
**Figure S1.** $^{1}H$ $^{13}C$ NMR HSQC-DEPT spectra of the OS of *B. holmesii* ATCC 51541 and *B. pertussis* 606 [overlay spectrum]; *Resonances placed in frames indicate variants of the residue F →3,4)-L-α-D-Hepp-(1→ in different environment; The remaining resonances of the initially identified residue G ($\delta_{H1}/\delta_{C1}$ 4.95/96.9) and ($\delta_{H2}/\delta_{C2}$ 3.85/73.4) were not resolved from those of residue F.

**Table S1.** $^{1}H$ $^{13}C$ NMR chemical shifts of the core oligosaccharides of *B. pertussis 606* and *B. holmesii* ATCC 51541 *

| Residue | Strain | Chemical Shifts (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | **H-1** | **H-2** | **H-3** | **H-4** | **H-5** | **H-6, H-6′** | **H-7** | **H-8, H-8′** |
| | | **C-1** | **C-2** | **C-3** | **C-4** | **C-5** | **C-6** | **C-7** | **C-8** |
| **Kdo** →4,7)-anhKdo*f* | Bp606 | | | 3.12 | 4.38 | 4.02 | 4.13 | 3.89 | 3.66, 3.60 |
| | | | 203.1 | 42.9 | 77.4 | 83.8 | 75.4 | 83.6 | 61.1 |
| | Bhol | | | 3.12 | 4.39 | 4.02 | 4.14 | 3.89 | 3.66, 3.60 |
| | | | 202.9 | 42.8 | 77.4 | 83.8 | 75.4 | 83.7 | 61.1 |
| **Kdo′** →4,7)-anhKdo*f* | Bp606 | | | 3.11 | 4.50 | 4.12 | 4.08 | 3.74 | 3.67, 3.58 |
| | | | 203.3 | 39.1 | 75.7 | 80.2 | 74.7 | 84.8 | 61.8 |
| | Bhol | | | 3.09 | 4.51 | 4.12 | 4.08 | 3.74 | 3.67, 3.58 |
| | | | 203.2 | 38.8 | 75.8 | 80.2 | 74.7 | 84.8 | 61.8 |
| **A** →4)-α-Glc*p*N-(1→ | Bp606 | 5.47 | 3.31 | 3.94 | 3.63 | 3.73 | 3.78, 3.73 | | |
| | | 97.4 | 54.5 | 70.3 | 74.9 | 71.9 | 60.5 | | |
| | Bhol | 5.48 | 3.33 | 3.94 | 3.63 | 3.74 | 3.78 | 3.73 | |
| | | 97.3 | 54.5 | 70.3 | 74.9 | 71.9 | 60.5 | | |
| **B** →2,7)-L-α-D-Hep*p*-(1→ | Bp606 | 5.38 | 3.86 | 3.90 | 3.84 | 3.46 | 4.18 | 3.70 | |
| | | 99.7 | 79.9 | 70.5 | 66.6 | 72.2 | 68.0 | 70.3 | |
| | Bhol | 5.39 | 3.85 | 3.91 | 3.84 | 3.45 | 4.17 | 3.70 | |
| | | 99.7 | 79.8 | 70.4 | 66.5 | 72.1 | 67.9 | 70.3 | |
| **C** L-α-D-Hep*p*-(1→ | Bp606 | 5.27 | 3.96 | 3.64 | 3.78 | 3.55 | 3.90 | 3.65, 3.62 | |
| | | 101.2 | 70.1 | 70.3 | 65.8 | 72.5 | 68.5 | 62.5 | |
| | Bhol | 5.27 | 3.96 | 3.74 | 3.81 | 3.54 | 3.94 | 3.62 | |
| | | 101.2 | 70.1 | 70.5 | 65.9 | 72.5 | 68.5 | 62.7 | |
| **D** α-Gal*p*NA-(1→ | Bp606 | 5.16 | 3.44 | 4.03 | 4.15 | 4.33 | | | |
| | | 94.5 | 50.5 | 66.7 | 69.7 | 72.3 | 175.1 | | |
| | Bhol | 5.17 | 3.47 | 4.04 | 4.16 | 4.33 | | | |
| | | 94.4 | 50.5 | 66.7 | 69.7 | 72.3 | 175.1 | | |
| **E** α-Glc*p*N-(1→ | Bp606 | 5.12 | 3.28 | 3.85 | 3.45 | 3.70 | 3.78, 3.72 | | |
| | | 96.0 | 54.1 | 69.8 | 69.4 | 72.2 | 60.2 | | |
| | Bhol | 5.12 | 3.28 | 3.86 | 3.44 | 3.70 | 3.78, 3.72 | | |
| | | 96.0 | 54.1 | 69.8 | 69.4 | 72.2 | 60.2 | | |
| **F** →3,4)-L-α-D-Hep*p*-(1→ | Bp606 | 5.07 | 3.90 | 3.84 | 4.23 | 3.54 | 3.95 | 3.67, 3.65 | |
| | | 97.7 | 73.5 | 79.9 | 71.7 | 71.3 | 68.9 | 62.7 | |
| | Bhol | 5.07 | 3.90 | 3.84 | 4.23 | 3.53 | 3.93 | 3.67, 3.65 | |
| | | 97.8 | 73.3 | 76.7 | 71.7 | 71.4 | 68.9 | 62.7 | |
| **H** α-Glc*p*A-(1→ | Bp606 | 4.97 | 3.52 | 3.69 | 3.39 | 4.04 | | | |
| | | 101.0 | 71.9 | 71.6 | 72.3 | 73.8 | 176.6 | | |
| | Bhol | 4.99 | 3.52 | 3.68 | 3.39 | 4.03 | | | |
| | | 101.0 | 71.9 | 71.6 | 72.3 | 73.8 | 176.6 | | |
| **I*** α-Glc*p*A-(1→ | Bp606 | 4.96 | 3.51 | 3.67 | 3.37 | 4.01 | | | |
| | | 101.1 | 72.1 | 71.5 | 72.2 | 73.8 | 176.7 | | |
| | Bhol | 4.95 | 3.52 | 3.67 | 3.38 | 4.01 | | | |
| | | 101.2 | 72.1 | 71.6 | 72.2 | 73.9 | 176.7 | | |

| Residue | Strain | Chemical Shifts (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | **H-1** | **H-2** | **H-3** | **H-4** | **H-5** | **H-6, H-6′** | **H-7** | **H-8, H-8′** |
| | | **C-1** | **C-2** | **C-3** | **C-4** | **C-5** | **C-6** | **C-7** | **C-8** |
| **J** →4,6)-β-Glc*p*-(1→ | Bp606 | 4.39 | 3.27 | 3.56 | 3.44 | 3.67 | 3.76, 3.89 | | |
| | | 101.4 | 73.4 | 76.4 | 78.9 | 72.9 | 67.2 | | |
| | Bhol | 4.40 | 3.27 | 3.55 | 3.44 | 3.66 | 3.76, 3.89 | | |
| | | 101.4 | 73.4 | 76.4 | 79.0 | 73.0 | 67.3 | | |

* The additional $CH_2$- signals at $\delta_{H1}/\delta_{C1}$ (3.13/40.5 ppm), $\delta_{H1'}/\delta_{C1'}$ (3.18/39.8 ppm) and $\delta_{H2}/\delta_{C2}$ (3.9/60.2 ppm), $\delta_{H2'}/\delta_{C2'}$ (4.09/62.0 ppm) for the *B. pertussis* 606 OS and at $\delta_{H1}/\delta_{C1}$ (3.17/40.0 ppm) and $\delta_{H2}/\delta_{C2}$ (4.07/62.2 ppm) for the *B. holmesii* OS V indicate the presence of phosphoethanolamine in the intact core oligosaccharides of these strains. P-EtN correlations were not resolved and the substitution position is only tentative.

**Table S2.** Selected inter-residue NOE and $^3J_{H,C}$-connectivities from the anomeric atoms of the core oligosaccharide of *B. pertussis* 606

| Residue | Atom H-1/C-1 Connectivities to | | | Inter-Residue |
|---|---|---|---|---|
| | **(ppm)** | **$\delta_C$** | **$\delta_H$** | **Atom/Residue** |
| **A** →4)-α-Glc*p*N-(1→ | 97.4/5.47 | 78.9 | 3.44 | C-4, H-4 of **J** |
| **B** →2,7)-L-α-D-Hep*p*-(1→ | 99.7/5.38 | 79.9 | 3.84 | C-3, H-3 of **F** |
| **C** L-α-D-Hep*p*-(1→ | 101.2/5.27 | 74.9 | 3.63 | C-6, H-6/6′ of **A** |
| **D** α-Gal*p*NA-(1→ | 94.5/5.15 | 67.2 | 3.76/3.89 | C-6, H-6/6′ of **J** |
| **E** α-Glc*p*N-(1→ | 96.0/5.12 | 70.3 | 3.70 | C-7, H-7 of **B** |
| **F**→3,4)-L-α-D-Hep*p*-(1→ | 97.7/5.07 | 83.7 | 4.02 | C-5, H-5 of **Kdo** |
| **H** α-Glc*p*A-(1→ | 101.0/4.97 | 79.9 | 3.86 | C-2, H-2 of **B** |
| **I** α-Glc*p*A-(1→ | 101.1/4.96 | 79.9 | 3.85 | C-2, H-2 of **B** |
| **J**→4,6)-β-Glc*p*-(1→ | 101.4/4.39 | 71.7 | 4.23 | C-4, H-4 of **F** |