Electronic Supplementary Information

Synthesis, glycosylation and NMR characterization of linear peracetylated D-galactose glycopolymers

Marco Pocci,* Silvana Alfei, Francesco Lucchesini, Sara Castellaro, Vincenzo Bertini

Dipartimento di Farmacia, Università di Genova
Via Brigata Salerno, 13 I-16147 Genova, Italy

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Table S1. Homopolymerization of 4 in DMF at 60 °C.

<table>
<thead>
<tr>
<th>Run</th>
<th>Monomer (mmol)</th>
<th>AIBN mg (%)</th>
<th>DMF mL</th>
<th>Time h</th>
<th>Polymer g (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4αp</td>
<td>0.188 (0.39)</td>
<td>2.0 (1.1)</td>
<td>48</td>
<td>P4αp 0.163 (87)</td>
</tr>
<tr>
<td>2</td>
<td>4βp</td>
<td>0.916 (1.92)</td>
<td>9.2 (1.0)</td>
<td>48</td>
<td>P4βp 0.839 (92)</td>
</tr>
<tr>
<td>3</td>
<td>4αβp</td>
<td>1.860 (3.90)</td>
<td>18.6 (1.0)</td>
<td>24</td>
<td>P4αβp 0.821 (44)</td>
</tr>
<tr>
<td>4</td>
<td>4αβp</td>
<td>2.18 (4.57)</td>
<td>21.8 (1.0)</td>
<td>50</td>
<td>P4αβp 1.99 (91)</td>
</tr>
<tr>
<td>5</td>
<td>4αβp</td>
<td>2.28 (4.76)</td>
<td>22.9 (1.0)</td>
<td>72</td>
<td>P4αβp 2.01 (88)</td>
</tr>
</tbody>
</table>

AIBN = azobisisobutironitrile; DMF = N,N-dimethylformamide; p = pyranose form; f = furanose form; * as enriched β-pyranose anomer.

Table S2. Typical glycosylation data of 5 with 2 in the presence of SnCl$_4$ or BF$_3$:Et$_2$O in CH$_2$Cl$_2$.

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate mg (mmol)</th>
<th>C μL (mmol)</th>
<th>2 mg (mmol)</th>
<th>5 : C : 2 Molar ratio</th>
<th>6αp mg (mmol)</th>
<th>6βp mg (mmol)</th>
<th>7αβf mg (mmol)</th>
<th>8 mg (mmol)</th>
<th>9βp mg (mmol)</th>
<th>10αβp mg (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5αp</td>
<td>108.2 (0.240)</td>
<td>35 (0.299)</td>
<td>78.3 (0.269)</td>
<td>1:1.3:1.1</td>
<td>41.8 (0.061)</td>
<td>5.2 (0.008)</td>
<td>-</td>
<td>27.2 (0.082)</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>5βp</td>
<td>250.9 (0.556)</td>
<td>70 (0.598)</td>
<td>173.1 (0.594)</td>
<td>1:1.1:1</td>
<td>-</td>
<td>111.0 (0.163)</td>
<td>-</td>
<td>85.5 (0.257)</td>
<td>22.3</td>
</tr>
<tr>
<td>3</td>
<td>5αβf</td>
<td>116.2 (0.257)</td>
<td>35 (0.299)</td>
<td>84.0 (0.299)</td>
<td>1:1.2:1.2</td>
<td>-</td>
<td>-</td>
<td>84.4 (0.124)</td>
<td>7.1 (0.021)</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>5βp</td>
<td>200.3 (0.444)</td>
<td>60 (0.473)</td>
<td>142.6 (0.490)</td>
<td>1:1.1:1.1</td>
<td>-</td>
<td>100.9 (0.148)</td>
<td>-</td>
<td>71.7 (0.215)</td>
<td>2.5</td>
</tr>
<tr>
<td>5</td>
<td>5αβp</td>
<td>122.9 (0.272)</td>
<td>252 (2.042)</td>
<td>95.1 (0.327)</td>
<td>1:1.5:1.2</td>
<td>-</td>
<td>36.9 (0.054)</td>
<td>-</td>
<td>22.9 (0.069)</td>
<td>7.4</td>
</tr>
</tbody>
</table>

C = promoter; * yield percent with respect to 2; $^b$β/α = 1.3; $^c$β/α = 2.0; $^d$β/α = 2.2.
Characterization of compounds 7αβf, 8, 9βp, and 10αβp

7αβf. Oil. νmax/cm⁻¹ (neat) 1748 (ester), 1650 (amide).

7βf. δH (300 MHz; CDCl₃, Me₄Si) 1.72-1.89 (m, 4H, H-2”” + H-3””)*, 2.07 (s, 3H, CH₃)*, 2.10 (s, 3H, CH₃), 2.13 (s, 3H, CH₃), 3.49-3.91 (m, 4H, H-6 + H-1””)*, 3.97 (t, 2H, J = 6.1, H-4””)*, 4.25 (dd, 1H, J₁ = 5.7, J₂ = 3.2, H-4), 4.43 (d, 2H, J = 5.6, H-1””)*, 4.98-5.03 (m, 1H, H-3), 5.04-5.09 (m, 2H, H-1 + H-2), 5.33 (dt, 1H, J₁ = 7.1, J₂ = 3.4, H-5), 6.81-6.91 (m, 3H, H-2ᵢv + H-6ᵢv + CH₂NH)*, 7.14-7.22 (m, 2H, H-3ᵢv + H-5ᵢv), 7.25 (bs, 1H, CF₃CONH)*, 7.38-7.53 (m, 3H, H-3”” + H-4”” + H-5””)*, 7.70-7.76 (m, 2H, H-2”” + H-6””)*. *Overlapped with those from 7αf. δC (75.5 MHz, CDCl₃, Me₄Si) 20.68 (CH₃)**, 20.78 (CH₃)**, 20.91 (CH₃)**, 25.88 (C-2”” or C-3””)**, 25.94 (C-2”” or C-3””)**, 41.75 (C-6), 43.37 (C-1””)**, 67.34 (C-1””), 67.54 (C-4””)**, 70.62 (C-5), 76.89 (C-3), 81.33 (C-2), 81.61 (C-4), 105.59 (C-1), 114.87 (C-2ᵢv)**, 115.96 (q, CF₃CO, J_CF = 288)**, 126.89
(C-2'')**, 128.13 (C-4'''), 128.63 (C-3'')**, 129.45 (C-3''')**, 131.65 (C-4''')**, 134.07 (C-1''), 157.10 (q, CF₃CO, JCF = 37)**, 158.86 (C-1''''), 167.54 (CO, amide), 169.80 (CO, ester)**, 170.31 (CO, ester), 171.18 (CO, ester). **Overlapped with those of 7αf or not assignable to the proper anomer.

7αf. δH (300 MHz; CDCl₃, Me₄Si) 1.72-1.89 (m, 4H, H-2''' + H-3''''), 2.07 (s, 3H, CH₃)*, 2.09 (s, 3H, CH₃), 2.11 (s, 3H, CH₃), 3.35-3.45 (m, 1H, H-6), 3.49-3.91 (m, 3H, H-6 + H-1'''), 3.97 (t, 2H, J = 6.1, H-4''''), 4.08 (dd, 1H, J₁ = 6.5, J₂ = 5.2, H-4), 4.43 (d, 2H, J = 5.6, H-1'''), 5.14-5.17 (m, 1H, H-5), 5.21 (d, 1H, J = 4.7, H-1), 5.56 (dd, 1H, J₁ = 7.2, J₂ = 6.5, H-3), 6.81-6.91 (m, 3H, H-2'''' + H-6'''' + CH₂NH)*, 7.14-7.22 (m, 2H, H-3'''' + H-5'''''), 7.25 (bs, 1H, CONH)*, 7.38-7.53 (m, 3H, H-3'''' + H-4'''' + H-5''), 7.70-7.76 (m, 2H, H-2'''' + H-6''). **Overlapped with those from 7βf.

The H-2 signal around 5.0 ppm is hidden under H-3 from the β-anomer (DQF-COSY). δC (75.5 MHz, CDCl₃, Me₄Si) 20.54 (CH₃), 20.67 (CH₃)**, 20.78 (CH₃)**, 20.91 (CH₃)**, 25.88 (C-2'''' or C-3'''')**, 25.94 (C-2'''' or C-3'''')**, 41.08 (C-6), 43.37 (C-1'''), 67.54 (C-4'''')**, 68.18 (C-1''), 71.80, 73.91, 76.46, 78.91, 99.68 (C-1), 114.87 (C-2'''')**, 115.96 (q, CF₃CO, JCF = 288)**, 126.89 (C-2'''), 128.06 (C-4'''), 128.63 (C-3'''), 129.45 (C-3''')**, 131.65 (C-4'''')**, 134.07 (C-1'''), 157.10 (q, CF₃CO, JCF = 37), 158.86 (C-1''''), 167.49 (CO, amide), 169.80 (CO, ester)**, 170.37 (CO, ester), 171.27 (CO, ester). **Overlapped with those of 7βf or not assignable to the proper anomer.

8. Mp 65-66 °C (from Et₂O/pentane/-30 °C). vmax/cm⁻¹ (KBr) 3334 (NH amide), 1716 (ester + amide). δH (300 MHz; CDCl₃, Me₄Si) 1.73-1.89 (m, 4H), 2.05 (s, 3H, CH₃), 3.98 (t, 2H, J = 5.9), 4.13 (t, 3H, J = 6.2), 4.45 (d, 2H, J = 5.7), 5.64 (bs, 1H, NH), 6.84-6.91 (m, 2H), 7.17-7.23 (m, 2H). δC (75.5 MHz, CDCl₃, Me₄Si) 20.95, 25.40, 25.84, 43.47, 64.11, 67.42, 114.96, 115.93 (q, JCF = 288), 128.04, 129.48, 157.06 (q, JCF = 37), 158.97, 171.25. m/z (CI) 334 (M⁺+1, 20%), 221 (100).

Anal. calcd for C₁₅H₁₉F₃NO₄: C, 54.05; H, 5.44; N, 4.20. Found: C, 54.26; H, 5.77; N, 4.06.
$9\beta p$. $[\alpha]_D^{22} = +17.2$ (c 0.255, CHCl$_3$). $\nu_{\text{max}}$/cm$^{-1}$ (KBr) 3375 (NH + OH), 1751 (ester), 1646 (amide). 
$\delta_H$ (300 MHz; CDCl$_3$, Me$_4$Si) 2.07 (s, 3H, $CH_3\beta$), 2.19 (s, 3H, $CH_3\alpha$), 2.20 (s, 3H, $CH_2\beta$), 2.65 (bs, 1H, OH), 3.47-3.70 (m, 2H, H-6), 3.92-4.06 (m, 2H, H-2 + H-5), 5.02 (dd, 1H, $J_1 = 3.4, J_2 = 10.2$, H-3), 5.41 (dd, 1H, $J_1 = 0.7, J_2 = 3.4$, H-4), 5.63 (d, 1H, $J = 8.2$, H-1), 6.63 (bt, 1H, $J = 5.6$, NH), 7.38-7.55 (m, 3H, aromatics), 7.72-7.79 (m, 2H, aromatics). $\delta_C$ (75.5 MHz, CDCl$_3$, Me$_4$Si) 20.72 (CH$_3$), 20.98 (3CH$_3$), 39.20 (C-6), 68.35, 68.52, 72.46, 73.03, 94.44 (C-1), 127.03 (C-2"), 128.66 (C-3"), 131.74 (C-4"), 133.92 (C-1"), 167.60 (CO, amide), 169.28 (CO, ester), 170.45 (CO, ester), 170.83 (CO, ester). Anal. calcd for C$_{19}$H$_{23}$NO$_5$: C, 55.74; H, 5.66; N, 3.42. Found: C, 55.64; H, 5.56; N, 3.13.

$10\alpha\beta p$. $\nu_{\text{max}}$/cm$^{-1}$ (KBr): 3390 (NH + OH), 1740 (ester), 1647 (amide). $\delta_H$ (300 MHz; DMSO-$d_6$, Me$_4$Si) 1.88 (s, $CH_3\beta$), 1.91 (s, 3H, $CH_3\alpha$), 2.01 (s, 3H, $CH_3\alpha$), 2.03 (s, 3H, $CH_3\beta$), 2.12 (s, 3H, $CH_3\alpha$), 2.13 (s, 3H, $CH_3\beta$), 3.10-3.29 (m, H-6$\alpha$ + H-6$\beta$), 3.44-3.64 (m, H-6$\alpha$ + H-6$\beta$), 4.12 (bt, 1H, $J = 7.0$, H-5$\beta$), 4.44 (bt, 1H, $J = 7.1$, H-5$\alpha$), 4.78 (dd, 1H, $J_1 = 7.8, J_2 = 6.5$, H-1$\beta$), 4.86-4.97 (m, H-2$\alpha$ + H-2$\beta$), 5.09 (dd, 1H, $J_1 = 10.3, J_2 = 3$, H-3$\beta$), 5.18-5.30 (m, H-1$\alpha$ + H-3$\alpha$ + H-4$\alpha$ + H-4$\beta$), 7.11 (dd, 1H, $J_1 = 4.8, J_2 = 0.9$, OH$\alpha$), 7.19 (d, 1H, $J = 6.5$, OH$\beta$), 7.43-7.56 (m, aromatics), 7.52-7.56 (m, aromatics), 8.45 (bdd, 1H, $J_1 = 7.1, J_2 = 4.1$, NH$\alpha$), 8.56 (bdd, 1H, $J_1 = 6.6, J_2 = 4.8$, NH$\beta$). $\delta_C$ (75.5 MHz; DMSO-$d_6$, Me$_4$Si) 20.31 (CH$_3$), 20.36 (CH$_3$), 20.47(CH$_3$), 20.52 (CH$_3$), 20.55 (CH$_3$), 20.58 (CH$_3$), 38.46 (C-6), 38.56 (C-6), 65.57 ($\alpha$-anomer), 67.15 ($\alpha$-anomer), 67.40 ($\beta$-anomer), 67.68 ($\alpha$-anomer), 68.26 ($\alpha$-anomer), 70.12 ($\beta$-anomer), 70.17 ($\beta$-anomer), 89.36 (C-1$\alpha$), 94.21 (C-1$\beta$), 127.05 (C-2"), 128.18 (C-3"), 131.14 (C-4"$\alpha$), 131.18 (C-4"$\beta$), 134.12 (C-1"$\beta$), 134.21 (C-1"$\alpha$), 166.38 (CO, amide), 169.12 (CO, ester), 169.53 (CO, ester), 169.54 (CO, ester), 169.95 (CO ester).
Figure S1. $^1$H NMR spectrum of 4αp in CDCl$_3$. 
Figure S2. $^{13}$C NMR spectrum of 4ap in CDCl$_3$. 
Figure S3. $^1$H NMR spectrum of 4βp containing small amounts of 4αp, 4αf and 4βf in CDCl₃.
Figure S4. $^{13}$C NMR spectrum of $4\beta p$ containing small amounts of $4\alpha p$, $4\alpha f$ and $4\beta f$ in CDCl$_3$. 
**Figure S5.** $^1$H NMR spectrum of 5αp in CDCl$_3$. 
Figure S6. $^{13}$C NMR spectrum of 5αp in CDCl$_3$. 
Figure S7. $^1$H NMR spectrum of $5\beta p$ in CDCl$_3$. 
Figure S8. $^{13}$C NMR spectrum of 5βp in CDCl$_3$. 
Figure S9. $^1$H NMR spectrum of 6αp in CDCl$_3$. 
Figure S10. $^{13}$C NMR spectrum of 6αp in CDCl$_3$. 
Figure S11. $^1$H NMR spectrum of 6βp in CDCl$_3$. 
Figure S12. $^{13}$C NMR spectrum of $6\beta p$ in CDCl$_3$. 
Figure S13. $^1$H NMR spectrum of $7\alpha\beta f$ in CDCl$_3$. 
Figure S14. $^{13}$C NMR spectrum of 7αβf in CDCl$_3$. 
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Figure S22. $^1$H and $^{13}$C NMR spectra of 12 in CDCl$_3$. 