A Chemo-Enzymatic Synthesis of D-Allosamine Derivatives from Tri-*O*-acetyl-D-glucal

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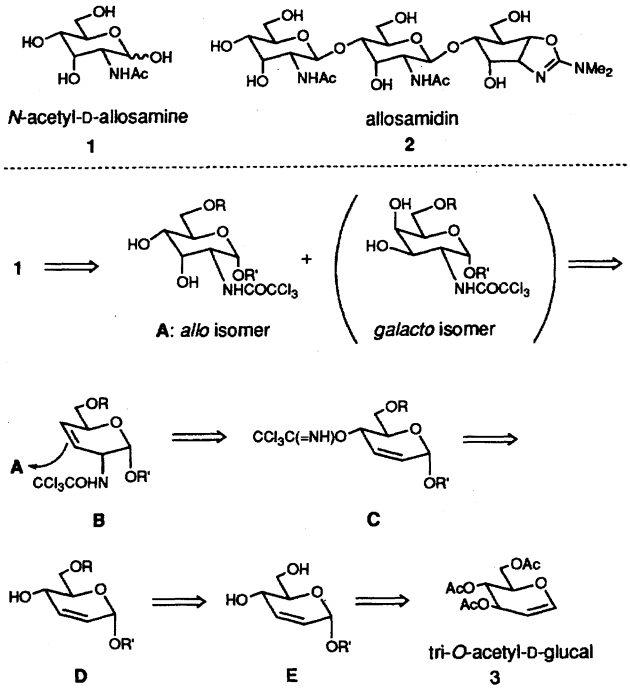
N-Acetyl-D-allosamine and its derivatives were synthesized from tri-*O*-acetyl-D-glucal based on lipase-catalyzed selective protection of primary alcohols, [3,3] sigmatropic rearrangement of allylic trichloroacetimidates, and stereoselective ruthenium-catalyzed dihydroxylation. In the course of this study, it was revealed that the *Pseudomonas* lipase-catalyzed acetylation occurred in a high yield (> 90%) exclusively at the primary alcohols of three Ferrier rearrangement products derived from tri-*O*-acetyl-D-glucal.

N-Acetyl-D-allosamine (2-acetamido-2-deoxy-D-allose, **1**) is one of the rare aminosugars, and the component of allosamidin (**2**),[1] a chitinase inhibitor. Recently, **2** and its derivatives have been the object of extensive studies on structure-activity relationships.[2] *N*-Acetyl-D-allosamine and its glycosides have been synthesized from *N*-acetyl-D-glucosamine,[3] *N*,*N*-diacetylchitobiose,[4] D-ribose,[5] 2,3-*O*-isopropylidene-D-glyceraldehyde,[6] and tri-*O*-acetyl-D-glucal.[7] All syntheses, however, have suffered from rather lengthy multisteps and tedious synthetic transformations. Our recent study on the chemo-enzymatic synthesis of deoxyamino sugars[8] prompted us to develop a short-step synthesis of **1** as its protected form, starting from readily available tri-*O*-acetyl-D-glucal (**3**).

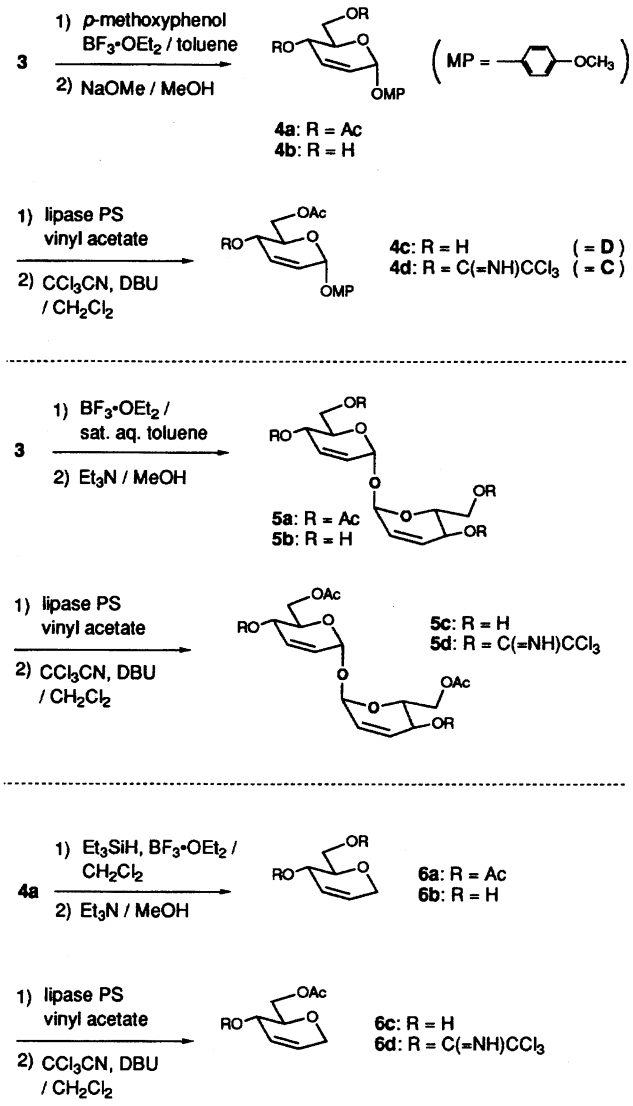
The synthetic plan is shown in Scheme 1. The derivative of **1** with the desired *allo*-configuration [**A**] would be obtained via a stereocontrolled dihydroxylation of 3,4-unsaturated sugar [**B**]. The intermediate [**B**] is secured by an approach based on [3,3] sigmatropic rearrangement[9] especially via an Overman-type thermal rearrangement[10,11] of the corresponding trichloroacetimidate [**C**]. When we use glucal derivative **3** as the starting material, the key step would be regioselective protection of two hydroxy groups of [**E**] to [**D**].



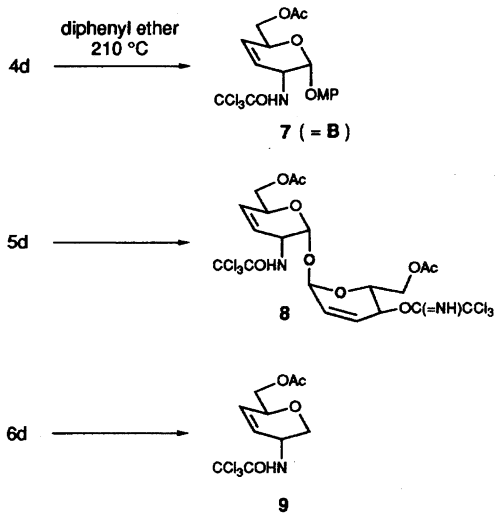
Scheme 1.

Reaction of tri-*O*-acetyl-D-glucal (**3**) and *p*-methoxyphenol in the presence of $BF_3 \cdot OEt_2$, followed by deacetylation, gave the Ferrier-rearrangement product **4b** [**E**] (92%) in an anomerically pure state.[12—14] The selective introduction of protective group (*R*) on the 6-position of **4b** was realized in a highly efficient manner (quantitative) by a lipase-catalyzed regioselective acetylation.[cf. 15,16] The absence of acetylation on the allylic secondary alcohol[17] (4-position) is ascribed to its (*S*)-absolute configuration.[18] The selective acylation on the structurally related substrates worked successfully. In addition, the reaction proceeded exclusively on the two primary alcohols (94% yield) of the dimeric substrate **5b**, which was prepared from tri-*O*-acetyl D-glucal via a Lewis acid-catalyzed dimerization[14,19,20] and the subsequent deprotection. Another candidate **6b**[21] was also a good substrate to give **6c** (95% yield, Scheme 2). Subsequent treatment of **4c** [**D**] with trichloroacetonitrile[22] in the presence of DBU[23] afforded **4d** [**C**] in a quantitative yield (Scheme 2).

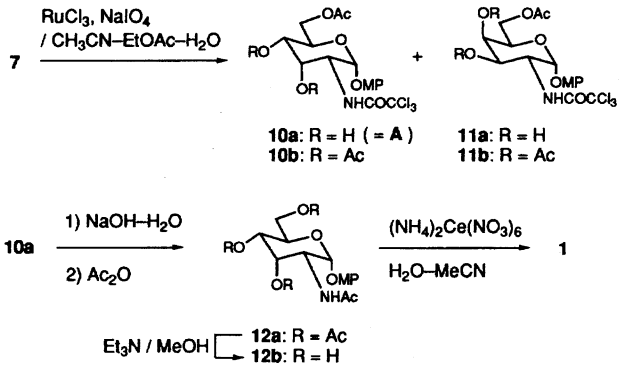
It was reported that the rearrangement of a similar allylic trichloroacetimidate proceeded only sluggishly in the case that the substrate had both 1α, 4α-configuration.[10] Indeed, also in our case, the desired rearrangement took place only at a very high temperature (210 °C) to give **7** [**B**] (54% yield based on the consumed starting material, 43% recovery of **4d**, Scheme 3).[cf. 24] Attempts for improving yield of rearrangement, however, resulted only in disappointment. The



Scheme 2.



Scheme 3.



Scheme 4.

reaction of more electron-donating **5d** afforded only a complex mixture, and the yield of product (**8**) formed via only one trichloroacetimidate rearrangement was as low as 8%. In the case that the sterically less hindered **6d** was submitted to the reaction, to our surprise, the high temperature was also required for the rearrangement, as in the case for **4d**, the yield of **9** being 25% (Scheme 3). In all cases, either a prolonged heating of the slow elevation of the reaction temperature lowered the yield. Moreover, the removal of moisture from the reaction mixture was necessary to obtain a higher yield.

The next task was the introduction of dihydroxy groups on **7**. Among many methods of a stereoselective dihydroxylation on the cyclic compound,[11,25] recently developed ruthenium-catalyzed dihydroxylation[26] was applied, because the reaction proceeds much faster than osmium-catalyzed reaction even at low temperature. This point would be advantageous for **7** bearing methoxyphenyl ether, a functional group susceptible to oxidation. As expected, the dihydroxylation proceeded at -11 °C within 2 min to give the desired diols **10a** and **11a** (77% yield based on the consumed starting material, 43% recovery of **7**). A prolonged reaction brought about a further decomposition of the product. The stereochemistry of the major product was determined to be an *allo*-isomer **10a** by a comparison of NMR spectra[11] of the products and the corresponding acetates, the ratio (**10a** : **11a**) being 11 : 1 (Scheme 4). Finally, the *N*-trichloroacetyl group was replaced[11] with a *N*-acetyl group to give *N*-acetyl-D-allosamine as its protected form (**12a**) in a quantitative yield. This was deprotected[27] via **12b** to **1** and its identity with an authentic sample was confirmed[3,28] (see Experimental).

In conclusion, the protected form of *N*-acetyl-D-allosamine (**12a**) was synthesized from tri-*O*-acetyl-D-glucal via 6 steps and 38% overall yield from a known compound (**4a**). Further studies on the substrate specificity of the lipase-catalyzed regioselective acylation on glycal derivatives and the utilization of those products are under way.

Experimental

IR spectra were measured as films on a JASCO IRA-202 spectrometer. ^{1}H NMR spectra were measured in $CDCl_3$ with TMS as the internal standard at 270 MHz on a JEOL JNM EX-270 or at 400 MHz on a JEOL JNM α-400 spectrometer unless otherwise stated. Mass spectra were recorded on Hitachi M-80B spectrometer at 70 eV. Optical rotations were recorded on a JASCO DIP 360 polarimeter. Silica gel 60 K070-WH (70—230 mesh) of Katayama Chemical Co. were used for preparative TLC and column chromatography.

***p*-Methoxyphenyl 2,3-Dideoxy-α-D-*erythro*-hex-2-enopyranoside (4b).** According to the reported procedure[13], *p*-methoxyphenyl 4,6-D-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside **4a** was prepared from tri-*O*-acetyl-D-glucal **3** in 92% yield, mp 76.0—76.5 °C [lit,[13] mp 78.5—79.5 °C]; $[\alpha]_D^{23}$ +179° (*c* 0.40, $CHCl_3$) [lit,[13] $[\alpha]_D^{22}$ +180° (*c* 0.4, $CHCl_3$)].

Acetate **4a** (1.64 g, 4.88 mmol) was dissolved in methanol (27 ml). To this was added triethylamine (3.84 ml) and the resulting mixture was stirred and heated at 70 °C for 7 h. Then the mixture was concentrated in vacuo. To the residue was added methanol and this mixture was further concentrated in vacuo. This procedure was repeated four times to remove any traces of triethylamine. The residue was recrystallized from diisopropyl ether to yield **4b** (1.23 g, quantitative) as colorless needles, mp 88.0—89.0 °C; $[\alpha]_D^{20}$ +154° (*c* 1.00, $CHCl_3$). IR ν_{max} 3300 (O–H), 2900 (aromatic C–H), 1520 (aromatic C=C), 1290, 1240, 1220, 1110, 1050, 980, 840, 770 cm^{-1}; ^1H NMR (270 MHz, D_2O) δ = 3.78 (d, *J* = 5.6, 12.5 Hz, 1H, H6), 3.82 (s, 3H, OMe), 3.84 (dd, *J* = 2.3, 12.5 Hz, 1H, H6′), 3.90 (ddd, *J* = 2.3, 5.6, 11.2 Hz, 1H, H5), 4.24 (ddd, *J* = 1.7, 2.3, 11.2 Hz, 1H, H4), 5.67 (dd, *J* = 1.3, 1.3 Hz, 1H, H1), 6.03 (ddd, 1H, *J* = 1.3, 2.3, 10.2 Hz, 1H, H3), 6.17 (ddd, *J* = 1.3, 1.7, 10.2 Hz, 1H, H2), 7.00 (ddd, *J* = 2.6, 5.9, 9.2 Hz, 2H, aromatic), 7.35 (ddd, *J* = 2.6, 5.9, 9.2 Hz, 2H, aromatic). Anal. Found: C, 61.65; H, 6.49%. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39%.

***p*-Methoxyphenyl 6-*O*-Acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (4c).** Diol **4b** (400 mg, 1.58 mmol) was dissolved in vinyl acetate (10 ml). To this was added *Pseudomonas* lipase PS (200 mg) and the mixture was stirred for 2 d at 20 °C. Then the mixture was filtered through a pad of Celite, and the residue was washed with ethyl acetate. The combined filtrate and washings were concentrated in vacuo. The residue was purified on a column of silica gel (40 g, 3 cm×10 cm) with ethyl acetate –hexane (1 : 4) and recrystallized from hexane to give **4c** (578 mg, 99% yield) as colorless needles, mp 68.5—69.0 °C; $[\alpha]_D^{22}$ +99.6° (*c* 1.00, $CHCl_3$). IR ν_{max} 3400 (O–H), 2900 (aromatic C–H), 1710 (C=O), 1510 (aromatic C=C), 1380, 1280, 1215, 1180, 1120, 1080, 1040, 980, 820, 770, 710, 650, 550, 510 cm^{-1}; ^1H NMR (270 MHz) δ = 2.00 (s, 3H, OAc), 2.25 (d, *J* = 6.9 Hz, 1H, 4-OH), 3.72 (s, 3H, OMe), 3.92 (ddd, *J* = 2.3, 4.6, 9.6 Hz, 1H, H5), 4.05 (ddd, *J* = 2.3, 6.9, 9.6 Hz, 1H, H4), 4.15 (dd, *J* = 2.3, 12.2 Hz, 1H, H6), 4.51 (dd, *J* = 4.6, 12.2 Hz, 1H, H6′), 5.48 (dd, *J* = 1.3, 2.3 Hz, 1H, H1), 5.85 (ddd, *J* = 2.3, 2.3, 10.2 Hz, 1H, H3), 6.03 (dd, *J* = 1.3, 10.2 Hz, 1H, H2), 6.76 (ddd, *J* = 5.9, 9.2, 2.3 Hz, 2H, aromatic), 6.97 (ddd, *J* = 5.9, 9.2, 2.3 Hz, 2H, aromatic); ^{13}C NMR (100 MHz) δ = 20.77, 55.59, 63.51, 70.83, 77.00, 94.14, 114.44, 118.60, 125.76, 133.74, 151.10, 155.01, 171.76. Anal. Found: C, 60.85; H, 6.18%. Calcd for $C_{15}H_{18}O_6$: C, 61.22; H, 6.16%.

6-*O*-Acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl 6-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5c). According to the reported procedure,[19] 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside **5a** was prepared from tri-*O*-acetyl-D-glucal **3**, mp 57.5—58.0 °C [lit,[19] mp 68—69 °C]; $[\alpha]_D^{23}$ +76° (*c* 0.15, $CHCl_3$) [lit,[19] $[\alpha]_D^{22}$ +79.4° (*c* 2.2, $CHCl_3$)].

The removal of acetate of **5a** (300 mg, 0.78 mmol) was performed in a similar manner to that described for **4a**. The crude residue was dissolved in ethanol (6 ml) and treated with Norit (30 mg). After Norit was filtered off, the filtrate was concentrated in vacuo and the residue (crude **5b**) was dissolved in anhydrous pyridine (4 ml). To this was added *Pseudomonas* lipase PS (200 mg) and the mixture was stirred for 4 d at 20 °C. Then the mixture was filtered through a pad of Celite, and the residue was washed with ethyl acetate. The combined filtrate and washings were concentrated in vacuo. To the residue was added toluene and the mixture was further concentrated in vacuo. This procedure was repeated three times to remove any traces of pyridine. The residue was purified on a column of silica gel (15 g, 1.5 cm×16 cm) with ethyl acetate–hexane (1 : 4) and recrystallized from hexane to give **5c** (228 mg, 94% yield) as pale yellow needles, mp 88.5—89.0 °C; $[\alpha]_D^{22}$ −54.0° (*c* 1.00, $CHCl_3$). IR ν_{max} 3470 (O–H), 3050, 2950, 1720 (C=O), 1460, 1420, 1370, 1260, 1230, 1200, 1140, 1120, 1100, 1080, 1055, 1040, 1000, 960, 905, 770, 740, 660, 620, 500 cm^{-1}; ^1H NMR (270 MHz) δ = 2.10 (s, 3H, OAc), 2.35 (d, *J* = 6.9 Hz, 1H, 4-OH), 3.82 (ddd, *J* = 2.3, 5.0, 9.6 Hz, 1H, H5), 4.08 (ddd, *J* = 2.3, 6.9, 9.6 Hz, 1H, H4), 4.24 (dd, *J* = 2.3, 12.2 Hz, 1H, H6), 4.51 (dd, *J* = 5.0, 12.2 Hz, 1H, H6′), 5.40 (dd, *J* = 1.0, 2.3 Hz, 1H, H1), 5.73 (ddd, *J* = 2.3, 2.3, 10.2 Hz, 1H, H3), 6.00 (dd, *J* = 1.0, 10.2 Hz, 1H, H2); ^{13}C NMR (100 MHz) δ = 20.82, 63.55, 63.64, 70.46, 90.64, 125.99, 133.49, 171.67. Anal. Found: C, 53.29; H, 6.47%. Calcd for $C_{16}H_{22}O_9$: C, 53.63; H, 6.19%.

6-*O*-Acetyl-1,5-anhydro-2,3-dideoxy-D-*erythro*-hex-2-enitol (6c): According to the reported procedure, 4,6-Di-*O*-acetyl-1,5-anhydro-2,3-dideoxy-D-*erythro*-hex-2-enitol (**6a**) was prepared from **4a**.[20] Its NMR spectrum was in good accordance with that reported previously.[20] In a similar manner to that described for **4c**, **6c** was prepared from **6a** via **6b** in 95%, $[\alpha]_D^{22}$ +24° (*c* 0.87, $CHCl_3$). IR ν_{max} 3450 (O–H), 2950, 2850, 1740 (C=O), 1450, 1370, 1260, 1180, 1120, 1040, 980, 820, 700 cm^{-1}; ^1H NMR (270 MHz) δ = 2.12 (s, 3H, OAc), 2.25 (d, 1H, *J* = 6.9 Hz, OH), 3.45 (ddd, 1H, *J* = 2.3, 5.3, 8.3 Hz, H5), 4.07 (ddd, 1H, *J* = 3.0, 6.9, 8.3 Hz, H4), 4.20 (m, 2H, H1, H1), 4.29 (dd, 1H, *J* = 2.3, 12.2 Hz, H6), 4.46 (dd, 1H, *J* = 5.3, 12.2 Hz, H6′), 5.83 (m, 2H, H2, H3); ^{13}C NMR (100 MHz) δ = 20.87, 63.38, 64.01, 65.49, 77.01, 127.68, 128.00, 171.80. Found: *m/z* 154.0613 ($M^+ - H_2O$). Calcd for $C_8H_{10}O_3$: M, 154.0628.

***p*-Methoxyphenyl 6-*O*-Acetyl-2,3-dideoxy-4-*O*-(1-imino-2,2,2-trichloroethyl)-α-D-*erythro*-hex-2-enopyranoside (4d).** Monoacetate **4c** (305 mg, 1.04 mmol) was dissolved in anhydrous dichloromethane (5.8 ml) and cooled to −17 °C with an ice-salt bath. To this cooled and stirred solution, trichloroacetonitrile (0.95 ml, 10.3 mmol), and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU, 97 μl, 0.74 mmol) were added and the mixture was further stirred for 15 min. After we confirmed the disappearance of the starting material by a TLC analysis, the mixture was concentrated in vacuo. The residue was purified on a column of silica gel (40 g, 3 cm×11 cm) with ethyl acetate–hexane (1 : 4) and recrystallized from hexane to give **4d** (466 mg, quant.) as colorless needles, mp 76.0—76.5 °C; $[\alpha]_D^{22}$ +159° (*c* 0.99, $CHCl_3$). IR ν_{max} 3350 (O–H), 3300 (N–H), 2900 (aromatic C–H), 1740 (ester C=O), 1670 (C=N), 1510 (aromatic C=C) 1240, 1220, 1190, 1150, 1100, 1070, 1040, 1000, 840, 820, 800, 770 cm^{-1}; ^1H NMR (270 MHz) δ = 2.04 (s, 3H, OAc), 3.78 (s, 3H, OMe), 4.24 (dd, *J* = 2.3, 11.7 Hz, 1H, H6), 4.36 (dd, *J* = 5.6, 11.7 Hz, 1H, H6′), 4.44 (ddd, *J* = 2.3, 5.6, 9.6 Hz, 1H, H5), 5.54 (ddd, *J* = 1.7, 2.3, 9.6 Hz, 1H, H4), 5.60 (br, 1H, H1), 6.05 (ddd, *J* = 2.3, 2.3, 10.2 Hz, 1H, H3), 6.20 (dd, *J* = 1.7, 10.2 Hz, 1H, H2), 6.84 (ddd, *J* = 5.9, 9.2, 2.3 Hz, 2H, aromatic), 7.07 (ddd, *J* = 5.9, 9.2, 2.3 Hz, 2H, aromatic), 8.49 (s, 1H, NH). Found: *m/z* 423.0016 ($M^+ + 1 - CH_3$). Calcd for $C_{16}H_{16}Cl_3NO_6$: M, 423.0041.

6-*O*-Acetyl-2,3-dideoxy-4-*O*-(1-imino-2,2,2-trichloroethyl)-α-D-*erythro*-hex-2-enopyranosyl 6-*O*-Acetyl-2,3-dideoxy-4-*O*-(1-imino-2,2,2-trichloroethyl)-α-D-*erythro*-hex-2-enopyranoside (5d). In a similar manner to that described for **4d**, **5d** was prepared as an oil (quantitative), $[\alpha]_D^{22}$ +62.6° (*c* 1.08, $CHCl_3$). IR ν_{max} 3350 (N–H), 2950 (aromatic C–H), 1750 (C=O), 1670 (C=N), 1380, 1300, 1240, 1190, 1150, 800, 770, 720, 650 cm^{-1}; ^1H NMR (270

MHz) δ = 2.10 (s, 2×3H, OAc), 4.20—4.40 (m, 2×3H, H5, H6, H6′), 5.48—5.54 (m, 2×2H, H1, H4), 5.90 (ddd, J = 2.3, 2.8, 10.2 Hz, 2×1H, H3), 6.15 (dd, J = 1.0, 10.2 Hz, 2×1H, H2), 8.50 (s, 2×1H, NH). Found: m/z 601.9320 ($M^+ + 1 - CH_3CO$). Calcd for $C_{18}H_{20}Cl_6N_2O_8$: M, 601.9348.

6-*O*-Acetyl-1,5-anhydro-2,3-dideoxy-4-*O*-(1-imino-2,2,2-trichloroethyl)-D-*erythro*-hex-2-enitol (6d). In a similar manner to that described for **4d**, **6d** was prepared as an oil (quantitative), $[\alpha]_D^{22}$ +81.3° (c 1.09, $CHCl_3$). IR ν_{max} 3350 (N–H), 2950, 2850, 1740 (C=O), 1660 (C=N), 1500, 1450, 1370, 1315, 1300, 1290, 1240, 1180, 1130, 1080, 1020, 990, 840, 800, 740, 690, 650 cm^{-1}; ^1H NMR (270 MHz) δ = 2.04 (s, 3H, OAc), 3.82 (ddd, 1H, J = 2.6, 5.6, 8.6 Hz, H5), 4.14—4.30 (m, 4H, H1, H1′, H6, H6′), 5.38 (dd, 1H, J = 1.7, 8.6 Hz, H4), 5.87 (ddd, J = 1.7, 1.7, 10.2 Hz, 1H, H3), 6.15 (ddd, J = 0.7, 1.7, 10.2 Hz, 1H, H2), 8.38 (s, 1H, NH). Found: m/z 314.9830 (M^+). Calcd for $C_{10}H_{12}Cl_3NO_4$: M, 314.9831.

***p*-Methoxyphenyl 6-*O*-Acetyl-2,3,4-trideoxy-2-trichloroacetamido-α-D-*erythro*-hex-3-enopyranoside (7).** Powdered molecular sieves 4A (500 mg) were flame-dried in a 30-ml two-necked flask, and the reaction vessel was further heated at 100 °C in vacuo for 1 h. Trichloroacetimidate **4d** (500 mg, 1.14 mmol) and diphenyl ether (3.3 ml) were charged and the mixture was stirred for 10 min at room temperature. Then the mixture was stirred in a preheated oil bath (210 °C) for 35 min. After cooling, the mixture was charged on a column of silica gel (52 g, 3 cm×15 cm) and eluted with ethyl acetate–hexane (2 : 5). The starting material (215 mg, 43%) was recovered and the desired fraction was further recrystallized from hexane to give **7** (154 mg, 30% yield, 54% based on the consumed starting material **4d**) as colorless needles, mp 84.4—85 °C; $[\alpha]_D^{24}$ +31.4° (c 1.00, $CHCl_3$). IR ν_{max} 3400 (N–H), 3000 (aromatic C–H), 2350, 1750 (ester C=O), 1700, 1550 (amide C=O), 1530, 1240, 1110, 1040, 840 cm^{-1}; ^1H NMR (270 MHz) δ = 2.10 (s, 3H, OAc), 3.80 (s, 3H, OMe), 4.20 (dd, J = 3.9, 11.6 Hz, 1H, H6), 4.26 (dd, J = 5.6, 11.6 Hz, 1H, H6′), 4.52 (dddd, J = 2.0, 2.0, 3.9, 5.6 Hz, 1H, H5), 4.90 (dddd J = 2.0, 3.4, 4.4, 8.3 Hz, 1H, H2), 5.62 (dd, J = 2.4, 4.4 Hz, 1H, H1), 5.78 (dddd, J = 2.0, 2.4, 3.4, 10.5 Hz, 1H, H3), 5.94 (ddd, J = 2.0, 2.0, 10.5 Hz, 1H, H4), 6.84 (ddd, J = 6.1, 9.3, 2.4 Hz, 2H, aromatic), 7.04 (ddd, J = 6.1, 9.2, 2.4 Hz, 2H, aromatic), 7.13 (d, J = 8.3 Hz, 1H, NH); ^{13}C NMR (100 MHz) δ = 20.78, 47.02, 55.63, 64.93, 67.04, 92.27, 95.27, 114.77, 117.88, 124.36, 127.72, 150.54, 155.51, 161.75, 170.79. Found: m/z 437.0184 (M^+). Calcd for $C_{17}H_{18}Cl_3NO_6$: M, 437.0198.

6-*O*-Acetyl-2,3-dideoxy-4-*O*-(1-imino-2,2,2-trichloroethyl)-α-D-*erythro*-hex-2-enopyranosyl 6-*O*-Acetyl-2,3,4-trideoxy-2-trichloroacetamido-α-D-*erythro*-hex-3-enopyranoside (8). In a similar manner to that described for **7**, **8** was prepared as an oil (8%), $[\alpha]_D^{22}$ +18° (c 0.14, $CHCl_3$). IR ν_{max} 3350 (N–H), 2950 (aromatic C–H), 1740 (C=O), 1720, 1670, 1510, 1240, 990, 830, 800 cm^{-1}; ^1H NMR (270 MHz) δ = 2.08 (s, 3H, OAc), 2.12 (s, 3H, OAc), 4.14—4.32 (m, 5H, H5′, H6, H6′, H6‴, H6⁗), 4.38 (m, 1H, H5), 4.86 (m, 1H, H2), 5.45—5.58 (m, 3H, H1′, H4′, H1), 5.68—6.20 (m, 4H, H2′, H3′, H3, H4), 6.99 (s, 1H, J = 9.2 Hz, NH), 8.50 (s, 1H, NH). Found: m/z 644.9546 ($M^+ + 1$). Calcd for $C_{20}H_{23}N_2O_9Cl_6$: M, 644.9533.

6-*O*-Acetyl-1,5-anhydro-2,3,4-trideoxy-2-trichloroacetamido-α-D-*erythro*-hex-2-enitol (9). In a similar manner to that described for **7**, **9** was prepared as an oil (25% yield), $[\alpha]_D^{21}$ +126° (c 0.95, $CHCl_3$). IR ν_{max} 3350 (N–H), 2950, 2860, 1740 (C=O), 1710, 1520, 1370, 1240, 1100, 1050, 830, 720 cm^{-1}; ^1H NMR (270 MHz) δ = 2.04 (s, 3H, OAc), 4.00—4.25 (m, 4H, H1, H1′, H6, H6′), 4.25—4.45 (m, 2H, H5, H2), 5.86 (ddd, 1H, J = 1.0, 2.2, 10.2 Hz, H3), 5.95 (ddd, 1H, J = 2.3, 3.8, 10.2 Hz, H4), 6.68 (d, 1H, J = 6.3 Hz, NH). Found: m/z 315.9908 ($M^+ + 1$). Calcd for $C_{10}H_{13}Cl_3NO_4$: M, 315.9908.

***p*-Methoxyphenyl 6-*O*-Acetyl-2-deoxy-2-trichloroacetamido-α-D-allopyranoside (10a) and *p*-Methoxyphenyl 6-*O*-Acetyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranoside (11a).** Trichloroacetamide **7** (30 mg, 0.068 mmol) was dissolved in a mixture of acetonitrile (0.4 ml) and ethyl acetate (0.4 ml) and the mixture was kept at −11 °C. To the mixture was added a solution of ruthenium tetroxide [80 μl, 0.043 equiv., prepared from ruthenium (III) chloride trihydrate (18 mg, 0.07 mmol) and sodium metaperiodate (321 mg, 1.50 mmol) in water (2 ml)]. The resulting mixture was vigorously stirred at that temperature for 4 min. Then the reaction was quenched by adding a saturated aqueous sodium thiosulfate solution (8 ml). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (5 ml) three times. The combined organic solution was concentrated in vacuo. The residue was charged on a column of silica gel (15 g, 1.5 cm×17 cm) with ethyl acetate–hexane (2 : 1). The starting material (10.7 mg, 35%) was recovered and further elution afforded **10a** (16.4 mg, 50% yield, 77% based on the consumed starting material **7**) as an oil, $[\alpha]_D^{24}$ +91° (c 0.96, $CHCl_3$). IR ν_{max} 3500 (O–H), 3450 (N–H), 2900 (aromatic C–H), 2350, 1720 (ester C=O), 1500 (aromatic C=C), 1370, 1240, 1220, 1120, 1050, 830 cm^{-1}; ^1H NMR (270 MHz) δ = 2.10 (s, 3H, OAc), 3.00 (d, J = 8.1 Hz, 1H, OH), 3.06 (d, J = 8.1 Hz, 1H, OH), 3.66 (ddd, J = 2.9, 8.1, 10.4 Hz, 1H, H4), 3.78 (s, 3H, OMe), 4.16 (ddd, J = 2.2, 4.6, 10.4 Hz, 1H, H5), 4.22—4.29 (m, 2H, H2,H3), 4.39 (dd, J = 2.2, 12.2 Hz, 1H, H6), 4.51 (dd, J = 4.6, 12.2 Hz, 1H, H6′), 5.46 (d, J = 4.2 Hz, 1H, H1), 6.82 (ddd, J = 6.1, 9.2, 2.4 Hz, 2H, aromatic), 7.00 (ddd, J = 6.1, 9.2, 2.4 Hz, 2H, aromatic), 7.50 (d, J = 8.1 Hz, 1H, NH); ^{13}C NMR (100 MHz) δ = 20.81, 51.00, 55.59, 60.42, 63.37, 66.12, 69.23, 92.08, 97.55, 114.67, 119.08, 150.28, 155.94, 161.77, 171.67. Found: m/z 395.0073 ($M^+ + 1 - AcOH - OH$). Calcd for $C_{15}H_{16}Cl_3NO_5$: M, 395.0092.

Further elution afforded **11a** (1.5 mg, 4.6% yield, 8.6% based on the consumed starting material **7**): Recrystallization from hexane gave an analytical sample, mp 132.0—133.0 °C; $[\alpha]_D^{23}$ +130° (c 0.52, $CHCl_3$). IR ν_{max} 3450 (O–H), 3350 (N–H), 2950 (aromatic C–H), 2350, 1740 (ester C=O), 1710, 1510 (aromatic C=C), 1370, 1240, 1220, 1100, 1050, 830 cm^{-1}; ^1H NMR (270 MHz) δ = 2.05 (s, 3H, OAc), 2.76 (d, J = 8.3 Hz, 1H, OH), 2.83 (d, J = 4.0 Hz, 1H, OH), 3.78 (s, 3H, OMe), 4.00—4.54 (m, 6H, H2, H3, H4, H5, H6, H6′), 5.48 (d, J = 3.6 Hz, 1H, H1), 6.84 (ddd, J = 5.9, 9.2, 2.4 Hz, 2H, aromatic), 7.00 (ddd, J = 5.9, 9.2, 2.4 Hz, 2H, aromatic), 7.07 (d, J = 8.9 Hz, 1H, NH). Found: m/z 427.0024 ($M^+ - 1 - CH_3CO$). Calcd for $C_{15}H_{16}Cl_3NO_7$: M, 426.9991.

***p*-Methoxyphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-α-D-allopyranoside (10b).** In a conventional manner, diol **10a** was acetylated to give **10b** as an oil, $[\alpha]_D^{22}$ +103° (c 0.44, $CHCl_3$). IR ν_{max} 3450 (N–H), 2940 (aromatic C–H), 2850, 1750 (ester C=O), 1720 (ester C=O), 1510 (aromatic C=C), 1440, 1370, 1220, 1100, 1040, 830, 750 cm^{-1}; ^1H NMR (270 MHz) δ = 2.00 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.20 (s, 3H, OAc), 3.80 (s, 3H, OMe), 4.19 (dd, J = 2.3, 12.2 Hz, 1H, H6), 4.29 (dd, J = 5.0, 12.2 Hz, 1H, H6′), 4.46 (ddd, J = 2.3, 5.0, 10.6 Hz, 1H, H5), 4.48 (ddd, J = 3.3, 4.3, 8.9 Hz, 1H, H2), 5.06 (dd, J = 3.0, 10.6 Hz, 1H, H4), 5.42 (d, J = 4.3 Hz, 1H, H1), 5.68 (dd, J = 3.0, 3.3 Hz, 1H, H3), 6.84 (ddd, J = 5.9, 9.2, 2.3 Hz, 2H, aromatic), 7.01 (ddd, J = 5.9, 9.2, 2.3 Hz, 2H, aromatic), 7.16 (d, J = 8.9 Hz, 1H, NH); MS m/z (rel intensity) 553 ($M^+ - 2$; 29), 519 (12), 432 (35), 397 (23), 331 (52), 271 (62), 253 (19), 235 (35), 217 (20), 185 (6), 151 (8), and 124 (100).

***p*-Methoxyphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-trichloroacetamido-α-D-galactopyranoside (11b).** In a conventional manner, diol **11a** was acetylated to give **11b** as an oil, $[\alpha]_D^{23}$ +108° (*c* 0.48, $CHCl_3$). IR ν_{max} 3350 (N–H), 2950 (aromatic C–H), 2350, 1750 (ester C=O), 1720, 1510 (aromatic C=C), 1440, 1380, 1230, 1050, 830 cm^{-1}; ^1H NMR (270 MHz) δ = 2.00 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.20 (s, 3H, OAc), 3.78 (s, 3H, OMe), 4.10 (dd, *J* = 7.1, 11.3 Hz, 1H, H6), 4.17 (dd, *J* = 5.9, 11.3 Hz, 1H, H6′), 4.42 (dd, *J* = 5.9, 7.1 Hz, 1H, H5), 4.65 (broad dd, *J* = 3.4, 8.9 Hz, 1H, H2), 5.51 (d, *J* = 3.4 Hz, 1H, H1), 5.46—5.54 (m, 2H, H3, H4), 6.84 (ddd, *J* = 2.4, 6.1, 9.3 Hz, 2H, aromatic), 7.01 (ddd, *J* = 2.4, 6.1, 9.3 Hz, 2H, aromatic), 6.97 (d, *J* = 9.5 Hz, 1H, NH). Found: *m/z* 438.0290 [$M^+ + 1 - (CH_3CO_2) \times 2$]. Calcd for $C_{17}H_{19}Cl_3NO_6$: M, 438.0276.

***p*-Methoxyphenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-acetamido-α-D-allopyranoside (12a).** To a solution **10a** (44.1 mg, 0.0932 mmol) in ethanol (2 ml), an aqueous sodium hydroxide (2 M, 375 μl, M = 1 mol dm^{-3}) was added and the mixture was stirred at 30 °C for 30 min. The reaction temperature was raised to 40 °C and the mixture was further stirred for 1.5 h. The mixture was concentrated in vacuo and to the residue was added acetic anhydride (1.5 ml), pyridine (1.5 ml), and a catalytic amount of DMAP. The mixture was stirred overnight at room temperature. The mixture was poured into ice-water and extracted three times with ethyl acetate. The organic layer was washed successively with saturated copper(II) sulfate solution (5 ml×2), saturated sodium hydrogencarbonate solution (5 ml×2), and brine (5 ml×2), dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified on a column of silica gel (40 g, 1.5 cm×5 cm) with ethyl acetate–hexane (2 : 3) to afford **12a** (42.8 mg, quant) as an oil, $[\alpha]_D^{24}$ +108° (*c* 0.96, $CHCl_3$). IR ν_{max} 3350 (N–H), 2950 (aromatic C–H), 2840, 1740 (ester C=O), 1680, 1660, 1520, 1510, 1460, 1440, 1370, 1240, 1220, 1180, 1100, 1040, 830, 800 cm^{-1}; ^1H NMR (270 MHz) δ = 1.99 (s, 3H, OAc), 2.01 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.21 (s, 3H, NHAc), 3.78 (s, 3H, OMe), 4.12 (ddd, *J* = 2.3, 12.2 Hz, 1H, H6), 4.24 (dd, *J* = 4.9, 12.2 Hz, 1H, H6′), 4.37 (ddd, *J* = 2.3, 4.9, 9.6 Hz, 1H, H5), 4.64 (ddd, *J* = 4.0, 4.0, 9.2 Hz, 1H, H2), 5.03 (dd, *J* = 3.0, 9.2 Hz, 1H, H4), 5.38 (d, *J* = 4.0 Hz, 1H, H1), 5.58 (dd, *J* = 3.0, 4.0 Hz, 1H, H3), 5.89 (d, *J* = 9.6 Hz, 1H, NH), 6.83 (ddd, *J* = 2.3, 5.9, 9.2 Hz, 2H, aromatic), 6.98 (dd, *J* = 2.3, 5.9, 9.2 Hz, 2H, aromatic); ^{13}C NMR (100 MHz) δ = 20.42, 20.57, 20.86, 23.03, 47.31, 55.54, 61.89, 63.82, 65.97, 68.38, 95.76, 114.54, 118.05, 149.99, 155.28, 169.04, 169.31, 170.42, 170.53. Found: *m/z* 454.1679 (M^+). Calcd for $C_{21}H_{28}NO_{10}$: M, 454.1711.

***N*-Acetyl-D-allosamine (1).** To a solution of **12a** (37.0 mg, 0.081 mmol) in methanol (2 ml) was added triethylamine (0.5 ml) and the mixture was stirred at room temperature for 7 h. Workup was carried out in a similar manner to that described for **4b** to give *p*-methoxyphenyl α-*N*-acetyl-D-allosaminide **12b** (23.2 mg, 87%). ^1H NMR (270 MHz) δ = 2.11 (s, 3H, NHAc), 3.78 (dd, *J* = 3.3, 10.6 Hz, 1H, H4), 3.80 (s, 3H, OMe), 3.82 (dd, *J* = 4.6, 12.2 Hz, 1H, H6), 3.89 (dd, *J* = 2.6, 12.2 Hz, 1H, H6′), 4.12 (ddd, *J* = 2.6, 4.6, 10.6 Hz, 1H, H5), 4.16 (dd, *J* = 3.3, 3.3 Hz, 1H, H3), 4.23 (dd, *J* = 3.3, 4.0 Hz, 1H, H2), 5.36 (d, *J* = 4.0 Hz, 1H, H1), 6.96 (ddd, *J* = 2.6, 5.3, 9.1 Hz, 2H, aromatic), 7.12 (ddd, *J* = 2.6, 5.3, 9.1 Hz, 2H, aromatic). This was employed for the next step without further purification.

The deacylated form **12b** as above (11.6 mg, 0.0353 mmol) was dissolved in a mixture of acetonitrile–water (4 : 1, 1 ml) which was cooled to 0 °C. To this was added diammonium cerium(IV) nitrate[27] (46.3 mg, 0.085 mmol, 2.4 mole ratio) and the resulting mixture was stirred for 130 min with ice-cooling. The reaction was quenched by adding 1,2,4-trimethoxybenzene (0.1 ml). The mixture was diluted with water (5 ml) and extracted with toluene (3 ml). The organic layer was washed twice with water (5 ml). The combined aqueous layer and washings were further extracted twice with toluene (1 ml) for the removal of traces of quinones. The aqueous layer was de-salted with AC-220-10 on Asahi Chemical Micro Acylyzer S1 and concentrated in vacuo. The residue was diluted with water (3 ml) and mixed with Celite (200 mg), and lyophilized. The residual powder was changed on a column of silica gel [Kanto Chemical, silica gel 60 (spherical, No. 37558-79), 2.5 ml, 0.4 cm×5 cm] and eluted with ethyl acetate–isopropyl alcohol–water (27 : 8 : 4). An elaborated fractionation afforded pure **1** (2.3 mg, 29.5%), $[\alpha]_D^{24}$ −68° (*c* 0.05, H_2O) [lit,[5] $[\alpha]_D^{24}$ −55° (*c* 0.2, H_2O), lit,[6] $[\alpha]_D^{24}$ −48.3° (*c* 0.74, H_2O, after 2 h of equilibration)]. ^1H NMR (400 MHz, D_2O) δ = 2.02 (s, NAc), 2.04 (s, NAc), 2.05 (s, NAc), 2.07 (s, NAc), 3.59—4.10 (m, H2-H6), 4.92 (d, *J* = 8.5 Hz, H1 of β-pyranoside), 5.12 (d, *J* = 3.9 Hz, H1 of α-pyranoside), 5.25 (d, *J* = 4.6 Hz, H1 of β-furanside), 5.43 (d, *J* = 4.9 Hz, H1 of α-furanoside). Its NMR spectrum was in good accordance with that reported previously.[28]

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