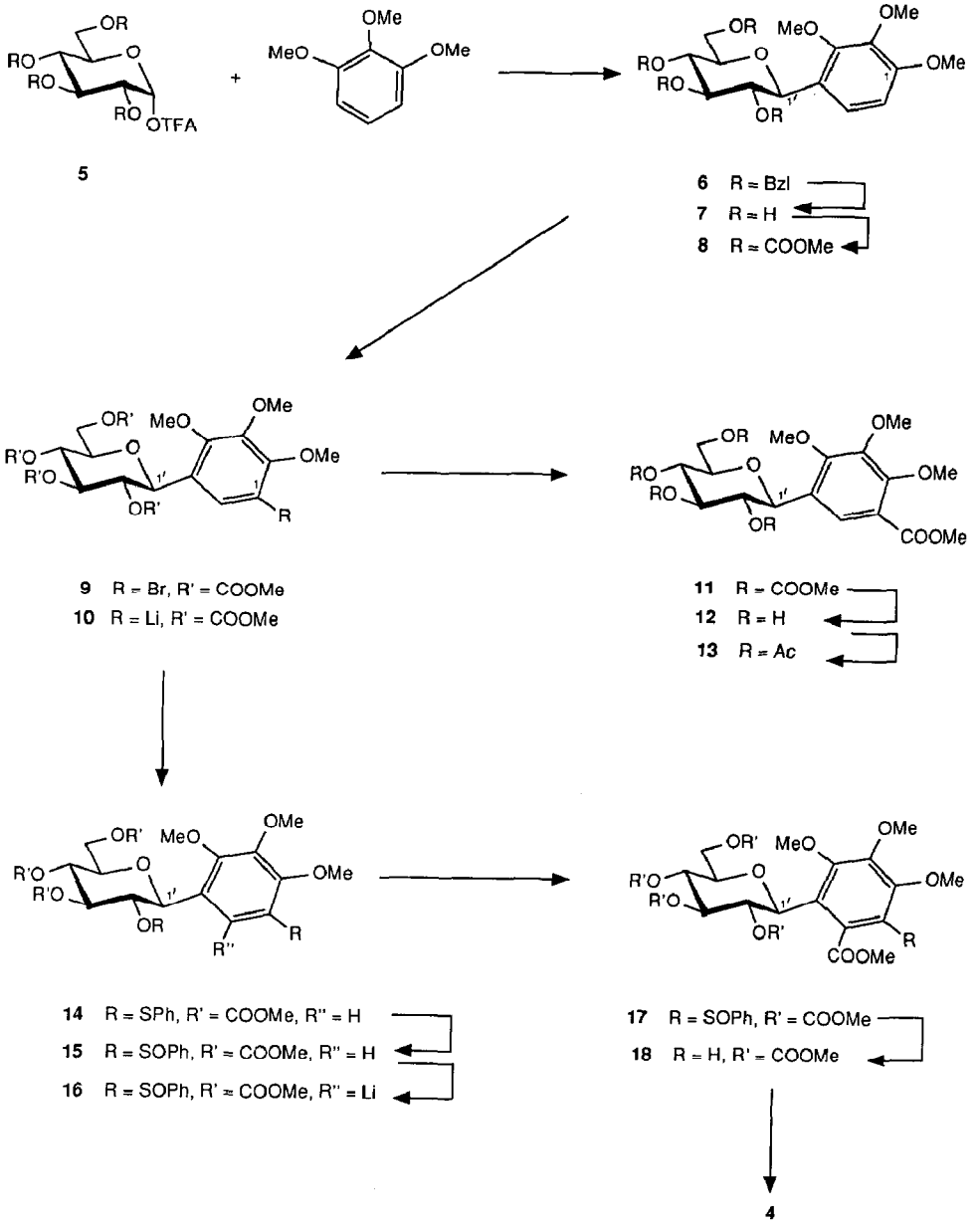
TABLE I

$^1$H-N.m.r. data (250 MHz) for solutions of **4, 12, 16**[a] in $CDCl_3$ (internal $Me_4Si$) ($\delta$ in p.p.m., $J$ in Hz)

| **4** | **12** | **16** |
|---|---|---|
| H-10b 4.84 (d, 10 Hz) | H-1 4.75 (d, 9.5 Hz) | H-1 5.23 (d, 9.4 Hz) |
| H-4a 4.29 (dd, 10 Hz) | H-2 5.3 (dd, 9.5 Hz) | H-2 5.83 (dd, 9.4 Hz) |
| H-4 5.52 (dd, 10 Hz), | H-3 5.4 (dd, 9.5 Hz) | H-3 5.20 (dd, 9.4 Hz) |
| H-3 5.13 (dd, 10 Hz) | H-4 5.20 (dd, 9.5 Hz) | H-4 5.05 (dd, 9.4 Hz) |
| H-2 3.90 (m) | H-5 3.90 (m) | H-5 3.90 (m) |

[a] The protons in the same line have identical locations at the sugar moiety (see formulae for numbering).

the sulfinyl group was selected. Therefore, the C-5-lithiated species **10** was reacted with diphenyl disulfide to furnish the phenyl sulfide **14**. Oxidation of **14** with 3-chloroperoxybenzoic acid gave a 1:2-mixture of the diastereomeric sulfoxides **15** which could be fractionated by chromatography on silica gel. Treatment of the major isomer with lithium di-isopropylamide at −90° gave the *C*-lithiated product **16**. Reaction of **16** with methyl chloroformate afforded the desired compound **17**, which, however, could not be



characterised by $^1$H-n.m.r. spectroscopy due to the hindered rotation in this fully substituted benzene derivative. Treatment of **17** with Raney nickel in methanol removed the phenylsulfinyl group and provided the "prebergenin"-type compound **18**, which was characterised by $^1$H-n.m.r. spectroscopy (Table I). Lactonisation of **18** by treatment with methanolic sodium methoxide gave 8,10-di-*O*-methylbergenin (**2**) which, with acetic anhydride in pyridine, gave the 3,4,11-triacetate **4**. The physical data for **4** were in full agreement with those published[1,3].

## EXPERIMENTAL

*General methods.* — Melting points are uncorrected. Optical rotations were determined with a Perkin–Elmer 241 MC polarimeter for solutions in $CHCl_3$ at 20°, unless noted otherwise. Flash chromatography was performed on silica gel (Merck, 230–400 mesh ASTM) with light petroleum (b.p. 40–65°)–ethyl acetate (LP–EA) mixtures. T.l.c. was performed on Silica Gel 60 $F_{254}$ (Merck). $^1$H-N.m.r. spectra were recorded on solutions in $CDCl_3$ (internal $Me_4Si$) with a Bruker WM 250 Cryospec or AC 250 Cryospec instrument.

*1,2,3-Trimethoxy-4-(2,3,4,6-tetra-*O*-benzyl-β-*D*-glucopyranosyl)benzene* (**6**). — To a solution of 2,3,4,6-tetra-*O*-benzyl-D-glucose (10.0 g, 18.5 mmol) in dry dichloromethane (80 mL) was added trifluoroacetic anhydride (7 mL). After 30 min, the mixture was concentrated *in vacuo*. To a solution of the residue in dichloromethane (80 mL) were added 1,2,3-trimethoxybenzene (8.0 g, 47.6 mmol) and boron trifluoride etherate (7 mL). The mixture was left for 30 min at room temperature, then diluted with chloroform (50 mL), washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography (4:1 LP–EA) of the residue gave **6** (7.5 g, 59%), isolated as a colourless oil, $[\alpha]_D$ +37° (*c* 1), $R_F$ 0.37. $^1$H-N.m.r. data (250 MHz): $\delta$ 7.34–6.90 (m, 21 H, 4 Ph and H-6), 6.69 (d, 1 H, $J_{5,6}$ 8.8 Hz, H-5), 4.94–4.46 (m, 8 H, 3.5 PhC$H_2$ and H-1'), 4.04 (d, 1 H, PhC*H*), 3.86 (s, 6 H, 2 OMe), 3.84 (s, 3 H, OMe), 3.85–3.57 (m, 6 H, H-2',3',4',5',6',6'').

*Anal.* Calc. for $C_{43}H_{46}O_8$ (690.84): C, 74.8; H, 6.7. Found: C, 74.2; H, 6.9.

*1,2,3-Trimethoxy-4-(2,3,4,6-tetra-*O*-methoxycarbonyl-β-*D*-glucopyranosyl)benzene* (**8**). — A solution of **6** (7.5 g, 10.8 mmol) in AcOH–MeOH (1:2, 150 mL) was hydrogenated in the presence of 10% Pd–C (500 mg) for 10 h at room temperature. Filtration and concentration afforded crude **7** (3.5 g, 98%) as colourless, hygroscopic crystals, $R_F$ 0.31 (5:1 $CHCl_3$–MeOH). To a solution of crude **7** (120 mg, 0.36 mmol) in pyridine (3 mL) were added dichloromethane (30 mL) and 4-dimethylaminopyridine (50 mg). A solution of methyl chloroformate (3 mL) in dichloromethane (7 mL) was then added dropwise during 30 min at −10°. The mixture was stirred for 90 min, diluted with dichloromethane (30 mL), washed successively with aqueous NaCl, 2M HCl, and water, dried ($MgSO_4$), and concentrated to dryness. Flash chromatography (1:1 LP–EA) of the residue gave **8** (180 mg, 90%), m.p. 112°, $[\alpha]_D$ −1.5° (*c* 1), $R_F$ 0.50. $^1$H-N.m.r. data (250 MHz): $\delta$ 7.07 (d, 1 H, $J_{5,6}$ 8.7 Hz, H-5), 6.69 (d, 1 H, H-6), 5.24 (dd, 1 H, $J_{3',4'}$ 9.4 Hz, H-3'), 5.14 (dd, 1 H, $J_{2',3'}$ 9.4 Hz, H-2'), 5.05 (dd, 1 H, $J_{4',5'}$ 9.4 Hz, H-4'), 4.82 (d, 1 H,

$J_{1',2'}$ 9.4 Hz, H-1'), 4.32–4.30 (m, 2 H, H-6',6''), 3.94–3.88 (m, 1 H, H-5'), 3.89, 3.85, 3.84, 3.81, 3.78, 3.77, 3.58 (7 s, 21 H, 3 OMe and 4 COOMe).

*Anal.* Calc. for $C_{23}H_{30}O_{15}\cdot H_2O$ (564.5): C, 48.9; H, 5.7. Found: C, 48.9; H, 5.5.

*1-Bromo-2,3,4-trimethoxy-5-(2,3,4,6-tetra-*O*-methoxycarbonyl-β-*D*-glucopyranosyl)benzene* (**9**). — To a solution of **8** (1.3 g 2.4 mmol) in chloroform (120 mL) was added bromine. The mixture was left for 15 min at room temperature, then washed successively with aqueous $NaHSO_3$, aqueous $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography (1:1 LP–EA) of the residue gave amorphous **9** (1.3 g, 88%), $[\alpha]_D$ −16° (*c* 1), $R_F$ 0.55. $^1$H-N.m.r. data (250 MHz): δ 7.30 (s, 1 H, H-6), 5.23 (dd, 1 H, $J_{2',3'}$ 9.3, $J_{3',4'}$ 9.3 Hz, H-3'), 5.11–5.01 (m, 2 H, H-2',4'), 4.79 (d, 1 H, $J_{1',2'}$ 9.9 Hz, H-1'), 4.31 (d, 2 H, H-6',6''), 3.95–3.88 (m, 1 H, H-5'), 3.89, 3.88, 3.87, 3.82, 3.79, 3.78, 3.61 (7 s, 21 H, 3 OMe and 4 COOMe).

*Anal.* Calc. for $C_{23}H_{29}BrO_{15}$ (625.39): C, 44.2; H, 4.7. Found: C, 43.9; H, 5.0.

*1,2,3-Trimethoxy-4-methoxycarbonyl-6-(2,3,4,6-tetra-*O*-methoxycarbonyl-β-*D*-glucopyranosyl)benzene* (**11**). — To a solution of **9** (0.3 g, 0.48 mmol) in dry tetrahydrofuran (30 mL) was added, dropwise, *n*-BuLi (1.0 mL, 1.6 mmol) at −100°, followed, after 5 min, by methyl chloroformate (1.5 mL). The mixture was stirred for 18 h at room temperature, then poured into aqueous $NaHCO_3$, and extracted thrice with ether, and the combined extracts were dried ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography (1:1 LP–EA) of the residue gave **11** (0.2 g, 69%), $R_F$ 0.43. $^1$H-N.m.r. data (250 MHz): δ 7.61 (s, 1 H, H-5), 5.31–5.02 (3 dd, 3 H, H-2',3',4'), 4.82 (d, 1 H, $J_{1',2'}$ 9.6 Hz, H-1'), 4.31 (d, 2 H, H-6',6''), 3.90–3.80 (m, 1 H, H-5'), 3.96, 3.93, 3.89, 3.86, 3.82, 3.78, 3.59 (7 s, 24 H, 3 OMe and 5 COOMe).

*1,2,3-Trimethoxy-4-methoxycarbonyl-6-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)benzene* (**13**). — A solution of **11** (150 mg, 0.25 mmol) in dry methanol (10 mL) was treated with methanolic M NaOMe (0.5 mL). After 4 h, the mixture was neutralised with acetic acid and concentrated *in vacuo* to give crude **12**. A solution of **12** in pyridine (5 mL) and acetic anhydride (5 mL) was left overnight at room temperature. The mixture was poured into ice and extracted several times with chloroform, and the combined extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (1:1 LP–EA) of the product gave amorphous **13** (138 mg, 80%), $[\alpha]_D$ −26° (*c* 1), $R_F$ 0.38. $^1$H-N.m.r. data (250 MHz): δ 7.60 (s, 1 H, H-5), 5.40–5.30 (2 dd, 2 H, H-2',3'), 5,20 (dd, 1 H, H-4'), 4.75 (d, 1 H, H-1'), 4.25, 4.14 (2 dd, 2 H, H-6',6''), 3.97, 3.93, 3.89, 3.87 (4 s, 12 H, 3 OMe and COOMe), 3.90 (m, 1 H, H-5'), 2.08, 2.06, 2.01, 1.82 (4 s, 12 H, 4 Ac).

*Anal.* Calc. for $C_{25}H_{32}O_{14}$ (556.53): C, 54.0; H, 5.8. Found: C, 54.4; H, 5.9.

*2,3,4-Trimethoxy-1-phenylthio-5-(2,3,4,6-tetra-*O*-methoxycarbonyl-β-*D*-glucopyranosyl)benzene* (**14**) — To a solution of **9** (1.1 g, 1.76 mmol) in dry tetrahydrofuran (60 mL) was added, dropwise, *n*-BuLi (3 mL, 4.8 mmol) at −100°, followed after 5 min by a solution of diphenyl disulfide (2.5 g, 11.5 mmol) in dry tetrahydrofuran (10 mL). The mixture was stirred for 30 min at room temperature, then treated with methyl chloroformate (4 mL), and stirred again for 30 min. The mixture was poured into saturated aqueous $NaHCO_3$, the aqueous layer was washed several times with ether, and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Flash

chromatography (1:1 LP–EA) of the residue gave **14** (0.62 g, 54%), $[\alpha]_D$ −16° (*c* 1), $R_F$ 0.55. $^1$H-N.m.r. data (250 MHz): $\delta$ 7.30–7.21 (m, 5 H, SPh), 7.04 (s, 1 H, H-6), 5.20 (dd, 1 H, $J_{2',3'}$ 9.3, $J_{3',4'}$ 9.3 Hz, H-3'), 5.08–4.93 (2 dd, 2 H, H-2',4'), 4.72 (d, 1 H, $J_{1',2'}$ 9.8 Hz, H-1'), 4.32–4.26 (m, 2 H, H-6',6''), 3.96–3.88 (m, 1 H, H-5'), 3.91, 3.86, 3.80, 3.79, 3.77, 3.76, 3.58 (7 s, 21 H, 3 OMe and 4 COOMe).

*Anal.* Calc. for $C_{29}H_{34}O_{15}S$ (654.65): C, 53.2; H, 5.2. Found: C, 53.3; H, 4.9.

*2,3,4-Trimethoxy-1-phenylsulfinyl-5-(2,3,4,6-tetra-*O*-methoxycarbonyl-β-*D*-glucopyranosyl)benzene* (**15**). — A solution of **14** (0.55 g, 0.84 mmol) in dichloromethane (30 mL) was treated at −5° with 3-chloroperoxybenzoic acid (0.4 g, 1.3 mmol; 55%). After 1 h, the mixture was poured into aqueous $NaHCO_3$, and the organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (1:2 LP–EA) of the residue gave a 1:2 mixture (0.47 g, 83%) of the two isomers.

The major isomer had $[\alpha]_D$ −12° (*c* 1), $R_F$ 0.30. $^1$H-N.m.r. data (250 MHz): $\delta$ 7.90 (s, 1 H, H-6), 7.98–7.46 (2 m, 5 H, SOPh), 5.26–5.19 (2 dd, 2 H, H-2',3'), 5.06 (dd, 1 H, $J_{3',4'}$ 9.5, $J_{4',5'}$ 9.5 Hz, H-4'), 4.79 (d, 1 H, $J_{1',2'}$ 9.5 Hz, H-1'), 4.38, 4.28 (2 dd, 2 H, H-6',6''), 3.97–3.88 (m, 1 H, H-5'), 3.92, 3.83, 3.80, 3.79, 3.76, 3.74, 3.54 (7 s, 21 H, 3 OMe and 4 COOMe).

*Anal.* Calc. for $C_{29}H_{34}O_{16}S{\cdot}H_2O$ (688.66): C, 50.6; H, 5.3. Found: C, 50.3; H, 5.5.

*2,3,4-Trimethoxy-6-methoxycarbonyl-1-phenylsulfinyl-5-(2,3,4,6-tetra-*O*-methoxycarbonyl-β-*D*-glucopyranosyl)benzene* (**17**). — To a solution of lithium di-isopropylamide (3.2 mmol) in dry tetrahydrofuran (20 mL) was added **15** (370 mg, 0.55 mmol) in portions at −90°. After 3 h, the mixture was treated at −75° with methyl chloroformate (5 mL), and stirring was continued for 10 h at −60°. The mixture was worked-up as described for **14**, to give **17** (240 mg, 60%), isolated as a colourless oil, $[\alpha]_D$ −15° (*c* 1), $R_F$ 0.30 (1:2 LP–EA). The compound was used directly in the next step.

*1,2,3-Trimethoxy-5-methoxycarbonyl-6-(2,3,4,6-tetra-*O*-methoxycarbonyl-β-*D*-glucopyranosyl)benzene* (**18**). — To a solution of **17** (240 mg, 0.33 mmol) in methanol (30 mL) was added Raney Ni W2 (0.5 g). Stirring was continued for 20 h at room temperature, the mixture was filtered, the insoluble material was washed with methanol, and the combined filtrate and washings were concentrated *in vacuo*. Flash chromatography (1:1 LP–EA) of the product gave **18** (180 mg, 90%), isolated as a colourless oil, $[\alpha]_D$ −7° (*c* 1), $R_F$ 0.30 (1:2 LP–EA). $^1$H-N.m.r. data (250 MHz): $\delta$ 6.99 (bs, 1 H, H-5), 5.83 (dd, 1 H, H-2'), 5.23 (d, 1 H, H-1'), 5.20 (dd, 1 H, H-3'), 5.05 (dd, 1 H, H-4'), 4.30 (m, 2 H, H-6',6''), 3.94, 3.91, 3.87, 3.86, 3.81, 3.78, 3.77, 3.57 (8 s, 24 H, 3 OMe and 5 COOMe), 3.90 (m, 1 H, H-5').

*Anal.* Calc. for $C_{25}H_{32}O_{17}{\cdot}0.5H_2O$ (613.53): C, 48.9; H, 5.4. Found: C, 48.8; H, 5.5.

*(3R,4R,4aS,10bS)-3,4-Diacetoxy-2-acetoxymethyltetrahydropyrano[5,6-c]dihydroisocoumarin* (**4**). — To a solution of **18** (100 mg, 0.17 mmol) in methanol (20 mL) was added methanolic M NaOMe (0.5 mL). After 30 min, the mixture was diluted with tetrahydrofuran (50 mL), 70% of the solvent was evaporated, and this procedure was repeated twice. Acetic acid (1 mL) was then added and the solution was concentrated to dryness to give crude **2**, a solution of which in pyridine (10 mL) and acetic anhydride (10 mL) was left overnight at room temperature. The mixture was poured on to ice (20 g)

and extracted three times with chloroform (50 mL), and the combined extracts were washed thrice with 0.5M HCl, dried ($MgSO_4$), and concentrated *in vacuo*. Flash chromatography (1:1 LP–EA) of the product gave **4** (56 mg, 70%), $[\alpha]_D$ −8° (*c* 1), $R_F$ 0.42. $^1$H-N.m.r. data (250 MHz): $\delta$ 7.46 (s, 1 H, H-7), 5.52 (dd, 1 H, H-4), 5.13 (dd, 1 H, H-3), 4.84 (d, 1 H, H-10b), 4.35–4.27 (m, 2 H, H-11,11'), 4.29 (dd, 1 H, H-4a), 3.90 (m, 1 H, H-2), 3.96, 3.92, 3.86 (3 s, 9 H, 3 OMe), 2.12, 2.11, 2.08 (3 s, 9 H, 3 Ac).

*Anal.* Calc. for $C_{22}H_{26}O_{12}$ (482.45): C, 54.8; H, 5.4. Found: C, 54.7; H, 5.7.

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