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# Tetra-*n*-propylammonium tetra-oxoruthenate(VII): a reagent of choice for the oxidation of diversely protected glycopyranoses and glycofuranoses to lactones †

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**Abstract**

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranose, 2,3,5-tri-*O*-allyl-D-ribofuranose, 2,3,5-tri-*O*-allyl- and -tri-*O*-benzyl-D-arabinofuranose, and 2-deoxy-3,5-di-*O*-allyl-D-*erythro*-pentofuranose were oxidized to their corresponding lactones **6–10** by dimethyl sulfoxide activated by oxalyl chloride, pyridinium dichromate in the presence of molecular sieves and acetic acid, and tetra-*n*-propylammonium tetra-oxoruthenate(VII) using 4-methylmorpholine *N*-oxide as co-oxidant. With the latter reagent, analytically pure lactones were obtained in 83–98% yield. A multistep preparation of 3,4,6-tri-*O*-benzyl-2-deoxy-D-*arabino*-hexono-1,5-lactone (**14**) from 3,4,6-tri-*O*-benzyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol (65% overall yield) is described.

*Key words:* Oxidation; Tetra-*n*-propylammonium tetra-oxoruthenate(VII); Hexono-1,5-lactone; Pentono-1,4-lactone

## 1. Introduction

Diversely protected carbohydrate 1,4- and 1,5-lactones and furanosidic lactones are useful precursors for the synthesis of natural products [1,2]. They were also

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employed for the synthesis of *C*-glycosyl compounds [3–9] and *C*-nucleosides [10]. These protected lactones are usually prepared by oxidation of the corresponding lactols [11].

Since these lactones were needed for the development of our program of synthesis of *C*-glycosyl compounds, we decided to examine the scope and limitations of several oxidation procedures disclosed since the work of Fletcher and co-workers [11]. We now report the results of our study, together with a new synthesis of 3,4,6-tri-*O*-benzyl-2-deoxy-D-*arabino*-hexono-1,5-lactone from 3,4,6-tri-*O*-benzyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol (3,4,6-tri-*O*-benzyl-D-glucal).

## 2. Results and discussion

Benzylated and allylated glycopyranoses and glycofuranoses derivatives were oxidized with several oxidants: dimethyl sulfoxide activated by oxalyl chloride [12], pyridinium dichromate (PDC) in the presence of molecular sieves and acetic acid [13], and 4-methylmorpholine *N*-oxide (NMO) in the presence of tetra-*n*-propylammonium tetra-oxoruthenate(VII) (tetra-*n*-propylammonium per-ruthenate [14], TPAP). Significant results, obtained with 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose [11] **1**, are reported in Table 1. Treatment of **1**, under Swern conditions [12], afforded 2,3,4,6-tetra-*O*-benzyl-D-glucono-1,5-lactone (**6**) in 60% yield after flash-chromatography, which was needed to remove polar impurities. The procedure, which gave very good results for the preparation of protected dicarbonyl sugars, namely PDC in dichloromethane in the presence of acetic acid and molecular sieves [13], allowed a clean transformation of **1** into **6**, but some lactone was lost during the removal of chromium salts by filtration.

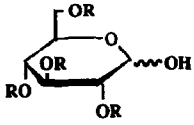
Tetra-*n*-propylammonium tetra-oxoruthenate(VII), with NMO as co-oxidant, was recently reported as a mild catalytic oxidant for the high-yield conversion of alcohols into aldehydes and ketones [14]. However, to the best of our knowledge, this reagent has not been employed for the oxidation of lactols to lactones. Treatment of **1** with 5 mol% of TPAP, in the presence of 1.5 equiv of NMO and

Table 1
Methods used for the obtention of 2,3,4,6-tetra-*O*-benzyl-D-glucono-1,5-lactone (**6**) from **1**

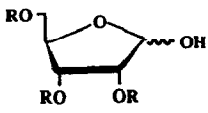
| Method | Solvent | Temp. (°C) | Time (h) | Yield (%) |
|---|---|---|---|---|
| Swern [a] | $CH_2Cl_2$/THF | −55 → rt | 4 | 60 [e] |
| PDC [b] | $CH_2Cl_2$ [c] | 0 → rt | 0.5 | 86 |
| TPAP [d] | $CH_2Cl_2$ | rt | 1 | 94 [f] |

[a] Reagents: oxalyl chloride (1.2 equiv)–$Me_2SO$ (2.2 equiv)–$Et_3N$ (5 equiv).
[b] Reagents: PDC (1 equiv)–AcOH (1.75 equiv)–3A molecular sieves.
[c] Distillated over PDC.
[d] Reagents: TPAP (5 mol%)–NMO (1.5 equiv)–3A molecular sieves.
[e] After flash-chromatography.
[f] Crude product of analytical purity.

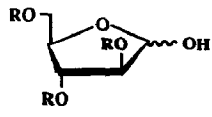
3A molecular sieves in dichloromethane for 1 h at room temperature, afforded **6** in 94% yield. In this case, lactone **6** was obtained directly in analytical purity and no purification was needed. This result was repeated many times without any problem on ~5 g quantities. In the presence of larger amounts of TPAP (10–15%), the reaction time was shortened but, with less than 5% TPAP, the reaction did not go to completion. Lactone **6** was also prepared previously by use of dimethylsulfoxide–acetic anhydride [11], silver carbonate on celite [15], or PCC [16] as oxidants. In our hands, TPAP in the presence of NMO was found to be the most convenient and efficient system.



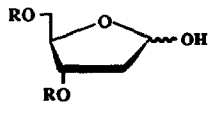
**1** R = Bn



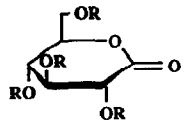
**2** R = $CH_2$-CH=$CH_2$



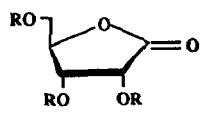
**3** R = $CH_2$-CH=$CH_2$
**4** R = Bn



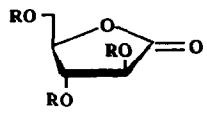
**5** R = $CH_2$-CH=$CH_2$



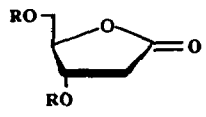
**6** R = Bn



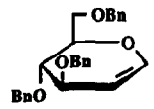
**7** R = $CH_2$-CH=$CH_2$



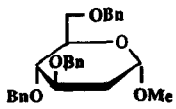
**8** R = $CH_2$-CH=$CH_2$
**9** R = Bn



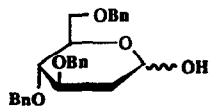
**10** R = $CH_2$-CH=$CH_2$



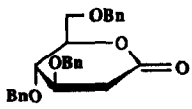
**11**



**12**



**13**



**14**

In the pentofuranose series, oxidation of **2–5** with TPAP in the presence of NMO afforded also the corresponding lactones **7–10** in good yield (Table 2). As for **1**, this procedure was convenient and fast, and gave analytically pure lactones without purification. With other oxidants such as PDC–acetic acid–molecular sieves [17], or PCC–molecular sieves [17], the desired lactones were obtained in lower yield (65–70%) after flash-chromatography. Pentofuranose derivatives **2**, **3**, and **5** were conveniently prepared by allylation of the corresponding methyl glycoside [18–20], followed by acidic hydrolysis.

A one-step preparation of 3,4,6-tri-*O*-benzyl-2-deoxy-D-*arabino*-hexono-1,5-lactone (**14**) by oxidation of 3,4,6-tri-*O*-benzyl-D-glucal (**11**) was previously reported [21]. However, in our hands, this procedure led to lactone **14** contaminated by variable amounts of an $\alpha,\beta$-unsaturated lactone. Although this by-product had an $R_f$ value close to that of **14**, it could be removed by recrystallization. Since Bolitt and Mioskowski [22] recently proposed an efficient preparation of 2-deoxy-glyco-

Table 2
Protected 1,4-lactones obtained from the oxidation of the corresponding D-ribono- or arabino-furanoses by TPAP

| Compound | Lactone | Time (min) | Yield (%) | [α] deg (solvent) |
|---|---|---|---|---|
| **2** | **7** | 20 | 83 | +46.0 ($CHCl_3$) |
| **3** | **8** | 20 | 92 | −22.1 ($CHCl_3$) |
| **4** | **9** [a] | 30 | 94 | +3.1 ($CHCl_3$) |
| **5** | **10** | 15 | 98 | +28.7 ($CHCl_3$) |

[a] Mp 65–66°C; lit. [24] mp 67°C, $[\alpha]_D$ +6.8° ($CHCl_3$).

sides by addition of an alcohol to protected 1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol without Ferrier rearrangement, we decided to evaluate an alternative approach to **14** which would use the 2-deoxy-glycose **13** available from **12**.

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranoside (**12**) was obtained in nearly quantitative yield from **11** and methanol (1.5 equiv) in the presence of triphenylphosphine hydrobromide (TPHB) in dichloromethane [22]. The crude mixture, containing mainly the α anomer, was directly hydrolyzed to **13** and was obtained crystalline in 85% yield. Oxidation of **13** with NMO, in the presence of 5% TPAP, afforded analytically pure 2-deoxy lactone **14** in 76% yield.

## 3. Experimental

*General methods.*—Melting points were determined with a Thomas–Hoover apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. $^1H$ NMR spectra were recorded with a Brucker AM 250 spectrometer for solutions in $CDCl_3$ (internal $Me_4Si$). Analytical TLC was performed on Merck aluminum precoated plates of Silica Gel 60 $F_{254}$, with detection by UV and by spraying with 6 N $H_2SO_4$ and heating for ~ 2 min at 300°C. The following solvents were used: (*A*) 3:7 ether-light petroleum; (*B*) 2:1 ether–light petroleum; (*C*) 1:1 ether–light petroleum; (*D*) 1:6 ether–light petroleum; (*E*) 3:7 EtOAc–light petroleum; (*F*) 4:1 ether–pentane; (*G*) 2:1 ether–pentane. Silica Gel 60 (E. Merck, 230–400 mesh) was used for flash chromatography. Elemental analyses were performed at the Service de Microanalyse of the University of Paris VI.

*2,3,4,6-Tetra-O-benzyl-D-glucono-1,5-lactone* (**6**).—*Method A (TPAP).* To a solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (Sigma; 4 g, 7.4 mmol) in $CH_2Cl_2$ (60 mL), were added 3A molecular sieves (2 g) and 4-methylmorpholine *N*-oxide (1.3 g, 11.1 mmol). After stirring at room temperature for 10 min, TPAP (129 mg, 0.37 mmol) was added, and the progress of the reaction was monitored by TLC (solvent *C*). After completion of the oxidation (1 h), the mixture was diluted with $CH_2Cl_2$ (40 mL), washed successively with 5% $Na_2SO_3$ in brine (15 mL), brine (15 mL), and satd $CuSO_4$ (15 mL), dried ($MgSO_4$), filtered through Celite, and concentrated under reduced pressure to give an oil (3.74 g, 94%) homogeneous on

TLC; $R_f$ 0.29 (solvent *C*); $[\alpha]_D$ +78.0° (*c* 1, $CHCl_3$); lit. [11] $[\alpha]_D$ +81.3° ($CHCl_3$). Anal. Calcd for $C_{34}H_{34}O_6$: C, 75.81; H, 6.34. Found: C, 75.66; H, 6.30.

*Method B (Swern).* To a cooled (−55°C) solution of oxalyl chloride (6 mmol) in $CH_2Cl_2$ (10 mL), was added dropwise a solution of $Me_2SO$ (11 mmol) in $CH_2Cl_2$ (3 mL) under Ar. The mixture was stirred for 2 min and **1** (5 mmol in 15 mL of THF) was added. The temperature was slowly raised to −30°C, $Et_3N$ (25 mmol) was added dropwise and the mixture was allowed to warm to room temperature and was kept for 4 h at this temperature. Water (25 mL) was then added, and the aqueous layer was extracted with $CHCl_3$ (2 × 25 mL). The organic layers were combined, washed successively with HCl (10%, 10 mL), $H_2O$ (10 mL), $NaHCO_3$ (5%, 10 mL) and $H_2O$ (2 × 10 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed on a column of silica gel (95:5 $CHCl_3$–EtOAc) to give lactone **6** (1.614 g, 60%).

*Method C (PDC).* Finely ground pyridinium dichromate (752 mg, 2 mmol) was added in one batch to a stirred solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (1.08 g, 2 mmol) in $CH_2Cl_2$ (15 mL) containing anhyd AcOH (200 μL, 3.5 mmol) and molecular sieves (2.6 g) at 0°C. After 30 min stirring at room temperature, ether (30 mL) was added in order to precipitate the chromium salts. The mixture was filtered through a layer of Celite and the filtrate concentrated under reduced pressure. Additional ether (30 mL) was added and the mixture was filtered through silica gel with solvent *D* to give the lactone **6** (919 mg, 86%).

*General procedure for the preparation of methyl allyl-glycofuranosides.*—To a solution of either methyl α,β-D-ribofuranoside [18], methyl α,β-D-arabinofuranoside [19] or methyl 2-deoxy-α,β-D-*erythro*-pentofuranoside [20] (35 mmol) in THF (100 mL), was added 80% NaH (105 mmol) in one portion previously washed with ether. Allyl bromide (105 mmol) was added after 30 min stirring at room temperature and the progress of reaction was monitored by TLC with solvent *F*. After completion of the reaction (~ 15 h), excess NaH was destroyed with EtOH (10 mL) and the mixture was diluted with water (50 mL). The aqueous layer was extracted with additional ether (3 × 20 mL). The organic layers were combined, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed on a column of silica gel with an ether–pentane gradient to give a mixture of the α and β anomers which could be separated for analysis:

*Methyl 2,3,5-tri-O-allyl-α,β-D-ribofuranosides.* —Yield 74%; α anomer; oil; $R_f$ 0.53 (solvent *G*); $[\alpha]_D$ −1.7° (*c* 1.7, $CHCl_3$); $^1H$ NMR: δ 5.60–5.80 (m, 3 H, 3 CH=), 4.88–5.10 (m, 6 H, 3 $CH_2$=), 4.69 (d, 1 H, $J_{1,2}$ 4.3 Hz, H-1), 3.96 (ddd, 1 H, $J_{4,5}$ 4.1 and $J_{4,5'}$ 7.2 $H_z$, H-4), 3.74–3.82 (m, 6 H, 3 $CH_2$ allyl), 3.64 (dd, 1 H, $J_{3,4}$ 3.1 Hz, H-3), 3.56 (dd, 1 H, $J_{2,3}$ 6.7 Hz, H-2), 3.28 (m, 2 H, H-5,5'), 3.20 (s, 3 H, $OCH_3$). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H 8.51. Found: C, 63.66; H, 8.39. β Anomer; oil; $R_f$ 0.25 (solvent *G*); $[\alpha]_D$ +33.0° (*c* 1.7, $CHCl_3$); $^1H$ NMR: δ 5.63–5.73 (m, 3 H, 3 CH=), 4.92–5.13 (m, 6 H, 3 $CH_2$=), 4.67 (s, 1 H, H-1), 4.00 (ddd, 1 H, $J_{4,5}$ 3.8 and $J_{4,5'}$ 5.6 Hz, H-4), 3.83–3.94 (m, 6 H, 3 $CH_2$ allyl), 3.77 (dd, 1 H, $J_{3,4}$ 6.9 Hz, H-3), 3.60 (d, 1 H, $J_{2,3}$ 4.6 Hz, H-2), 3.38 (dd, 1 H, $J_{4,5}$ 3.8 and $J_{5,5'}$ 10.6 Hz, H-5), 3.30 (dd, 1 H, $J_{5,5'}$ 10.6 Hz, H-5'), 3.20 (s, 3 H, $OCH_3$). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.87; H, 8.26.

*Methyl 2,3,5-tri-*O*-allyl-α,β-*D*-arabinofuranosides.*—Yield 92%; α anomer; oil; $R_f$ 0.55 (solvent *G*); $[\alpha]_D$ −52.22° (*c* 0.72, $CHCl_3$); $^1$H NMR: 5.82–5.96 (m, 3 H, 3 CH=), 5.15–5.30 (m, 6 H, 3 $CH_2$=), 4.82 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.08–4.10 (m, 6 H, 3 $CH_2$ allyl), 4.05 (m, 1 H, H-4), 3.95 (m, 1 H, H-2), 3.73 (m, 1 H, H-3), 3.52 (m, 1 H, H-5), 3.37 (m, 4 H, H-5′, $OCH_3$). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.93; H, 8.67. β Anomer: oil; $R_f$ 0.77 (solvent *G*); $[\alpha]_D$ +66.65° (*c* 0.6, $CHCl_3$); $^1$H NMR: 5.82–5.90 (m, 3 H, 3 CH=), 5.16–5.28 (m, 6 H, 3 $CH_2$=), 4.87 (s, 1 H, H-1), 4.01–4.12 (m, 7 H, H-4 and 3 $CH_2$ allyl), 3.86 (d, 1 H, $J_{2,3}$ 2.9 Hz, H-2), 3.76 (dd, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 3.62 (m, 2 H, H-5,5′), 3.34 (s, 3 H, $OCH_3$). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.27; H, 8.36.

*Methyl 2-deoxy-3,5-di-*O*-allyl-α,β-*D*-*erythro*-pentofuranosides.*—Yield 80%; $R_f$ 0.73 (solvent F); $[\alpha]_D$ −1.64° (*c* 1.55, $CHCl_3$); $^1$H NMR: δ 5.51–5.58 (m, 3 H, 3 CH=), 4.88–5.05 (m, 6 H, 3 $CH_2$=), 4.51 (s, 1 H, H-1), 3.70–3.87 (m, 6 H, 3 $CH_2$ allyl), 3.50 (m, 1 H, H-4), 3.40 (m, 1 H, H-3), 3.48–3.38 (m, 2 H, H-5,5′), 3.00 (s, 3 H, $OCH_3$), 1.50–1.80 (m, 2 H, H-2,2′). Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 62.98; H, 8.15.

*General procedure for the acidic hydrolysis of methyl glycofuranosides.*—To a solution of an *O*-allylated methyl pentofuranoside (37.6 mmol) in AcOH (120 mL), was added dropwise 6 N HCl (20 mL) at 65°C. After completion of the reaction (TLC), the mixture was diluted with $CH_2Cl_2$, neutralized with $Na_2CO_3$, and extracted with $CH_2Cl_2$ (3 × 50 mL). After concentration under reduced pressure, the residue was purified by chromatography over silica gel to give the corresponding *O*-allylated pentofuranose:

*2,3,5-Tri-*O*-allyl-*D*-ribofuranose* (**2**).—Yield 89%; $R_f$ 0.50 (solvent *F*); $[\alpha]_D$ + 4.8° (*c* 1.17, $CHCl_3$), $^1$H NMR: δ 5.84–6.06 (m, 3 H, 3 CH=), 5.17–5.37 (m, 6 H, 3 $CH_2$=), 4.15 (ddd, 1 H, $J_{4,5}$ 3.5 and $J_{4,5'}$ 5.2 Hz, H-4), 4.04–4.10 (m, 6 H, 3 $CH_2$ allyl), 4.00 (dd, 1 H, $J_{3,4}$ 5.4 Hz, H-3), 3.94 (dd, 1 H, and $J_{2,3}$ 7.7 Hz, H-2), 3.79 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1), 3.59 (dd, 1 H, $J_{5,5'}$ 10.8 Hz, H-5), 3.46 (dd, 1 H, H-5′). Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 61.94; H, 7.90.

*2,3,5-Tri-*O*-allyl-*D*-arabinofuranose* (**3**).—Yield 88%; $R_f$ 0.62 (solvent *F*); $[\alpha]_D$ + 12.37° (*c* 0.7, $CHCl_3$), $^1$H NMR: δ 5.90–6.12 (m, 3 H, 3 CH=), 5.20–5.30 (m, 6 H, 3 $CH_2$=), 4.50 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.06–4.13 (m, 6 H, 3 $CH_2$ allyl), 4.10 (m, 1 H, H-4), 3.90 (dd, 1 H, $J_{2,3}$ 6.8 Hz, H-2), 3.80 (dd, 1 H, $J_{3,4}$ 7.2 Hz, H-3), 3.40 (m, 2 H, H-5,5′). Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 61.83; H, 8.10.

*2-Deoxy-3,5-di-*O*-allyl-*D*-erythro-pentofuranose* (**5**).—Yield 74%; $R_f$ 0.25 (solvent *F*); $[\alpha]_D$ + 31.73° (*c* 2.61, $CHCl_3$); $^1$H NMR: δ 5.55–5.60 (m, 3 H, 3 CH=), 4.55–5.13 (m, 6 H, 3 $CH_2$=), 3.85 (m, 1 H, H-4), 3.73–3.92 (m, 6 H, 3 $CH_2$ allyl), 3.70 (m, 1 H, H-3), 3.59 (s, 1 H, H-1), 3.45 (m, 1 H, H-5′), 3.40 (m, 1 H, H-5), 2.01 (m, 1 H, H-2), 1.70 (m, 1 H, H-2′). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.67; H, 8.46. Found: C, 61.25; H, 8.35.

*General procedure for the oxidation of pentofuranose derivatives* **2–5** *to lactones* **7–10**.—To a solution of **2**, **3**, **5**, or **4** (ref 18) (5 mmol) in $CH_2Cl_2$ (40 mL) were added 3A molecular sieves (1.35 g) and 4-methylmorpholine *N*-oxide (878 mg, 7.5 mmol). After stirring at room temperature for 10 min, TPAP (87 mg, 0.25 mmol)

was added. After completion of the reaction (TLC, solvent *C*; see Table 2), the product was extracted as for **6**. Three new lactones were characterized as follows:

*2,3,5-Tri*-O-*allyl*-D-*ribono-1,4-lactone* (**7**).—$R_f$ 0.60 (solvent *F*). $^1$H NMR: δ 5.71–5.98 (m, 3 H, 3 CH=), 5.12–5.36 (m, 6 H, 3 $CH_2$=), 4.50 (m, 1 H, $J_{4,5}$ 2.7 and $J_{4,5'}$ 6.4 Hz, H-4), 4.39 (m, 1 H $J_{2,3}$ 5.4 Hz, H-2), 4.36 (m, 1 H, $J_{3,4}$ 4.7 Hz, H-3), 3.92–4.24 (m, 6 H, 3 $CH_2$ allyl), 3.61 (m, 2 H, $J_{5,5'}$ 11.1 Hz, H-5,5'). Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.69; H, 7.46. Found: C, 62.60; H, 7.57.

*2,3,5-Tri*-O-*allyl*-D-arabino-*1,4-lactone* (**8**).—$R_f$ 0.62 (solvent *F*); $^1$H NMR: δ 5.62–5.82 (m, 3 H, 3 CH=), 4.96–5.20 (m, 6 H, 3 $CH_2$=), 4.30 (dd, 1 H, $J_{5,5'}$ 12.1 Hz, H-5), 4.20 (dd, 1 H, H-5'), 4.00–4.10 (m, 6 H, 3 $CH_2$ allyl), 3.98 (m, 1 H, H-3), 3.85 (d, 1 H, $J_{2,3}$ 1.2 Hz, H-2), 3.65 (dd, 1 H, $J_{4,5}$ 5.4 and $J_{4,5'}$ 3.7 Hz, H-4). Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.69; H, 7.46. Found: C, 62.54; H, 7.65.

*2-Deoxy-3,5-di*-O-*allyl*-D-erythro-*pentono-1,4-lactone* (**10**).—$R_f$ 0.57 (solvent *F*); $^1$H NMR: δ 5.71–5.86 (m, 2 H, 2 CH=), 5.11–5.25 (m, 4 H, 2 $CH_2$=), 4.51 (m, 1 H, H-4), 4.33 (dd, 1 H, $J_{5,5'}$ 12.4 Hz, H-5), 4.23 (dd, 1 H, H-5'), 4.16 (m, 1 H, H-3), 3.91–3.96 (m, 4 H, 2 $CH_2$ allyl), 2.8 (dd, 1 H, $J_{2,2'}$ 18.1 and $J_{2',3}$ 6.8 Hz, H-2'), 2.5 (dd, 1 H, $J_{2,3}$ 1.9 Hz, H-2). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.26; H, 7.55. Found: C, 62.24; H, 7.62.

*Methyl 3,4,6-tri*-O-*benzyl-2-deoxy*-α-D-arabino-*hexopyranoside* (**12**).—Triphenylphosphine hydrobromide (85 mg, 0.25 mmol) was added to a solution of 3,4,6-tri-*O*-benzyl-D-glucal [23] (2.08 g, 5 mmol) in $CH_2Cl_2$ (20 mL) containing anhyd MeOH (305 μL, 7.5 mmol). The reaction was complete after stirring for 3 h at room temperature. The mixture was treated with satd aq $NaHCO_3$ (2 mL) and extracted with $CH_2Cl_2$ (15 mL). The organic layer was washed with $H_2O$ (2 × 10 mL), dried ($MgSO_4$), and evaporated to give **12** as an oil (2.156 g, 97%); $R_f$ 0.58 (solvent *A*); $[\alpha]_D$ +50.3° (*c* 0.9, $CH_2Cl_2$); $^1$H NMR: δ 7.35 (m, 15 H, 3 Ph), 4.52–4.90 (m, 6 H, 3 $CH_2$Ph), 4.64 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 3.97 (ddd, 1 H, $J_{4,5}$ 11.4, $J_{5,6}$ 8.5 and $J_{5,6'}$ 5 Hz, H-5), 3.70 (m, 4 H, H-3,4,6,6'), 3.32 (s, 3 H, $OCH_3$), 2.29 (ddd, 1 H, $J_{2,2'}$ 13, $J_{2',3}$ 5 and $J_{1,2'}$ 1 Hz, H-2'), 1.73 (ddd, 1 H, $J_{2,3}$ 11.5 Hz, H-2). Anal. Calcd for $C_{28}H_{32}O_5$: C, 74.98; H, 7.19. Found: C, 74.59; H, 7.19.

*3,4,6-Tri*-O-*benzyl-2-deoxy*-D-arabino-*hexopyranose* (**13**).—To a solution of **12** (2.15 g, 4.8 mmol) in 1:2 AcOH–$H_2O$ (64 mL), was added HCl (1 N, 4.8 mL, 4.8 mmol). The sol was refluxed during 5 h. The mixture was extracted with $CH_2Cl_2$ (30 mL) and the organic layer was washed with 5% $NaHCO_3$ and $H_2O$ until neutral pH, then dried ($MgSO_4$) and evaporated. The crude product was crystallized from 3:7 EtOAc–petroleum ether to give **13** as white crystals (1.76 g, 85%); mp 90–92°C; $R_f$ 0.3 (solvent *B*); $[\alpha]_D$ +79.9° (*c* 0.75, $CH_2Cl_2$). $^1$H NMR: δ 7.3 (m, 15 H, 3 Ph), 5.41 (s, 1 H, OH), 4.9 (m, 1 H, H-1), 4.6 (m, 6 H, 3 $CH_2$Ph), 4.04 (m, 1 H, H-5), 3.7 (m, 2 H, H-6,6'), 3.5 (m, 2 H, H-3,4), 2.28 (m, 1 H, H-2'), 1.66 (m, 1 H, H-2). Anal. Calcd for $C_{27}H_{30}O_5$: C, 74.62; H, 6.95. Found: C, 74.21; H, 6.96.

*3,4,6-Tri*-O-*benzyl-2-deoxy*-D-arabino-*hexono-1,5-lactone* (**14**).—Compound **13** (500 mg) was oxidized according to method A to give lactone **14** (378 mg, 76%); mp 83°C (abs EtOH); $R_f$ 0.5 (solvent *A*); $[\alpha]_D$ +48° (*c* 0.65, EtOH); lit. [21] mp 83°C (abs EtOH), $[\alpha]_D$ +48° (EtOH). $^1$H NMR: δ 7.44 (m, 15 H, 3 Ph), 4.69 (m, 6 H, 3 $CH_2$Ph), 4.42 (dd, 1 H, $J_{4,5}$ 7.2 Hz, H-5), 4.04 (m, 2 H, H-3,4), 3.78 (d, 2 H, $J_{5,6}$

3,84 Hz, H-6,6'), 2.93 (dd, 1 H, $J_{2',3}$ 4.3 and $J_{2,2'}$ 16.5 Hz, H-2'), 2.81 (dd, 1 H, $J_{2,3}$ 5.0 Hz, H-2). Anal. Calcd for $C_{27}H_{28}O_5$: C, 74.98; H, 6.52. Found: C 74.48; H, 6.59.

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