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Synthesis of glycoprotein N-chain core fragment GlcNAcβ1-4(Fucα1-6)GlcNAc

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Spectral characteristics of oligosaccharides.

^{1}H NMR spectra were recorded on a Bruker AVANCE spectrometer at 303K. Chemical shifts δ for characteristic protons are given in ppm with the use of HOD (4.750), $CHCl_3$ (δ 7.270), or CHD_2OD (δ 3.500) as reference and coupling constants J, in Hz. The signals in ^{1}H NMR spectra were assigned using a technique of spin–spin decoupling (double resonance) and 2D-^{1}H,^{1}H- COSY experiments. The values of optical rotation were measured on a digital polarimeter Perkin Elmer 341 at 25°C. Mass spectra were measured on a MALDI-TOF Vision-2000 spectrometer using dihydroxybenzoic acid as a matrix.

5: ^{1}H NMR (700 MHz, $CDCl_3$-CD_3OH, 3:1): 1.892 – 2.014 (m, 2H, CH_2 sp); 2.069, 2.080, 2.148, 2.160, 2.184 and 2.225 (6s, 6 x 3H, $NCOCH_3$); 3.373-3.426 and 3.578 – 3.632 (2m, 2 x 1H, NCH_2 sp); 3.651-3.700 (m, 1H, OCH sp); 3.800 (dd, 1H, H-6’’a, $J_{5,6''}$ 3.5, $J_{6',6''}$ 12.3); 3.852 (ddd, 1H, H-5b, $J_{5,6'}$ 2.2, $J_{5,6''}$ 4.1, $J_{4,5}$ 10.1); 3.933-4.057 (m, 6H, OCH sp, H-2b, H-2a, H-4a, H-5a, H-6’a); 4.176 (dd, 1H, H-6’b, $J_{5,6'}$ 2.1, $J_{6',6''}$ 12.3); 4.512-4.550 (m, 2H, H-1b, H-6’’b); 4.799 (d, 1H, H-1a, $J_{1,2}$ 8.4); 5.131-5.180 (m, 2H, H-3a, H-4b); 5.317 (dd, 1H, H-3b, $J_{2,3}$ 10.4, $J_{3,4}$ 9.4). R_f 0.37 (chloroform–methanol, 6:1). MS m/z calculated for $C_{29}H_{42}F_3N_3O_{16}$ [M^-]: 746; found: 746.

6: ^{1}H NMR (800 MHz, D_2O): 1.924-1.988 (m, 2H, CH_2 sp); 2.054 and 2.081 (2s, 2 x 3H, $NCOCH_3$); 3.088 (m ≈ t, 2H, NCH_2 sp, J 7.0); 3.491 (dd, 1H, H-4b, $J_{3,4}$ 8.8, $J_{4,5}$ 9.8); 3.496-3.545 (m, 2H, H-5a, H-5b); 3.580 (dd, 1H, H-3b, $J_{3,4}$ 8.8, $J_{2,3}$ 10.3); 3.615 (dd, 1H, H-4a, $J_{3,4}$ 8.3, $J_{4,5}$ 9.6); 3.676 (dd, 1H, H-6’’a, $J_{5,6''}$ 5.6, $J_{6',6''}$ 12.1); 3.692-3.774 (m, 5H, OCH sp, H-2a, H-3a, H-2b, H-6’’b); 3.869 (dd, 1H,H-6’a, $J_{5,6'}$ 2.0, $J_{6',6''}$ 12.1); 3.930 (dd, 1H, H-6’b, $J_{5,6'}$ 2.1, $J_{6',6''}$ 12.3); 4.006-4.038 (m, 1H, OCH sp); 4.501 (d, 1H, H-1a, $J_{1,2}$ 8.1); 4.594 (d, H-1b, $J_{1,2}$ 8.5). R_f 0.55 (methanol–1 M aq. Py•AcOH, 5:1). $[\alpha]_{546}$ -31.6 (c 0.5, H_2O). MS, m/z calculated for $C_{19}H_{35}N_3O_{11}$ [M^-]: 481; found: 481.

7: ^{1}H NMR (700 MHz, D_2O): 1.934-2.029 (m, 2H, CH_2 sp); 2.064 and 2.118 (2s, 2 x 3H, $NCOCH_3$); 3.128 (m ≈ t, 2H, NCH_2 sp, $J_{6,8}$); 3.501 (dd, 1H, H-4b, $J_{3,4}$ 9.1, $J_{4,5}$ 9.5); 3.551 (ddd, 1H, H-5b, $J_{5,6'}$ 2.0,

$J_{5,6''}$ 5.5, $J_{4,5}$ 9.5); 3.590 (dd, 1H, H-3b, $J_{3,4}$ 9.2, $J_{2,3}$ 10.1); 3.699-3.826 (m, 7H); 3.944 (dd, 1H, H-6'b, $J_{5,6'}$ 1.9, $J_{6',6''}$ 12.3); 3.977-4.041 (m, 1H, OCH sp); 4.168 (dd, 1H, H-6''a, $J_{5,6''}$ 3.3, $J_{6',6''}$ 11.0);4.314 (dd ≈ d, 1H, H-6'a, J 10.7); 4.546 (d, 1H, H-1a, $J_{1,2}$ 8.4); 4.645 (d, H-1b, $J_{1,2}$ 8.5). R_f 0.53 (isopropanol–acetonitrile–water, 4:3:2).). $[\alpha]_{546}$ +33.0 (c 0.5, H_2O). MS, m/z calculated for $C_{19}H_{35}N_3O_{14}S$ $[M^-]$: 561; found: 561.

9: ^{1}H NMR (700 MHz, $CDCl_3$): 1.100 (d, 3H, H-6c, $J_{5,6}$ 6.4); 1.734-1.863 (m, 2H, CH_2 sp); 1.892, 1.945, 1.976 (2), 1.984, 2.043, 2.049, 2.098 and 2.141 (9s, 9 x 3H, $NCOCH_3$); 3.192-3.261 and 3.433-3.483 (2m, 2 x 1H, NCH_2 sp); 3.520-3.632 (m, 3H); 3.696-3.758 (m, 2H); 3.767-3.843 (m, 2H); 3.868-3.957 (m, 2H, H-2a, OCH sp); 4.067 (dd ≈ d, 1H, H-6'b, $J_{6',6''}$ 12.2); 4.197 (br. q., 1H, H-5c, J 6.5); 4.363 (dd, 1H, H-6''b, $J_{5,6''}$ 3.9, $J_{6',6''}$ 12.4); 4.404 (d, 1H, H-1b, $J_{1,2}$ 7.7); 4.873 (d, 1H, H-1a, $J_{1,2}$ 8.2); 5.001 (dd ≈ t, 1H, H-4b, J 9.6); 5.059-5.137 (m, 3H, H-3a, H-3c, H-4c); 5.264 (d, 1H, H-1c, $J_{1,2}$ 3.0); 5.313-5.364 (m, 2H, H-3b, H-2c); 5.679 and 5.883 (2d, 2 x 1H, 2 NHAc, $J_{2,NH}$ 8.0); 7.301-7.343 (m, 1H, $NHCOCF_3$). R_f 0.35 (ethyl acetate–isopropanol, 10:1). MS, m/z calculated for $C_{41}H_{58}F_3N_3O_{23}$ $[M^-]$: 1018; found: 1018.

10: ^{1}H NMR (700 MHz, D_2O): 1.251 (d, 3H, H-6c, $J_{5,6}$ 6.6);1.937-1.985 (m, 2H, CH_2 sp); 2.063 and 2.099 (2s, 2 x 3H, $NCOCH_3$); 3.087 (m ≈ t, 2H, NCH_2 sp, J 6.9); 3.462-3.529 (m, 2H, H-4b, H-5b); 3.585 (dd ≈ t, 1H, H-3b, J 9.4); 3.643-3.741 (m, 4H); 3.739-3.790 (m, 4H); 3.802-3.846 (m, 2H, H-2c, H-4c); 3.903-3.965 (m, 3H, H-3c, H-6'a, H-6'b); 4.000-4.044 (m, 1H, OCH sp); 4.123 (br. q., 1H, H-5c, $J_{5,6}$ 6.6); 4.502 (d, 1H, H-1a, $J_{1,2}$ 8.3); 4.657 (d, H-1b, $J_{1,2}$ 8.4); 4.927 (d, 1H, H-1c, $J_{1,2}$ 3.8). R_f 0.52 (methanol–1 M aq. Py•AcOH, 5:1). $[\alpha]_{546}$ -89.6 (c 0.5, H_2O). MS, m/z calculated for $C_{25}H_{45}N_3O_{15}$ $[M^-]$: 627; found: 627.