

## Note

**C-Arylation at the anomeric centre of sugars by bromomagnesium phenolates: synthesis of 1,1- and 5,5-bis(2-hydroxyaryl)-C-glycosyl derivatives**

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The phenolates of coordinating metals are carbon nucleophiles as well as Lewis acids, and this dual reactivity has been exploited in the arylation reactions of electrophilically activated substrates, including hydroxylated carbonyl compounds<sup>1</sup> and glycol derivatives<sup>2</sup>. The bromomagnesium salts of phenols have been used for the C-arylation of reducing sugars at the anomeric site<sup>3–9</sup>, and we now report on the application of this reaction to various aldose derivatives and a dialdose.

Readily available 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**2**), 2,3,4,6-tetra-

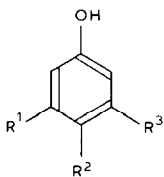
TABLE I

SYNTHESIS AND PROPERTIES OF DIARYL-C-GLYCOSYL COMPOUNDS

Entry	Phenol	Carbohydrate	Product <sup>a</sup>	Yield (%) <sup>b</sup>	$[\alpha]_D^{20}$ <sup>c</sup>
1	<b>1a</b>	<b>2</b>	<b>7</b>	67	–13
2	<b>1a</b>	<b>3</b>	<b>8</b>	62	+26
3	<b>1a</b>	<b>4</b>	<b>9a</b>	79	–9.6
4	<b>1b</b>	<b>4</b>	<b>9b</b>	74	+32
5	<b>1a</b>	<b>5</b>	<b>10a</b>	69	+22
6	<b>1b</b>	<b>5</b>	<b>10b</b>	68	+26.5
7	<b>1a</b>	<b>6</b>	<b>11</b>	71	+34
8	<b>1a</b>	<b>12</b>	<b>13a</b>	96	–50
9	<b>1b</b>	<b>12</b>	<b>13b</b>	94	–7.7

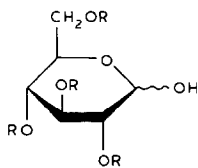
<sup>a</sup>Isolated as oily or glassy substances. <sup>b</sup>Based on the starting carbohydrate. <sup>c</sup>In chloroform (*c* 1).

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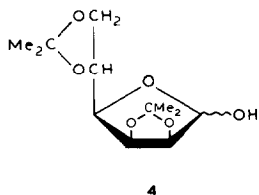
**1a**  $R^1 = H, R^2, R^3 = OCH_2O$

**1b**  $R^1 = R^3 = OMe, R^2 = H$

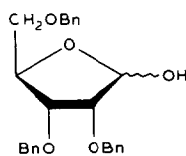


**2**  $R = Bn$

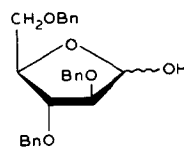
**3**  $R = Me$



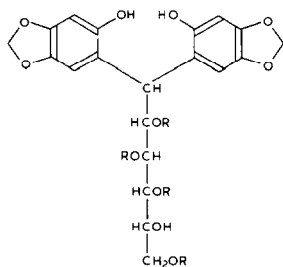
**4**



**5**

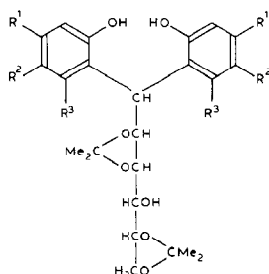


**6**



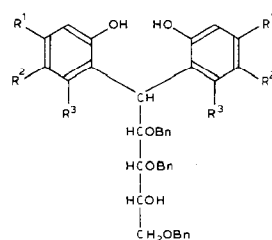
**7**  $R = Bn$

**8**  $R = Me$



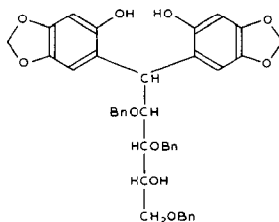
**9a**  $R^1, R^2 = OCH_2O, R^3 = H$

**9b**  $R^1 = R^3 = OMe, R^2 = H$



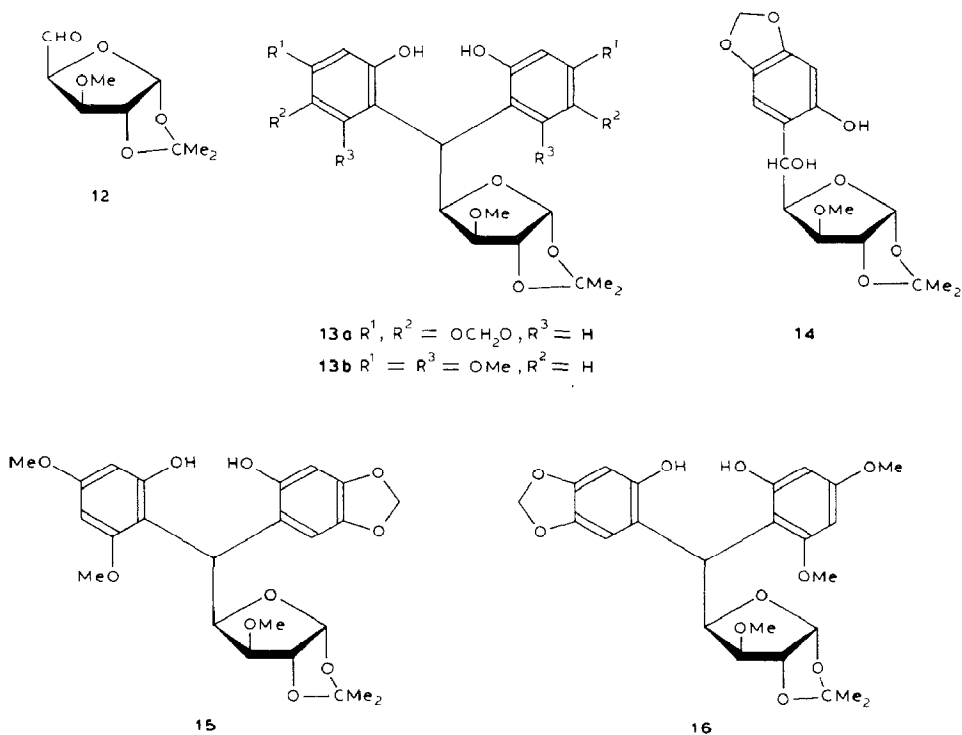
**10a**  $R^1, R^2 = OCH_2O, R^3 = H$

**10b**  $R^1 = R^3 = OMe, R^2 = H$



11

*O*-methyl-D-glucopyranose (**3**), 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (**4**), 2,3,5-tri-*O*-benzyl-D-ribofuranose (**5**), and 2,3,5-tri-*O*-benzyl-D-arabinofuranose (**6**) were each allowed to react with the bromomagnesium salts of 3,4-methylenedioxyphenol (**1a**) and 3,5-dimethoxyphenol (**1b**). Reactions with a 1:1 ratio of the reactants were unproductive but, with a 1:4 molar ratio of phenolate to sugar in dichloromethane, the 1,1-bis-arylated alditol derivatives **7-11** were



obtained in high yields. The results are collected in Table I (entries 1–7). No C-arylation was observed in these reactions, but moderate mono-C-arylation occurred with the salts of naphthols and certain alkyl-substituted phenols.

The structures of **7–11** were confirmed by elemental analysis and 200-MHz  $^1\text{H}$ -n.m.r. spectroscopy. The resonance for H-1 of the carbohydrate moieties appears as a doublet at 4.1–5.3 p.p.m., in agreement with data for analogous methine-bridged dinuclear phenolic compounds<sup>10,11</sup>, and the presence of the two diastereotopic phenolic rings in the molecule was deduced by the non-equivalence of the resonances in the region for aromatic protons.

On application of the arylation procedure to 1,2-*O*-isopropylidene-3-*O*-methyl-D-xylitol-pentodialdofuranose (**12**), the bromomagnesium salts of **1a** and **1b** reacted smoothly and gave the 5,5-bis-arylated derivatives **13a** and **13b** in good yields (Table I, entries 8 and 9), the identities of which were confirmed by their  $^1\text{H}$ -n.m.r. spectra, which contained resonances for two non-equivalent aromatic moieties.

The mechanism of the formation of the diarylalkane derivatives **13** was indicated by the addition of **1a** to **12** (2:1 molar ratio) at  $-30^\circ$  in  $\text{CH}_2\text{Cl}_2$ , which gave 64% of the carbinol **14**<sup>12</sup>. As expected, when **14** reacted in dichloromethane with 4 mol. equiv. of **1a** at  $40^\circ$ , **13a** (77%) was obtained, thus demonstrating that **14** is the reaction intermediate<sup>10–13</sup>.

When **14** reacted with an excess of the bromomagnesium salt of **1b**, 71% of an unresolvable 1:1 mixture of the C-5 epimers **15** and **16** was obtained.

The above results show that 1,1-bis-arylated C-glycosyl derivatives with identical or different phenolic moieties can be formed readily from aldose derivatives in which the anomeric position is unsubstituted.

#### EXPERIMENTAL

*General.* — I.r. spectra were recorded with a Perkin-Elmer 983 spectrophotometer.  $^1\text{H}$ -N.m.r. spectra ( $\text{CDCl}_3$ , internal  $\text{Me}_4\text{Si}$ ) were recorded on a Bruker CXP200 (200 MHz) spectrometer and  $[\alpha]_D$  values were measured with a Perkin-Elmer 241 polarimeter, using a 1-dm cell. Column chromatography was carried out on Kieselgel 60G (Merck). Microanalyses were performed by the Dipartimento di Chimica dell'Università di Sassari.

2,3,5-Tri-*O*-benzyl-D-ribofuranose (**5**), m.p. 46–49°,  $[\alpha]_D^{20} +42^\circ$  (c 2, 1,4-dioxane), was prepared by the method reported<sup>14</sup>. Compounds **1–4**, **6**, and **12** were commercial products.

The bromomagnesium phenolates were prepared by reacting **1a** or **1b** with ethereal  $\text{EtMgBr}$ . The ether was then evaporated under vacuum at ambient temperature. The salts were monoetherates, as shown by the  $^1\text{H}$ -n.m.r. data and elemental analyses.

Sonicated reactions were carried out with a Branson Model B-3200E2 ultrasonic cleaner.

*Reactions of bromomagnesium phenolates with 2–6 and 12.* — To a solution of the bromomagnesium salt (4 mmol) in dichloromethane (100 mL) was added a solution of the sugar derivative (1 mmol) in dichloromethane (20 mL) with stirring at room temperature. The mixture was sonicated for 10 h at 40°, the reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$ , and the mixture was extracted with ethyl acetate ( $3 \times 50$  mL). The combined extracts were dried and concentrated under reduced pressure. Flash chromatography (hexane–ethyl acetate mixtures) of the residue gave the following compounds.

The yields and the  $[\alpha]_D$  values are recorded in Table I.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1,1-bis(2-hydroxy-4,5-methylenedioxyphenyl)-D-glucitol (**7** from **1a** and **2**).  $^1\text{H}$ -N.m.r. data ( $\text{CDCl}_3$ ):  $\delta$  2.92 (s, 1 H, OH), 3.53 (m, 2 H, H-6a,6b), 3.65 (dd, 1 H,  $J_{3,4}$  3.5,  $J_{4,5}$  6.9 Hz, H-4), 3.78 (m, 1 H, H-3), 4.08 (m, 1 H, H-5), 4.12 (d, 1 H,  $J_{1,2}$  10.2 Hz, H-1), 4.55 (d, 1 H, H-2), 4.3–4.8 (m, 8 H, 4  $\text{CH}_2\text{Ph}$ ), 5.50 (s, 1 H, OH), 5.80 (m, 4 H, 2  $\text{OCH}_2\text{O}$ ), 6.32, 6.47, 6.48, and 6.63 (4 s, each 1 H, H-3',3'',6',6''), 6.9–7.4 (m, 20 H, 4 Ph), 8.62 (s, 1 H, OH);  $\nu_{\text{max}}$  3340, 2880, 1630, 1490, 1170, 1040, 940, and 740  $\text{cm}^{-1}$ .

*Anal.* Calc. for  $\text{C}_{48}\text{H}_{46}\text{O}_{11}$ : C, 72.17; H, 5.80. Found: C, 72.29; H, 5.78.

1-Deoxy-1,1-bis(2-hydroxy-4,5-methylenedioxyphenyl)-2,3,4,6-tetra-*O*-methyl-D-glucitol (**8** from **1a** and **3**).  $^1\text{H}$ -N.m.r. data ( $\text{CDCl}_3$ ):  $\delta$  2.85 (bs, 1 H, OH), 3.35, 3.38, and 3.42 (4 s, each 3 H, OMe), 3.3–3.5 (m, 4 H, H-3,4,6a,6b), 3.87 (m, 1 H, H-5), 4.23 (dd, 1 H,  $J_{1,2}$  5.3,  $J_{2,3}$  6.4 Hz, H-2), 4.55 (d, 1 H, H-1), 5.78 (m, 4 H,  $\text{OCH}_2\text{O}$ ), 6.37, 6.42, 6.59, 6.62 (4 s, each 1 H, H-3',3'',6',6''), 7.60

and 8.20 (2 bs, each 1 H, OH);  $\nu_{\max}$  3390, 2960, 1690, 1490, 1290, 1150, 950, and 740  $\text{cm}^{-1}$ .

*Anal.* Calc. for  $\text{C}_{24}\text{H}_{30}\text{O}_{11}$ : C, 58.29; H, 6.12. Found: C, 58.35; H, 6.20.

1-Deoxy-1,1-bis(2-hydroxy-4,5-methylenedioxyphenyl)-2,3:5,6-di-*O*-isopropylidene-D-mannitol (**9a** from **1a** and **4**).  $^1\text{H}$ -N.m.r. data ( $\text{CDCl}_3$ ):  $\delta$  1.09, 1.28, 1.46, and 1.53 (4 s, each 3 H, 2  $\text{Me}_2\text{C}$ ), 3.16 (bs, 1 H, HO-4), 3.46 (d, 1 H,  $J_{4,5}$  6.4 Hz, H-4), 3.98 (m, 3 H, H-5,6a,6b), 4.32 (t, 1 H,  $J_{1,2} = J_{2,3} = 2.9$  Hz, H-2), 5.08 (d, 2 H, H-1,3), 5.83 (m, 4 H, 2  $\text{OCH}_2\text{O}$ ), 6.30, 6.47, 6.65, and 6.72 (4 s, each 1 H, H-3',3'',6',6''), 5.90 (s, 1 H, OH), 7.50 (bs, 1 H, OH);  $\nu_{\max}$  3380, 2980, 1625, 1480, 1210, 1180, 930, and 740  $\text{cm}^{-1}$ .

*Anal.* Calc. for  $\text{C}_{26}\text{H}_{30}\text{O}_{11}$ : C, 60.23; H, 5.83. Found: C, 60.37; H, 5.94.

1-Deoxy-1,1-bis(2-hydroxy-4,6-dimethoxyphenyl)-2,3:5,6-di-*O*-isopropylidene-D-mannitol (**9b** from **1b** and **4**).  $^1\text{H}$ -N.m.r. data ( $\text{CDCl}_3$ ):  $\delta$  1.04, 1.24, 1.38, and 1.42 (4 s, each 3 H, 2  $\text{Me}_2\text{C}$ ), 3.17 (d, 1 H,  $J_{4,\text{OH}}$  6.9 Hz, OH), 3.70, 3.72, 3.92, and 3.94 (4 s, each 3 H, 4 OMe), 3.6–4.0 (m, 4 H, H-4,5,6a,6b), 4.26 (d, 1 H,  $J_{2,3}$  6.4 Hz, H-3), 5.22 (d, 1 H,  $J_{1,2}$  10.5 Hz, H-1), 5.63 (dd, 1 H, H-2), 6.0–6.2 (m, 4 H, H-3',3'',5',5''), 7.90 (bs, 1 H, OH), 8.08 (bs, 1 H, OH);  $\nu_{\max}$  3370, 2980, 1615, 1455, 1210, 1150, 940, and 755  $\text{cm}^{-1}$ .

*Anal.* Calc. for  $\text{C}_{28}\text{H}_{38}\text{O}_{11}$ : C, 61.08; H, 6.96. Found: C, 60.91; H, 7.09.

2,3,5-Tri-*O*-benzyl-1-deoxy-1,1-bis(2-hydroxy-4,5-methylenedioxyphenyl)-D-ribitol (**10a** from **1a** and **5**).  $^1\text{H}$ -N.m.r. data ( $\text{CDCl}_3$ ):  $\delta$  2.90 (bs, 1 H, OH), 3.44 (dd, 1 H,  $J_{4,5b}$  6.4,  $J_{5a,5b}$  9.9 Hz, H-5b), 3.53 (dd, 1 H,  $J_{3,4}$  2.6,  $J_{2,3}$  6.9 Hz, H-3), 3.58 (dd, 1 H,  $J_{4,5a}$  2.9 Hz, H-5a), 4.09 (m, 1 H, H-4), 4.30 (d, 1 H,  $J_{1,2}$  11.2 Hz, H-1), 4.35–4.95 (m, 7 H, 3  $\text{CH}_2\text{Ph}$  and H-2), 5.85 (m, 4 H, 2  $\text{OCH}_2\text{O}$ ), 6.18, 6.37, 6.58, and 6.61 (4 s, each 1 H, H-3',3'',6',6''), 7.0–7.4 (m, 15 H, 3 Ph), 7.6 (bs, 1 H, OH), 8.61 (bs, 1 H, OH);  $\nu_{\max}$  3330, 2880, 1630, 1480, 1210, 1170, 940, and 750  $\text{cm}^{-1}$ .

*Anal.* Calc. for  $\text{C}_{40}\text{H}_{38}\text{O}_{10}$ : C, 70.78; H, 5.64. Found: C, 70.91; H, 5.77.

2,3,5-Tri-*O*-benzyl-1-deoxy-1,1-bis(2-hydroxy-4,6-dimethoxyphenyl)-D-ribitol (**10b** from **1b** and **5**).  $^1\text{H}$ -N.m.r. data ( $\text{CDCl}_3$ ):  $\delta$  2.90 (bs, 1 H, OH), 3.47 (dd, 1 H,  $J_{4,5b}$  2.1,  $J_{5a,5b}$  10.5 Hz, H-5b), 3.59 (dd, 1 H,  $J_{4,5a}$  3.5 Hz, H-5a), 3.69, 3.72, 3.75, and 3.77 (4 s, each 3 H, OMe), 3.70 (m, 1 H, H-3), 4.06 (m, 1 H, H-4), 4.40 (d, 1 H,  $J_{1,2}$  6.4 Hz, H-1), 4.4–4.7 (m, 7 H, 3  $\text{CH}_2\text{Ph}$  and H-2), 6.03, 6.06, 6.13, and 6.22 (4 d, each 1 H,  $J_{\text{meta}}$  2.3 Hz, H-3',3'',5',5''), 7.1–7.4 (m, 15 H, 3 Ph), 7.75 (bs, 1 H, OH), 8.44 (bs, 1 H, OH);  $\nu_{\max}$  3390, 2930, 1630, 1460, 1224, 1160, 920, and 740  $\text{cm}^{-1}$ .

*Anal.* Calc. for  $\text{C}_{42}\text{H}_{46}\text{O}_{10}$ : C, 70.97; H, 6.52. Found: C, 70.06; H, 6.56.

2,3,5-Tri-*O*-benzyl-1-deoxy-1,1-bis(2-hydroxy-4,5-methylenedioxyphenyl)-D-arabinitol (**11** from **1a** and **6**).  $^1\text{H}$ -N.m.r. data ( $\text{CDCl}_3$ ):  $\delta$  2.90 (s, 1 H, OH), 3.50–3.80 (m, 3 H, H-4,5a,5b), 4.03 (m, 1 H, H-3), 4.12 (m, 1 H, H-2), 4.18 (d, 1 H,  $J_{1,2}$  10.2 Hz, H-1), 4.45–4.90 (m, 6 H, 3  $\text{CH}_2\text{Ph}$ ), 5.85 (m, 4 H, 2  $\text{OCH}_2\text{O}$ ), 6.33, 6.49, 6.64, and 6.75 (4 s, each 1 H, H-3',3'',6',6''), 7.0–7.4 (m, 15 H, 3 Ph), 7.60 (bs, 1 H, OH), 8.30 (bs, 1 H, OH);  $\nu_{\max}$  3450, 2900, 1640, 1395, 1190, 1050, 920, and 740  $\text{cm}^{-1}$ .

*Anal.* Calc. for  $C_{40}H_{38}O_{10}$ : C, 70.78; H, 5.64. Found: C, 70.89; H, 5.78.

5-Deoxy-5,5-bis(2-hydroxy-4,5-methylenedioxyphenyl)-1,2-*O*-isopropylidene-3-*O*-methyl- $\alpha$ -D-xylofuranose (**13a** from **1a** and **12**).  $^1\text{H-N.m.r.}$  data ( $\text{CDCl}_3$ ):  $\delta$  1.33 and 1.57 (2 s, each 3 H,  $\text{Me}_2\text{C}$ ), 3.25 (s, 3 H, OMe), 3.48 (d, 1 H,  $J_{3,4}$  2.5 Hz, H-3), 4.57 (d, 1 H,  $J_{1,2}$  3.7 Hz, H-2), 4.65 (d, 1 H,  $J_{4,5}$  10.7 Hz, H-5), 4.85 (dd, 1 H, H-4), 5.85 (bs, 4 H, 2  $\text{OCH}_2\text{O}$ ), 5.88 (s, 1 H, OH), 5.93 (d, 1 H, H-1), 6.29, 6.47, 6.58, and 6.80 (4 s, each 1 H, H-3', 3'', 6', 6''), 6.35 (bs, 1 H, OH);  $\nu_{\text{max}}$  3375, 2930, 1630, 1480, 1210, 1180, 930, and 730  $\text{cm}^{-1}$ .

*Anal.* Calc. for  $C_{23}H_{24}O_{10}$ : C, 60.00; H, 5.25. Found: C, 59.77; H, 5.38.

5-Deoxy-5,5-bis(2-hydroxy-4,6-dimethoxyphenyl)-1,2-*O*-isopropylidene-3-*O*-methyl- $\alpha$ -D-xylofuranose (**13b** from **1b** and **12**).  $^1\text{H-N.m.r.}$  data ( $\text{CDCl}_3$ ):  $\delta$  1.30 and 1.54 (2 s, each 3 H,  $\text{Me}_2\text{C}$ ), 3.05 (s, 3 H, OMe), 3.34 (d, 1 H,  $J_{3,4}$  2.9 Hz, H-3), 3.71, 3.74, 3.92, and 3.93 (4 s, each 3 H, 4 ArOMe), 4.47 (d, 1 H,  $J_{1,2}$  3.9 Hz, H-2), 5.01 (d, 1 H,  $J_{4,5}$  10.5 Hz, H-5), 5.50 (dd, 1 H, H-4), 5.86 (d, 1 H, H-1), 6.08, 6.11, 6.15, and 6.16 (4 d, each 1 H,  $J$  3 Hz, H-3', 3'', 5', 5''), 7.92 (bs, 1 H, OH), 8.20 (bs, 1 H, OH);  $\nu_{\text{max}}$  3480, 2950, 1630, 1480, 1220, 1160, 1030, and 740  $\text{cm}^{-1}$ .

*Anal.* Calc. for  $C_{25}H_{32}O_{10}$ : C, 60.97; H, 6.55. Found: C, 60.77; H, 6.90.

(5S)-5-(2-Hydroxy-4,5-methylenedioxyphenyl)-1,2-*O*-isopropylidene-3-*O*-methyl- $\alpha$ -D-xylofuranose (**14**). — To a stirred solution of the bromomagnesium salt of **1a** (10 mmol) in dichloromethane (250 mL) was added a solution of **12** (5 mmol) in dichloromethane (250 mL) at  $-30^\circ$ . The mixture was kept at  $-30^\circ$  for 20 h, quenched with saturated aqueous  $\text{NH}_4\text{Cl}$ , and extracted with ether ( $3 \times 200$  mL). The combined extracts were dried and concentrated. Flash chromatography (hexane–ethyl acetate, 85:15) of the residue gave **14** (1.10 g, 64%),  $[\alpha]_D^{20} -42^\circ$  (c 0.5, chloroform).  $^1\text{H-N.m.r.}$  data ( $\text{CDCl}_3$ ):  $\delta$  7.92 (s, 1 H, OH), 6.58 (s, 1 H, H-6'), 6.45 (s, 1 H, H-3'), 5.98 (d, 1 H,  $J_{1,2}$  3.8 Hz, H-1), 5.90 (s, 2 H,  $\text{OCH}_2\text{O}$ ), 5.05 (d, 1 H,  $J_{4,5}$  8.0 Hz, H-5), 4.61 (d, 1 H,  $J_{1,2}$  3.8 Hz, H-2), 4.38 (dd, 1 H,  $J_{4,5}$  8.0,  $J_{3,4}$  3.2 Hz, H-4), 3.49 (d, 1 H,  $J_{3,4}$  3.2 Hz, H-3), 3.39 (s, 3 H, OMe), 3.32 (bs, 1 H, OH), 1.49 and 1.32 (2 s, each 3 H,  $\text{Me}_2\text{C}$ );  $\nu_{\text{max}}$  3440, 2960, 1640, 1380, 1180, 1060, and 750  $\text{cm}^{-1}$ .

*Anal.* Calc. for  $C_{16}H_{20}O_8$ : C, 56.46; H, 5.92. Found: C, 56.51; H, 5.96.

5-Deoxy-5,5-bis(2-hydroxy-4,5-methylenedioxyphenyl)-1,2-*O*-isopropylidene-3-*O*-methyl- $\alpha$ -D-xylofuranose (**13a**). — To a stirred solution of the bromomagnesium salt of **1a** (4 mmol) in dichloromethane (25 mL) was added a solution of **14** (1 mmol) in dichloromethane (20 mL) at room temperature. The mixture was sonicated for 10 h at  $40^\circ$ , then quenched, and worked-up as above. Flash chromatography (hexane–ethyl acetate, 75:25) of the crude product afforded **13a** (0.35 g, 77%), which was identical to the product described above.

(5R)-5-Deoxy- and (5S)-5-deoxy-5-(2-hydroxy-3,5-dimethoxyphenyl)-5-(2-hydroxy-4,5-methylenedioxyphenyl)-1,2-*O*-isopropylidene-3-*O*-methyl- $\alpha$ -D-xylofuranose (**15** and **16**). — To a stirred solution of the bromomagnesium salt of **1b** (4 mmol) in dichloromethane (25 mL) was added a solution of **14** (1 mmol) in dichloromethane (20 mL) at room temperature. The mixture was sonicated for 10 h

at 40°, then quenched, and worked-up as above. Flash chromatography (hexane–ethyl acetate, 80:20) of the crude product afforded epimers **15** and **16** as an inseparable 1:1 mixture (0.34 g, 71%). <sup>1</sup>H-N.m.r. data (CDCl<sub>3</sub>): δ 1.25, 1.29, 1.53, and 1.55 (4 s, each 3 H, Me<sub>2</sub>C), 3.03 and 3.45 (2 s, each 3 H, OMe), 3.47 (bs, 2 H, H-3), 3.72, 3.75, 3.80, and 3.82 (4 s, each 3 H, 4 ArOMe), 4.49 and 4.54 (2 d, each 1 H, *J*<sub>1,2</sub> 3.5 Hz, H-2), 4.78 and 5.02 (2 d, each 1 H, *J*<sub>4,5</sub> 10 Hz, H-5), 5.40 and 5.51 (2 bd, each 1 H, H-4), 5.7–6.2 (m, 10 H, H-1, OCH<sub>2</sub>O, and aromatics), 6.36, 6.41, 6.45, and 6.60 (4 s, each 1 H, aromatics), 6.90, 7.06, 7.90, and 8.15 (4 s, each 1 H, OH).

*Anal.* Calc. for C<sub>24</sub>H<sub>28</sub>O<sub>10</sub>: C, 60.50; H, 5.92. Found: C, 60.19; H, 6.27.

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