

Table S1. ¹H and ¹³C NMR chemical shifts and homonuclear coupling constants of neokestose.

| Residue | Atom number | ¹ H (ppm) | <i>J</i> (Hz) | ¹³ C (ppm) | HMBC correlations |
|----------------|----------------|-------------------------|------------------|--------------------------|----------------------|
| β-Fruf-(2→ | 1a | 3.70 | | 61.04 | |
| | 1b | 3.63 | | - | |
| | 2 | - | | 104.51 | |
| | 3 | 4.14 | 8.5 | 77.62 | |
| | 4 | 4.09 | 8.1 | 75.17 | |
| | 5 | 3.82 | | 81.96 | 75.2 |
| | 6a | 3.75 | | 63.24 | |
| | 6b | 3.66 | | - | 82.0 |
| →6)-α-Glcp-(1→ | 1 | 5.35 | 3.8 | 92.82 | 104.4,73.2,72.3 |
| | 2 | 3.51 | 3.8, 10.0 | 71.82 | |
| | 3 | 3.70 | n.d. | 73.25 | |
| | 4 | 3.47 | 9.8, 9.8 | 70.00 | |
| | 5 | 3.89 | | 72.35 | |
| | 6a | 3.88 | | 61.14 | |
| | 6b | 3.74 | | | |
| →2)-β-Fruf | 1a | 3.61 | | 62.28 | 104.5, 77.1 |
| | 1b | 3.61 | | - | |
| | 2 | - | | 104.51 | |
| | 3 | 4.17 | 8.7 | 77.07 | 62.3 |
| | 4 | 4.015 | 8.9 | 74.76 | 82.1 |
| | 5 | 3.84 | | 82.16 | |
| | 6a | 3.79 | | 63.16 | |
| | 6b | 3.74 | | - | |