SUPPLEMENTARY INFORMATION

Selective Biocatalytic Deacylation Studies on Furanose Triesters: A Novel and Efficient Approach Towards Bicyclonucleosides[1]

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The characterization data of the compounds **2b-c**, **3b-c** and **9b-d** have been disclosed here.

3,5-Di-*O*-propanoyl-1,2-*O*-(1-methylethylidene)-4-*C*-propanoyloxymethyl-*β*-L-*threo*-pentofuranose (2b): It was obtained as a colorless oil (2.8 g; 80 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.91 (d, J = 4.0 Hz, 1H), 5.30 (s, 1H), 4.53 (dd, J = 1.0 and 4.0 Hz, 1H), 4.31-4.18 (m, 3H), 4.02 (d, J = 11.6 Hz, 1H), 2.33-2.23 (m, 6H), 1.53 (s, 3H), 1.26 (s, 3H), 1.10-1.03 (m, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 172.66, 172.56, 171.68, 112.53, 104.24, 84.84, 76.23, 62.23, 61.46, 28.67, 26.47, 26.33, 25.78, 25.34, 8.00, 7.93, 7.87; IR (thin film) 2985, 2945, 1746, 1462, 1423, 1381, 1164, 1082, 1019, 882, 808 cm^{-1}; HRMS *m/z* calculated for $[C_{18}H_{28}O_9Na]^+$ 411.1631, observed 411.1652.

4-*C*-Butanoyloxymethyl-3,5-di-*O*-butanoyl-1,2-*O*-(1-methylethylidene)-*β*-L-*threo*-pentofuranose (2c): It was obtained as a colorless oil (3.2 g; 82 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.97 (d, J = 3.9 Hz, 1H), 5.35 (s, 1H), 4.58 (d, J = 3.9 Hz, 1H), 4.32 (d, J = 7.8 Hz, 1H), 4.29 (d, J = 7.8 Hz, 1H), 4.27 (d, J = 11.6 Hz, 1H), 4.07 (d, J = 11.6 Hz, 1H), 2.34-2.27 (m, 6H), 1.68-1.60 (m, 9H), 1.33 (s, 3H), 0.98-0.91 (m, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 173.23, 173.15, 172.26, 113.91, 105.61, 86.25, 86.14, 77.60, 63.53, 62.83, 36.41, 36.29, 36.18, 36.06, 27.15, 26.71, 18.66, 18.60, 13.95; IR (thin film) 2967,

2878, 1745, 1461, 1418, 1383, 1305, 1250, 1165, 1078, 1016, 862 cm^{-1}; HRMS *m/z* calculated for $[C_{21}H_{34}O_9Na]^+$ 453.2101, observed 453.2133.

3,5-Di-*O*-propanoyl-4-*C*-hydroxymethyl-1,2-*O*-(1-methylethylidene)-α-D-*xylo*-pentofuranose (3b): It was obtained as a colorless oil (876 mg; 88 %). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.91 (d, J = 3.74 Hz, 1H), 5.22 (s, 1H), 4.56 (brs, 1H), 4.18 (d, J = 11.4 Hz, 1H), 4.04 (d, J = 11.4 Hz, 1H), 3.75 (d, J = 11.8 Hz, 1H), 3.65 (d, J = 11.8 Hz, 1H), 2.28-2.26 (m, 5H), 1.50 (s, 3H), 1.26 (s, 3H), 1.09-1.04 (m, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 172.79, 172.09, 112.32, 103.88, 86.93, 85.00, 76.33, 61.67, 61.17, 28.68, 26.36, 25.92, 25.40, 8.02, 7.85; IR (thin film) 3506, 2984, 2943, 1745, 1462, 1380, 1351, 1325, 1263, 1164, 1079, 1018, 882 cm^{-1}; HRMS *m/z* calculated for $[C_{15}H_{24}O_8Na]^+$ 355.1369, observed 355.1367.

3,5-Di-*O*-butanoyl-4-*C*-hydroxymethyl-1,2-*O*-(1-methylethylidene)-α-D-*xylo*-pentofuranose (3c): It was obtained as a colorless oil (1.0 g; 93 %). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.90 (d, J = 4.1 Hz, 1H), 5.22 (s, 1H), 4.57-4.55 (m, 1H), 4.18 (d, J = 11.4 Hz, 1H), 4.02 (d, J = 11.4 Hz, 1H), 3.74 (d, J = 11.9 Hz, 1H), 3.66 (d, J = 11.9 Hz, 1H), 2.40 (brs, 1H), 2.26-2.20 (m, 4H), 1.61-1.53 (m, 4H), 1.51 (s, 3H), 1.26 (s, 3H), 0.88 (t, J = 7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 172.03, 171.34, 112.35, 103.88, 86.85, 85.19, 76.37, 61.65, 61.25, 35.09, 34.86, 28.69, 25.95, 25.45, 17.35, 17.23,12.62; IR (thin film) 3435, 2927, 2360, 1742, 1381, 1163, 1076 cm^{-1}; HRMS *m/z* calculated for $[C_{17}H_{28}O_8Na]^+$ 383.1682, observed 383.1660.

3-*O*-Acetyl-4-*C*-acetoxymethyl-5-*O*-butanoyl-1,2-*O*-(1-methylethylidene)-β-L-*arabino*-pentofuranose (9b): It was obtained as a viscous oil (462 mg; 94 %). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.98 (d, J = 3.9 Hz, 1H), 5.35 (s, 1H), 4.61 (d, J = 3.9 Hz, 1H), 4.35 (d, J = 11.5 Hz, 1H), 4.28 (t, J = 11.2 Hz, 2H), 4.08 (d, J = 11.6 Hz, 1H), 2.32 (t, J = 7.4 Hz, 2H), 2.11 (s, 3H), 2.07 (s, 3H), 1.64 (m, 2H), 1.60 (s, 3H), 1.33 (s, 3H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 173.2, 170.56, 169.62, 113.80, 105.59, 86.00, 77.07, 63.28, 62.82, 36.23, 27.02, 26.56, 21.11, 20.94, 18.61, 13.90, 13.74; IR (thin film) 2993, 2948,

1751, 1736, 1461, 1432, 1391, 1373, 1235, 1166, 1117, 1079, 1026, 903, 851 cm^{-1}; HRMS *m/z* calculated for $[C_{17}H_{26}O_9Na]^+$ 397.1469, observed 397.1466.

3-*O*-Acetyl-4-*C*-acetoxymethyl-1,2-*O*-(1-methylethylidene)-5-*O*-pentanoyl-*β*-L-*arabino*-pentofuranose (9c): It was obtained as a viscous oil (474 mg; 93 %). ^1H NMR ($CDCl_3$, 300 MHz): δ 5.97 (d, J = 3.5 Hz, 1H), 5.60 (s, 1H), 4.60 (d, J = 2.8 Hz, 1H), 4.35-4.25 (m, 3H), 4.08 (d, J = 11.6 Hz, 1H), 2.34 (t, J = 7.5 Hz, 2H), 2.10 (s, 3H), 2.07 (s, 3H), 1.60 (br s, 5H), 1.33 (m, 5H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 173.58, 170.74, 169.78, 113.01, 105.78, 86.22, 77.86, 63.53, 63.04, 34.27, 34.17, 27.35, 27.24, 26.77, 22.69, 21.41, 21.13, 14.17; IR (thin film) 2993, 2948, 1751, 1736, 1461, 1432, 1391, 1373, 1235, 1166, 1117, 1079, 1026, 903, 851 cm^{-1}; HRMS *m/z* calculated for $[C_{18}H_{28}O_9Na]^+$ 411.1626, observed 411.1615.

3-*O*-Acetyl-4-*C*-acetoxymethyl-5-*O*-benzoyl-1,2-*O*-(1-methylethylidene)-*β*-L-*arabino*-pentofuranose (9d): It was obtained as a viscous oil (504 mg; 94 %). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.03 (d, J = 7.5 Hz, 2H), 7.54 (d, J = 7.1, 1H), 7.44 (d, J = 7.6 Hz, 2H), 6.02 (d, J = 3.5 Hz, 1H), 5.51 (s, 1H), 4.65-4.54 (m, 3H), 4.34 (d, J = 11.6 Hz, 1H), 4.21 (d, J = 11.6 Hz, 1H), 2.12 (s, 3H), 2.05 (s, 3H), 1.61 (s, 3H), 1.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 169.00, 168.00, 164.00, 132.05, 128.55, 127.24, 112.23, 104.17, 84.79, 84.40, 76.09, 62.42, 61.40, 25.47, 24.87, 19.56, 19.40; IR (thin film) 2993, 2948, 1751, 1736, 1461, 1432, 1391, 1373, 1235, 1166, 1117, 1079, 1026, 903, 851 cm^{-1}; HRMS *m/z* calculated for $[C_{20}H_{24}O_9Na]^+$ 431.1313, observed 431.1294.