Supporting Information

Experimental

Methyl 2,3-*O*-isopropylidene 2-*C*-(methyl)-β-D-erythrofuranoside (8). Tosylate **7** (prepared as described previously : Ho, P.-T. *Tetrahedron Lett.* **1978**, 1623)(1.68 g, 4.7 mmol) was dissolved in a mixture of anhydrous $CHCl_3$ (10 mL) and ether (40 mL). Lithium aluminum hydride (0.64 g) was added and the mixture was heated with stirring at 30 °C for 20 h. Ethyl acetate (3 mL) and water (1.5 mL) were then slowly added to the reaction mixture, the mixture was filtered, and the filtrate was concentrated at 30 °C *in vacuo*. The crude product was purified by silica gel chromatography (1:10 ethyl acetate:hexanes) to give **8** as a syrup (0.70 g, 80% yield). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 112.3, 109.3, 91.1, 86.1, 71.3, 54.5, 27.7, 27.4, 19.6; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.63 (H1), 4.26 (H3), 3.76 (H4, H4'), 3.22 (OCH_3), 1.34, 1.32, 1.29 (CH_3); ES+ $[M+Na]^+$ *m/z* 211.0.

2-*C*-(Methyl)-D-erythrose (9). Compound **8** (0.58 g, 3.1 mmol) was dissolved in a mixture of MeOH (20 mL) and water (10 mL), Dowex HCR-W2 (H^+) ion-exchange resin (1.0 g) was added (all ion-exchange resins used in this work were purchased from Sigma Chemical Co. and converted to the indicated ionic forms by standard methods), and the suspension was heated with stirring in an oil bath for 1 h at 80 °C. After cooling the reaction mixture, the resin was removed by filtration and the filtrate concentrated at 30 °C *in vacuo*. The crude residue was purified by chromatography on Dowex 50WX8-400 ion-exchange resin in the Ca^{2+} form to give **9** as a syrup (0.38 g, 92% yield). ^{13}C NMR (75 MHz, D_2O) δ: 103.9, 101.7, 79.5, 77.4, 75.5, 75.2, 72.8, 71.4, 22.8, 19.5; HRMS (FAB+) calcd for $C_5H_{10}O_4Na$ $[M+Na]^+$ 157.0477, found 157.0456.

1-Deoxy-D-xylulose (1-deoxy-D-*threo*-pent-2-ulose) (2). 2-*C*-(Methyl)-D-erythrose (**9**) (0.24 g) was dissolved in H_2O (5 mL) and MoO_3 (10 mg) was added. The mixture was heated at 70 °C for 40 min. HPLC (Phenomenex Rezex calcium column, 7.8

x 50 mm, H_2O solvent , 0.6 mL/min, 85 °C, RI detector) indicated that the ratio **2**:**9** was 95:5. The reaction mixture was then cooled to room temperature and deionized with batchwise, consecutive additions of excess Dowex HCR-W2 (H^+) and Dowex 1X8-50 (OAc^-) ion-exchange resins. The resins were removed by filtration and the filtrate concentrated at 30 °C *in vacuo*. The crude residue was purified by chromatography on Dowex 50WX8-400 ion-exchange resin in the Ca^{2+} form to give **2** as a syrup (0.22 g, 95% yield). ^{13}C NMR (75 MHz, D_2O) δ: 214.5, 107.6, 104.2, 82.7, 82.3, 78.7, 77.6, 76.5, 73.0, 71.0, 63.7, 27.3, 25.2, 22.3; HRMS (FAB+) calcd for $C_5H_{10}O_4Na$ $[M+Na]^+$ 157.04773, found 157.04942.

D-Xylulose (D-*threo*-pent-2-ulose) (12). Compound **5** (prepared as described previously : Ho, P.-T. *Tetrahedron Lett.* **1978**, 1623)(0.24 g, 1.3 mmol) was dissolved in H_2O (10 mL), Dowex 50 H^+ resin (1.0 g) was added, and the suspension was heated with stirring in an oil bath for 1 h at 80 °C. After cooling the reaction mixture, the resin was removed by filtration and the filtrate was concentrated at 30 °C *in vacuo*. The crude residue was purified by chromatography on Dowex 50WX8-400 ion-exchange resin in the Ca^{2+} form to give **10** as a syrup (0.17 g, 89% yield). ^{13}C NMR (75 MHz, D_2O) δ: 103.0, 98.5, 81.9, 80.2, 72.4, 72.0, 71.7, 71.3, 64.7, 63.9; ; HRMS (FAB+) calcd for $C_5H_{10}O_4$ $[M+H-OH]^+$ 134.0579, found 134.0622.

2-*C*-(Hydroxymethyl)-D-erythrose (**10**) (0.17 g, 1.1 mmol) was dissolved in H_2O (5 mL), MoO_3 (10 mg) was added, and the mixture was heated at 70 °C for 3 h. HPLC (see above for conditions) indicated that the ratio **12**:**10** was 85:15. Compound **12** was not isolated, but was identified by HPLC (see above for conditions) by comparison of its retention time to that of an authentic sample.

2-*C*-(Benzyloxymethyl)-D-erythrose (11). Methyl 2,3-*O*-isopropylidene-2-*C*-(hydroxymethyl)-β-D-erythrofuranoside (**6**) (prepared as described previously : Ho, P.-T. *Tetrahedron Lett.* **1978**, 1623)(1.61 g, 7.9 mmol) was dissolved in benzyl chloride (8 mL), KOH pellets (4.0 g) were added, and the suspension was stirred at 100 °C for 3 h. After

cooling to room temperature, the crude product was purified by silica gel chromatography (1:4 ethyl acetate:hexanes) to give methyl 2,3-*O*-isopropylidene-2-*C*-(benzyloxymethyl)-β-D-erythrofuranoside as an oil (1.4 g, 60% yield). ^{13}C NMR (75 MHz, D_2O) δ: 138.1, 128.0, 127.4, 127.3, 113.5, 108.6, 93.5, 82.4, 73.3, 71.7, 68.9, 54.5, 27.6; HRMS (FAB+) calcd for $C_{16}H_{21}O_5$ $[M-H]^+$ 293.13892, found 293.14082.

Methyl 2,3-*O*-isopropylidene-2-*C*-(benzyloxymethyl)-β-D-erythrofuranoside (0.42 g, 1.4 mmol) was suspended in dilute H_2SO_4 (0.1% v/v, 20 mL) and the solution was heated at reflux for 12 h. After cooling, the reaction mixture was deionized with batchwise addition of excess Dowex 1X8-50 (HCO_3^-) ion-exchange resin. The resin was removed by filtration and the filtrate was concentrated at 30 °C *in vacuo*. The crude product was purified by chromatography on Dowex 50WX8-400 ion-exchange resin in the Ca^{2+} form to give **11** as a syrup (0.25 g, 75% yield). ^{13}C NMR (75 MHz, D_2O) δ: 138.9, 138.7, 130.2, 129.9, 129.7, 102.9, 98.6, 81.6, 79.6, 75.0, 74.9, 72.7, 72.4, 72.3, 72.1, 71.6, 71.5; HRMS (FAB+) calcd for $C_{12}H_{16}O_5Na$ $[M+Na]^+$ 263.08960, found 263.08984.

1-*O*-Benzyl-D-xylulose (1-*O*-benzyl-D-*threo*-pent-2-ulose) (13). 2-*C*-(Benzyloxymethyl)-D-erythrose (**11**) (0.25 g, 1.0 mmol) was dissolved in H_2O (5 mL), MoO_3 (10 mg) was added, and the mixture was heated at 70 °C for 3 h. HPLC (see above for conditions) indicated that the ratio **13**:**11** was 88:12. After cooling to room temperature, the reaction mixture was deionized with batchwise, consecutive additions of excess Dowex HCR-W2 (H^+) and Dowex 1X8-50 (OAc^-) ion-exchange resins. The resins were removed by filtration and the filtrate was concentrated at 30 °C *in vacuo*. The crude residue was purified by chromatography on Dowex 50WX8-400 ion-exchange resin in the Ca^{2+} form to give **13** as a syrup (0.15 g, 62% yield). ^{13}C NMR (75 MHz, D_2O) δ: 212.3, 138.8, 138.7, 138.0, 130.3, 130.2, 130.1, 130.0, 129.9, 129.8, 106.9, 104.0, 82.0, 78.3, 77.3, 77.0, 76.3, 74.9, 74.7, 74.5, 73.6, 73.4, 72.4, 71.7, 71.4, 63.4; HRMS (FAB+) calcd for $C_{12}H_{16}O_5Na$ $[M+Na]^+$ 263.08960, found 263.08728.