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An expedient synthesis of D-callipeltose

Ainoliisa J. Pihko,[a,b] K. C. Nicolaou[a,*] and Ari M. P. Koskinen[b,*]

[a]*Department of Chemistry and The Skaggs Institute for Chemical Biology, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA 92037, USA and Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA*

[b]*Laboratory of Organic Chemistry, Department of Chemical Technology, Helsinki University of Technology, FIN-02015 HUT, Finland*

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Abstract—Methyl D-callipeltose **12** and D-callipeltose **4** were synthesized from D-glucal **5** in 10 and 11 steps, respectively. The synthesis features an azide displacement reaction of an α-nosyloxy ketone **7** and a highly diastereoselective *C*-methylation of α-azido ketone **8**.

1. Introduction

Callipeltoside A **1** belongs to a new class of cyclodepsipeptides called callipeltins. The molecules were isolated in 1996 from the shallow water lithistid sponge *Callipelta* sp., a native of New Caledonia.[1,2] They were found to inhibit in vitro proliferation of KB and P338 cells and to protect cells infected with HIV. Structurally, **1** consists of a macrocyclic lactone linked to a unique dienyne cyclopropane side chain and the deoxy amino sugar, callipeltose, **4** (Fig. 1). The absolute stereochemistry of the molecule has not been established.

There has been considerable synthetic interest in **1** although no total synthesis has been reported to date.[3–7] The deoxy amino sugar **4** contains an unusual five-membered oxazolidinone ring fused to the sugar backbone at positions 3 and 4. Both enantiomers of **4** have been synthesized—methyl L-callipeltose in 10 steps from L-rhamnose[8] and methyl D-callipeltose in 14 steps from methyl D-mannose.[9] Herein we report an expedient synthesis of α-D-callipeltose **4** from D-glucal **5**.

2. Results and discussion

The α,β-unsaturated ketone **6** was synthesized from D-glucal in three steps (Scheme 1).[10] A sequence of tosylation (TsCl, pyr.)[11] and reduction with $LiAlH_4$[12,13] effected deoxygenation of the 6-position of D-glucal **5**.

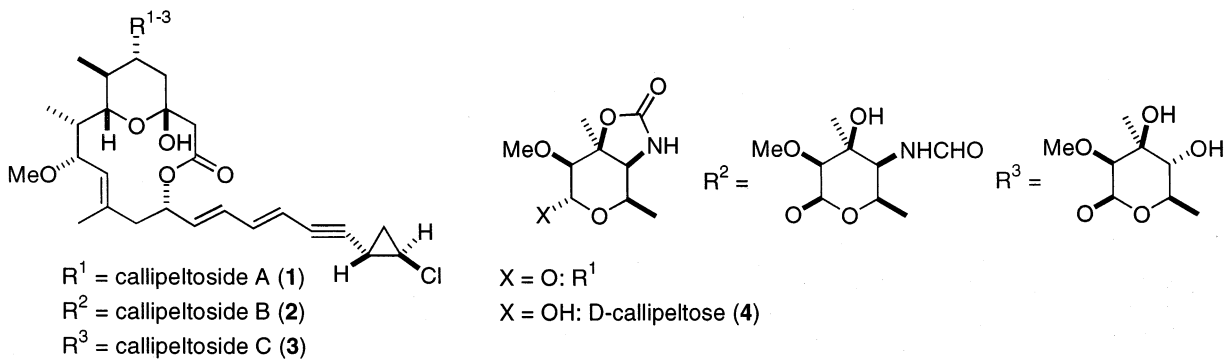

Figure 1. Structures of callipeltosides A–C, **1**–**3**.

* Corresponding authors. Tel.: +1 858 784 2400; fax: +1 858 784 2103 (K.C.N.); tel.: +358 9 451 2527; fax: +358 9 451 2538 (A.M.P.K.); e-mail: kcn@scripps.edu; ari.koskinen@hut.fi

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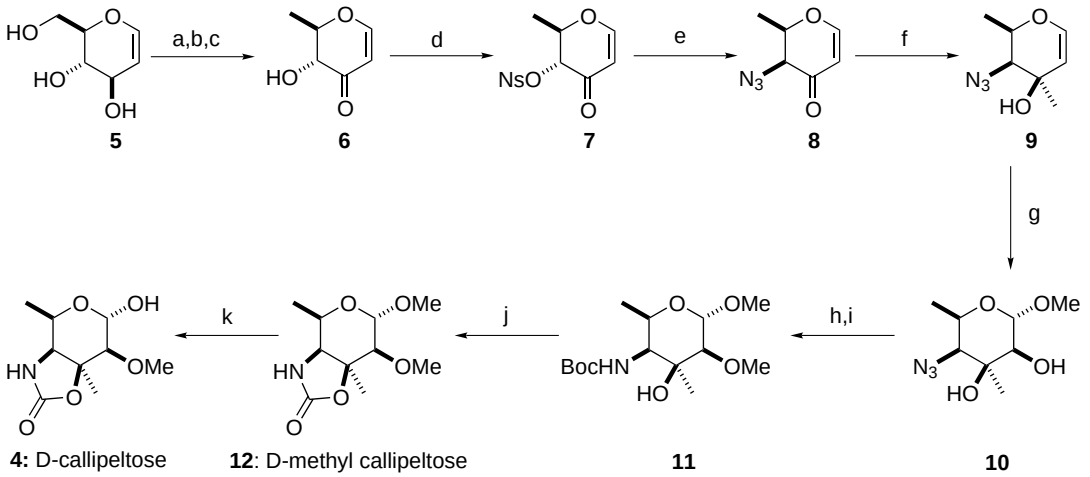

Scheme 1. Synthesis of D-callipeltose. Reagents and conditions: (a) TsCl, py, CH_2Cl_2, 0°C→rt, 78%; (b) $LiAlH_4$, THF, Δ, 59%; (c) MnO_2, CH_2Cl_2, rt, 66%; (d) NsCl, py, CH_2Cl_2, 0°C→rt, 80%; (e) n-Bu_4NN_3, CH_2Cl_2, 0°C→rt, 95%; (f) MeLi, THF, −100°C, 77%; (g) m-CPBA, $NaHCO_3$, MeOH, 0°C→rt, 60%; (h) MeI, Ag_2O, Et_2O, Δ, 72%; (i) H_2, 10% Pd/C, Boc_2O, EtOAc, rt, 62%; (j) t-BuOK, THF, 0°C→rt, 69%; (k) 2 M H_2SO_4 in 1:1 H_2O/dioxane, 60–70°C, 48%. Rt = room temperature, NsCl = nosyl chloride, py = pyridine, m-CPBA = m-chloroperbenzoic acid, Boc = t-butoxycarbonyl.

The resulting D-rhamnal was oxidized with MnO_2[14] to give α,β-unsaturated ketone **6**. The next task was to introduce a nitrogen atom at the 4-position of the sugar by azide displacement of a suitable leaving group.

For this purpose, several leaving groups, including mesylate,[15] triflate[15] and imidazolyl sulfonate,[16] were examined, but only the nosylate group[17] could be displaced at an acceptable rate without decomposition. The nosylate **7** was obtained by the action of nosyl chloride and pyridine on **6** in 80% yield along with ca. 3–5% of its C-(4) epimer. Sodium azide was found to be too basic for the displacement reaction; stirring **7** overnight in DMSO with NaN_3 at room temperature gave, in addition to recovered starting material, ca. 1:1 mixture of both epimers of **8**, presumably due to product enolization. However, tetra-n-butylammonium azide[18,19] furnished the desired azide **8** in 90% yield along with 5–10% of its C-(4) epimer.[20] The C-methylation with methyllithium in THF at −100°C gave the tertiary alcohol **9** in 77% yield as a single diastereomer.[14,21] The observed selectivity is rationalized through a synergy of steric and stereoelectronic considerations, as described in Fig. 2: the axially disposed azide group prevents attack from the *Re* face of the carbonyl, and the electronegativity of the nitrogen favors attack from the opposite (*Si*) face.

The next objective was to install the final two stereocenters of the sugar. Epoxidation accompanied by concomitant stereo- and regioselective opening of the epoxide is a useful method to functionalize the double bond in glucals.[22–28] Thus, reaction of **9** with m-CPBA in methanol in the presence of $NaHCO_3$ led to the stereoselective formation of **10** in 60% yield. Methylation of the newly created alcohol with MeI and Ag_2O[29] cleanly alkylated the secondary hydroxyl group. Subsequent palladium-catalyzed hydrogenation reduced the azide to the corresponding amine, which, in the presence of Boc-anhydride, furnished amide **11**,[30] setting the stage for the oxazolidinone ring closure. Thus, exposure of the tertiary alcohol **11** to potassium t-butoxide in THF, following the procedure of Davies et al., furnished the methyl glycoside **12**.[31] Finally, the glycoside was hydrolyzed with 2 M sulfuric acid in water/dioxane (1:1) at 60°C,[32,33] concluding the synthesis of D-callipeltose **4** in 11 steps from commercially available D-glucal **5**.

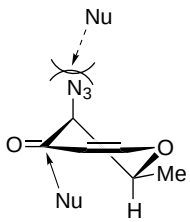

Figure 2. Preferred approach of nucleophile in the conversion of **8** to **9**.

3. Conclusion

In conclusion, methyl D-callipeltose **12** and D-callipeltose **4** were synthesized in a highly selective manner starting from D-glucal **5** in 10 and 11 steps, respectively. Key features of this synthesis, the shortest reported to date for **4**, include: (i) readily available starting materials; (ii) use of an α-nosyloxy ketone **7** en route to azide **8**; and (iii) a highly diastereoselective C-methylation rationalized in Fig. 2.

4. Experimental

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, if

necessary. Anhydrous solvents were obtained by passing them through commercially available activated alumina columns. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. All reagents were purchased at highest commercial quality and used without further purification, unless otherwise stated. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and acidic PMA (2.5% phosphomolybdic acid, 1.5% *o*-phosphoric acid and 5% sulfuric acid in water) or 1% aqueous potassium permanganate solution and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker DRX-600, DRX-500 or AMX-400 instruments and calibrated using residual undeuterated solvents as an internal reference ($CDCl_3$ 7.26 ppm, MeOH 3.34 ppm). The following abbreviations are used to explain the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; b = broad. IR spectra were recorded on a Perkin–Elmer 1600 series FT-IR spectrometer. Optical rotations were recorded on a Perkin–Elmer 241 polarimeter. High resolution mass spectra (HRMS) were recorded on an IonSpec mass spectrometer under MALDI-FTMS conditions with NBA or DHB as the matrix. Low resolution mass spectra were recorded on a Hewlett Packard 5971A benchtop GC/MS. Melting points (mp) are uncorrected and were recorded on a Thomas–Hoover Unimelt capillary melting point apparatus.

4.1. D-Rhamnal

To a stirred solution of D-glucal **5** (2.50 g, 17.1 mmol) in pyridine (42 mL) and CH_2Cl_2 (42 mL), cooled at 0°C, was added tosyl chloride (4.89 g, 25.7 mmol) and the cooling bath was removed. After stirring for 2.5 h at ambient temperature, the reaction mixture was cooled again to 0°C, quenched with water (5 mL) and stirred for 30 min. More water (20 mL) was added, the organic layer was separated and washed with sat. aq. $CuSO_4$ (3×20 mL) and water (3×20 mL). The combined aqueous phases (excluding the first water layer) were extracted with CH_2Cl_2 (2×20 mL) and those organic extracts were washed with water (2×10 mL). The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4), filtered and concentrated to provide crude 6-*O*-tosyl-D-glucal as a yellow oil (3.99 g, 78% yield). R_f 0.55 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 6.24 (dd, J = 6.1, 1.6 Hz, 1H), 4.74 (dd, J = 6.1, 2.1 Hz, 1H), 4.48 (dd, J = 11.4, 3.8 Hz, 1H), 4.27 (app. d, J = 11.4 Hz, 2H), 3.91 (ddd, J = 10.0, 3.8, 2.1 Hz, 1H), 3.77 (dd, J = 10.0, 7.3 Hz, 1H), 2.45 (s, 3H).

To a stirred solution of 6-*O*-tosyl-D-glucal (3.99 g, 13.3 mmol) in THF (30 mL) at 0°C was added $LiAlH_4$ (0.9 M solution in THF, 44.2 mL, 39.9 mmol) dropwise and the reaction mixture was heated to reflux. After stirring the reaction for 1 h, the mixture was cooled to 0°C and quenched slowly with H_2O (1.5 mL), 15% NaOH (1.5 mL) and H_2O (4.5 mL). The resulting slurry was diluted with Et_2O, filtered through a pad of Celite (Et_2O rinse) and concentrated. Purification by dry-column flash chromatography[34] (silica, 20–100% EtOAc/hexanes) provided D-rhamnal as a white solid (1.02 g, 59% yield). R_f 0.37 (EtOAc); mp 72–73°C (Et_2O/hexanes) (lit.[35] 71–73°C (EtOAc/hexanes)); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.32 (dd, J = 6.0, 1.6 Hz, 1H), 4.72 (dd, J = 6.0, 2.2 Hz, 1H), 4.21 (app. d, J = 6.3 Hz, 1H), 3.87 (dq, J = 9.8, 6.3 Hz, 1H), 3.43 (app. t, J = 8.6 Hz, 1H), 1.39 (d, J = 6.3 Hz, 3H).

4.2. 1,5-Anhydro-2,6-dideoxy-D-*erythro*-hex-1-enit-ulose 6

To a stirred solution of D-rhamnal (100 mg, 0.768 mmol) in CH_2Cl_2 (7.5 mL) at room temperature was added MnO_2 (200 mg, 2.30 mmol). After 3 h, more MnO_2 (200 mg, 2.30 mmol) was added and the stirring was continued. After 15 h, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered through a pad of Celite (EtOAc rinse) and concentrated. Purification by flash chromatography (silica, 40–50% EtOAc/hexanes) provided 65 mg of **6** as a white volatile solid (66% yield). R_f 0.66 (EtOAc); mp 91–92°C (Et_2O/hexanes) (lit.[36] 92–93°C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (app. d, J = 5.7 Hz, 1H), 5.46 (d, J = 5.7 Hz, 1H), 4.20 (dqd, J = 12.9, 6.4, 0.7 Hz, 1H), 3.54 (s, 1H), 1.57 (d, J = 6.4 Hz, 3H).

4.3. 1,5-Anhydro-2,6-dideoxy-4-*O*-nosyl-D-*erythro*-hex-1-enit-3-ulose 7

To a stirred solution of **6** (0.212 g, 1.65 mmol) in CH_2Cl_2 (8.0 mL) at 0°C were added pyridine (0.667 mL, 8.25 mmol) and nosyl chloride (0.733 g, 3.31 mmol). The reaction mixture was allowed to warm to room temperature over 2 h, and after stirring the mixture for a further 3 h more nosyl chloride (0.367 g, 1.66 mmol) and pyridine (0.667 mL, 8.25 mmol) were added. After 12 h the reaction mixture was cooled to 0°C and water (2 mL) was added. After stirring for 30 min more water (10 mL) was added, the aqueous layer was separated and extracted with CH_2Cl_2 (2×10 mL), the combined organic layers were washed with brine (5 mL), dried (Na_2SO_4), filtered and concentrated. Purification by dry-columm flash chromatography (silica, 15–30% EtOAc/hexanes) provided **7** as a yellow crystalline solid (0.411 g, 80% yield). R_f 0.60 (50% EtOAc/hexanes); mp 93°C; $[\alpha]_D$ +138.8 (c 1.07, $CHCl_3$); IR (film) 3108, 1695, 1598, 1533, 1353, 1256, 1188, 1026, 854, 780 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (app. d, J = 9.2 Hz, 2H), 8.19 (app. d, J = 9.2 Hz, 2H), 7.35 (d, J = 5.9 Hz, 1H), 5.37 (d, J = 5.9 Hz, 1H), 5.02 (d, J = 12.1 Hz, 1H), 4.54 (dq, J = 12.1, 6.2 Hz, 1H), 1.63 (d, J = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.0, 163.5, 150.8, 142.1, 129.7, 124.1, 105.0, 79.6, 77.4, 17.4; HRMS (MALDI) calcd for $C_{12}H_{11}NO_7S$ (M^+) m/z: 313.0256, found 313.0286.

4.4. 1,5-Anhydro-4-azido-2,6-dideoxy-D-*threo*-hex-1-enit-3-ulose 8

To a stirred solution of **7** (190 mg, 0.606 mmol) in CH_2Cl_2 (3.3 mL) at 0°C was added *n*-Bu_4NN_3 (0.651 g, 2.29 mmol) [CAUTION][19] in CH_2Cl_2 (0.5 mL) via cannula. The reaction mixture was allowed to warm to room temperature over 1.5 h and stirred at that temperature for 1 h. Water (5 mL) was added, the aqueous layer was extracted with CH_2Cl_2 (2×10 mL), the combined organic extracts were washed with brine (5 mL) and dried (Na_2SO_4), filtered and concentrated. Purification by dry-column flash chromatography (silica, 10–20% EtOAc/hexanes) provided **8** as a yellow oil (88 mg, 95% yield). R_f 0.43 (33% EtOAc/hexanes); $[\alpha]_D$ −78.0 (*c* 0.383, $CHCl_3$); IR (film) 3378, 2919, 2106, 1675, 1593, 1414, 1274, 1050 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, $J=6.0$ Hz, 1H), 5.49 (dd, $J=6.0$, 0.9 Hz, 1H), 4.53 (qd, $J=6.6$, 3.1 Hz, 1H), 3.81 (d, $J=3.1$ Hz, 1H), 1.48 (d, $J=6.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.1, 163.6, 104.9, 76.9, 63.8, 15.3; HRMS (MALDI) calcd for $C_6H_8NO_2$ ($MH-N_2^+$) *m*/*z*: 126.0550, found 126.0554.

4.5. 1,5-Anhydro-4-azido-2,6-dideoxy-3-*C*-methyl-D-*lyxo*-hex-1-enitol 9

To a stirred solution of **8** (95 mg, 0.620 mmol) in THF (3.1 mL) at −100°C was added MeLi (1.5 M solution in Et_2O, 0.500 mL, 0.744 mmol) dropwise. After 1.5 h, sat. aq. NH_4Cl (1.0 mL) was added and the reaction mixture was allowed to warm to room temperature. The aqueous layer was extracted with EtOAc (2×5 mL), the combined organic extracts were washed with brine (5 mL), dried (Na_2SO_4), filtered and concentrated. Purification by dry-column flash chromatography (silica, 10–25% EtOAc/hexanes) provided **9** as a yellow oil (81 mg, 77% yield). R_f 0.15 (20% EtOAc/hexanes); $[\alpha]_D$ +84.2 (*c* 0.483, $CHCl_3$); IR (film) 3413, 2919, 2097, 1637, 1449, 1378, 1232, 1132, 1049, 944, 820, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.27 (d, $J=6.3$ Hz, 1H), 4.70 (dd, $J=6.3$, 2.2 Hz, 1H), 4.19 (qd, $J=6.5$, 0.9 Hz, 1H), 3.34 (br s, 1H), 2.24 (br s, 1H) 1.45 (d, $J=6.6$ Hz, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 104.8, 72.1, 68.8, 68.4, 29.5, 18.0. Low resolution mass spectrum (GC/MS) calcd for $C_7H_{11}N_3O_2$ (M^+) 169, found 169.

4.6. Methyl 4-azido-4,6-dideoxy-3-*C*-methyl-α-D-*talo*-pyranoside 10

To a stirred solution of **9** (100 mg, 0.591 mmol, 100 mol%) in MeOH (3.1 mL) at 0°C were added $NaHCO_3$ (153 mg, 1.86 mmol, 315 mol%) and *m*-CBPA (55–60%, 0.321 g, 1.86 mmol, 315 mol%). After stirring for 1 h sat. aq. $NaHCO_3$ (2 mL) was added, the aqueous layer was extracted with EtOAc (2×10 mL), the combined organic extracts were washed with brine (5 mL) and dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography (silica, 20–30% EtOAc/hexanes) provided **10** as an oil (76 mg, 60% yield). R_f 0.28 (33% EtOAc/hexanes); $[\alpha]_D$ +143.8 (*c* 0.417, $CHCl_3$); IR (film) 3449, 2921, 2109, 1449, 1343, 1261, 1126, 1061, 997, 944, 814 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.76 (s, 1H), 4.03 (qd, $J=6.5$, 1.2 Hz, 1H), 3.62 (br s, 1H), 3.36 (s, 3H), 3.30 (d, $J=11.0$ Hz, 1H), 3.24 (s, 1H), 2.71 (d, $J=11.0$ Hz, 1H), 1.39 (s, 3H), 1.34 (d, $J=6.5$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 102.0, 73.2, 70.0, 64.2, 55.5, 23.5, 18.1; HRMS (MALDI) calcd for $C_8H_{15}N_3O_4Na$ ($M+Na^+$) *m*/*z*: 240.0955, found 240.0956.

4.7. Methyl 4-azido-4,6-dideoxy-3-*C*,2-*O*-dimethyl-α-D-*talo*-pyranoside

To a stirred solution of **10** (70 mg, 0.322 mmol) in Et_2O (2.0 mL) at room temperature were added MeI (0.200 mL, 3.22 mmol) and freshly prepared Ag_2O[29] (0.224 g, 0.967 mmol). The reaction mixture was protected from light and heated to reflux. After stirring under reflux for 5 h, the reaction was diluted with EtOAc (10 mL), filtered through a pad of Celite (EtOAc rinse) and concentrated. Purification by flash chromatography (silica, 5–15% EtOAc/hexanes) provided the azidomethyl glycoside as an oil (53 mg, 72% yield). R_f 0.33 (33% EtOAc/hexanes); $[\alpha]_D$ +164.8 (*c* 0.708, $CHCl_3$); IR (film) 3483, 2931, 2105, 1455, 1349, 1102, 1055, 597 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.79 (s, 1H), 4.00 (qd, $J=6.5$, 1.6 Hz, 1H), 3.72 (d, $J=1.0$ Hz, 1H), 3.49 (s, 3H), 3.36 (s, 3H), 3.11 (br s, 1H) 2.90 (s, 1H), 1.40 (d, $J=1.0$ Hz, 3H), 1.35 (d, $J=6.5$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 98.4, 82.0, 70.1, 69.6, 64.3, 59.8, 55.2, 24.5, 17.9; HRMS (MALDI) calcd for $C_9H_{17}N_3O_4Na$ ($M+Na^+$) *m*/*z*: 254.1111, found 254.1112.

4.8. Methyl 4-(*tert*-butoxycarbonylamino)-4,6-dideoxy-3-*C*,2-*O*-dimethyl-α-D-*talo*-pyranoside 11

To a stirred solution of the methyl glycoside (26 mg, 0.112 mmol) and Boc_2O (49 mg, 0.225 mmol) in EtOAc (0.50 mL) at room temperature under argon was carefully added Pd/C (10%, 2 mg). The reaction flask was evacuated and placed under an H_2 atmosphere. After 4 h more Pd/C (10%, 2 mg) was added. After stirring for 1 h the reaction flask was purged with argon, the mixture was filtered through a pad of Celite and concentrated. Purification by flash chromatography (silica, 10–20% EtOAc/hexanes with 2% Et_3N) provided **11** as an oil (21 mg, 62% yield). R_f 0.28 (33% EtOAc/hexanes); $[\alpha]_D$ +59.4 (*c* 0.500, $CHCl_3$) IR (film) 3429, 2929, 1716, 1503, 1170, 1060 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.30 (d, $J=10.4$ Hz, 1H), 4.73 (s, 1H), 4.01 (qd, $J=6.4$, 1.7 Hz, 1H), 3.49 (dd, $J=10.4$, 1.7 Hz, 1H), 3.47 (s, 3H), 3.37 (s, 3H), 3.23 (s, 1H) 2.91 (s, 1H), 1.44 (s, 9H), 1.41 (s, 3H), 1.15 (d, $J=6.4$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.5, 98.6, 83.0, 79.3, 68.0, 65.0, 59.4, 58.4, 55.2, 28.3, 23.8, 17.1; HRMS (MALDI) calcd for $C_{14}H_{27}NO_6Na$ ($M+Na^+$) *m*/*z*: 328.1730, found 328.1731.

4.9. α-D-Methyl callipeltose 12

To a stirred solution of **11** (28 mg, 0.0917 mmol) in THF (0.50 mL) at 0°C was added *t*-BuOK (0.9 M solution in THF, 0.204 mL, 0.183 mmol) dropwise and

the cooling bath was removed. After 4 h at room temperature more *t*-BuOK (0.051 mL, 0.46 mmol) was added. After 1 h sat. aq. NH_4Cl (1 mL) was added, the aqueous layer was extracted with EtOAc (2×5 mL), the combined organic extracts were washed with brine (5 mL) and dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography (silica, 1–3% MeOH/CH_2Cl_2) provided 15 mg of **12** as a white solid (69% yield). R_f 0.28 (5% MeOH/CH_2Cl_2); mp 145–146°C (hexanes) (lit.[8] 147–148°C); $[\alpha]_D$ +91.6 (*c* 1.06, $CHCl_3$) (lit.[9] $[\alpha]_D$ +76 (*c* = 1.0, $CHCl_3$)); IR (film) 3295, 2931, 1747, 1376, 1267, 1104, 1060, 670 cm^{-1}; ^1H NMR (500 MHz, MeOH-d_4) δ 4.48 (d, J = 6.1 Hz, 1H), 3.94 (qd, J = 6.5, 2.0 Hz, 1H), 3.52 (s, 3H), 3.45 (d, J = 2.0 Hz, 1H), 3.41 (s, 3H), 3.38 (d, J = 6.1 Hz, 1H), 1.50 (s, 3H), 1.12 (d, J = 6.5 Hz, 3H); ^1H NMR (400 MHz, $CDCl_3$) δ 6.69 (br s, 1H), 4.60 (d, J = 5.6 Hz, 1H), 3.89 (qd, J = 6.5, 2.0 Hz, 1H), 3.53 (s, 3H), 3.41 (s, 3H), 3.37 (d, J = 2.0 Hz, 1H), 3.19 (d, J = 5.6 Hz, 1H), 1.54 (s, 3H), 1.17 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 101.6, 81.9, 81.1, 63.7, 61.4, 60.6, 55.0, 23.3, 15.6; HRMS (MALDI) calcd for $C_{10}H_{17}NO_5Na$ (M+Na^+) m/z: 254.0999, found 254.1001.

4.10. α-D-Callipeltose 4

A solution of **12** (4.3 mg, 0.186 mmol) in H_2SO_4 (2 M in H_2O/1,4-dioxane (1:1), 0.20 mL) was heated to 60°C for 30 h. Saturated aq. $NaHCO_3$ (1 mL) was added, the solution was saturated with NaCl and extracted with 25% EtOH/$CHCl_3$ (20×1 mL). The combined organic extracts were washed with brine and dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography (silica, 5% MeOH/CH_2Cl_2) afforded D-callipeltose **4** as a film (1.9 mg, 48% yield). R_f 0.13 (5% MeOH/CH_2Cl_2); $[\alpha]_D$ +25.3 (*c* 0.150, $CHCl_3$); IR (film) 3313, 2924, 1737, 1449, 1273, 1261, 1061, 667 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.56 (s, 1H), 5.13 (d, J = 5.9 Hz, 1H), 4.06 (qd, J = 6.5, 1.9 Hz, 1H), 3.60 (s, 3H), 3.38 (d, J = 1.9 Hz, 1H), 3.24 (d, J = 5.9 Hz, 1H), 2.99 (br s, 1H), 1.56 (s, 3H), 1.17 (d, J = 6.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 95.0, 81.9, 81.8, 63.6, 61.3, 60.8, 23.3, 15.8; HRMS (MALDI) calcd for $C_9H_{15}NO_5Na$ (M+Na^+) m/z: 240.0842, found 240.0843.

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