**Supplementary information**

**Nematocidal activity of 6-*O*-octanoyl- and 6-*O*-octyl-d-allose against larvae of *Caenorhabditis elegans***. Hirofumi Sakoguchi, Tomoya Shintani, Hironobu Ishiyama, Ryo C. Yanagita, Yasuhiro Kawanami, and Masashi Sato

General remarks

1H- and 13C-NMR spectra were measured on a JEOL JMN-ECA 600 spectrometer; tetramethylsilane (TMS) was used as an internal standard. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on a Waters Xevo G2-XS Tof spectrometer. Optical rotation data were obtained on a JASCO P-1010 polarimeter. Wakogel® C-200 and C-300 (silica gel, Wako Pure Chemical Laboratory, Osaka, Japan) were used for column chromatography. All other chemicals and reagents were purchased from chemical companies and used without further purification.

6-*O*-Octyl-d-allose (**6**)

To a suspension of NaH (19.8 mg, 0.5 mmol, 4 eq., 60% dispersion in mineral oil, washed with *n*-hexane) in THF (100 µL) was added a solution of 1,2-*O*-(1-methylethylidene)-3,5-bis-*O*-(phenylmethyl)-α-d-allofuranose (**8**) [1] (49.8 mg, 0.124 mmol) in THF (830 µL), and the reaction mixture was stirred for 1 h at 0 °C. Then, to the reaction mixture were added 1-bromooctane (23 µL, 0.14 mmol, 1.1 eq.) and 18-Crown-6-ether (17 mg, 0.062 mmol, 0.5 eq.), and the reaction mixture was stirred for 8.5 h at rt. The reaction mixture was quenched with H2O, extracted with EtOAc (10 mL × 3), washed with brine (10 mL), dried over Na2SO4 overnight, filtered, and concentrated *in vacuo*. The resulting residue was purified by medium-pressure column chromatography (silica gel (Wakogel C-200), 30% EtOAc/*n*-hexane) to afford an ether **9** (27.9 mg, 0.0544 mmol, 44%, 71% based on recovered starting material). 1H NMR: (600 MHz, CDCl3, 0.043 M, 298 K) δ 0.88 (3H, t, *J* = 6.9 Hz, H-14), 1.24–1.30 (10H, m, H-9–13), 1.35 (3H, s, H-16), 1.52 (2H, m, H-8), 1.58 (3H, s, H-17), 3.37 (2H, td, *J* = 6.7, 1.7 Hz, H-7), 3.55 (2H, d, *J* = 6.0 Hz, H-6), 3.95 (1H, td, *J* = 8.0, 2.0 Hz, H-5), 4.04 (1H, dd, *J* = 8.6, 4.5 Hz, H-3), 4.23 (1H, dd, *J* = 8.6, 2.0 Hz, H-4), 4.51 (1H, t, *J* = 4.0 Hz, H-2), 4.56 (1H, d, *J* = 11.8 Hz, H-18a), 4.68 (1H, d, *J* = 11.8 Hz, H-19a), 4.72 (1H, d, *J* = 11.8 Hz, H-18b), 4.73 (1H, d, *J* = 11.8 Hz, H-19b), 5.69 (1H, d, *J* = 3.6 Hz, H-1), 7.24-7.36 (10H, m, Phenyl) ppm. [α]26.2D  +63.7° (*c* 1.08, CHCl3). HR-ESI-MS *m*/*z*: 535.3030 (MNa+, calculated for C31H44O6Na, 535.3036).

To a solution of **9** (27.9 mg) in EtOH/EtOAc (1:1, 1.17 mL) was added Pd/C (10.7 mg) , and the reaction mixture was stirred for 22 h under H2 atmosphere. The reaction mixture was filtered and the filtrate was concentrated *in vacuo* to afford a crude diol (13.8 mg). The diol was dissolved in TFA/H2O (9:1, 145 µL) and the reaction mixture was stirred for 10 min at rt. The reaction mixture was concentrated *in vacuo* below 30 °C, and the resultant residue was purified by medium-pressure column chromatography (silica gel, 90% → 100% EtOAc/*n*-hexane) to afford an allose ether (6.8 mg). The same procedure was repeated to afford 3.3 mg of the same compound. They were combined and purified by HPLC (column, YMC-pack ODS-AM12S05-1520WT; solvent, 65% MeOH/H2O; flow rate, 8.0 mL/min; retention time, 19.0 min) to afford **6** (1.68 mg, 5.75 µmol, 9.1%).

1H NMR: (600 MHz, CD3OD, 0.0096 M, 296 K, β-pyranose/α-pyranose/β-furanose/α-furanose = 16:6.1:2.2:1) for the β-pyranose: δ 0.90 (3H, t, *J* = 7.0 Hz, H-14), 1.30–1.38 (10H, m, H9–13), 1.56 (2H, m, H-8), 3.23 (1H, dd, *J* = 7.9, 3.0 Hz, H-2), 3.45–3.53 (3H, m, H-4, H-7), 3.55 (1H, dd, *J* = 10.8, 6.1 Hz, H-6a), 3.71 (1H, dd, *J* = 10.8, 2.0 Hz, H-6b), 3.80 (1H, ddd, *J* = 9.8, 6.0, 2.0 Hz, H-5), 4.03 (1H, t, *J* = 3.0 Hz, H-3), 4.80 (1H, d, *J* = 8.1 Hz, H-1) ppm; for the α-pyranose: δ 5.00 (1H, br.d, *J* = 2.9 Hz, H-1) ppm; for the β-furanose: δ 5.10 (1H, d, *J* = 1.7 Hz, H-1); for the α-furanose: δ 5.20 (1H, d, *J* = 4.3 Hz, H-1). Other peaks for the α-pyranose and β- and α-furanoses had weak intensities. 13C NMR: (150 MHz, CD3OD, 0.0096 M, 297 K) for the β-pyranose: δ 14.5 (C-14), 23.8 (C-13), 27.3 (C-9), 30.5, 30.6, 30.8, 33.1 (C-12), 69.3 (C-4), 72.0 (C-6), 72.8 (C-7), 73.0 (C-3), 73.5 (C-2), 74.4 (C-5), 95.4 (C-1) ppm. [α]20.5D  +11° (*c* 0.084, MeOH). HR-ESI-MS *m*/*z*: 315.1765 (MNa+, calculated for C14H28O6Na, 315.1784).

**Reference**

[1] Haines AH. Evidence on the structure of coyolosa. Synthesis of 6, 6′-ether linked hexoses. Tetrahedron Lett. 2004;45:835-837.