113. Synthesis of Allosamidin

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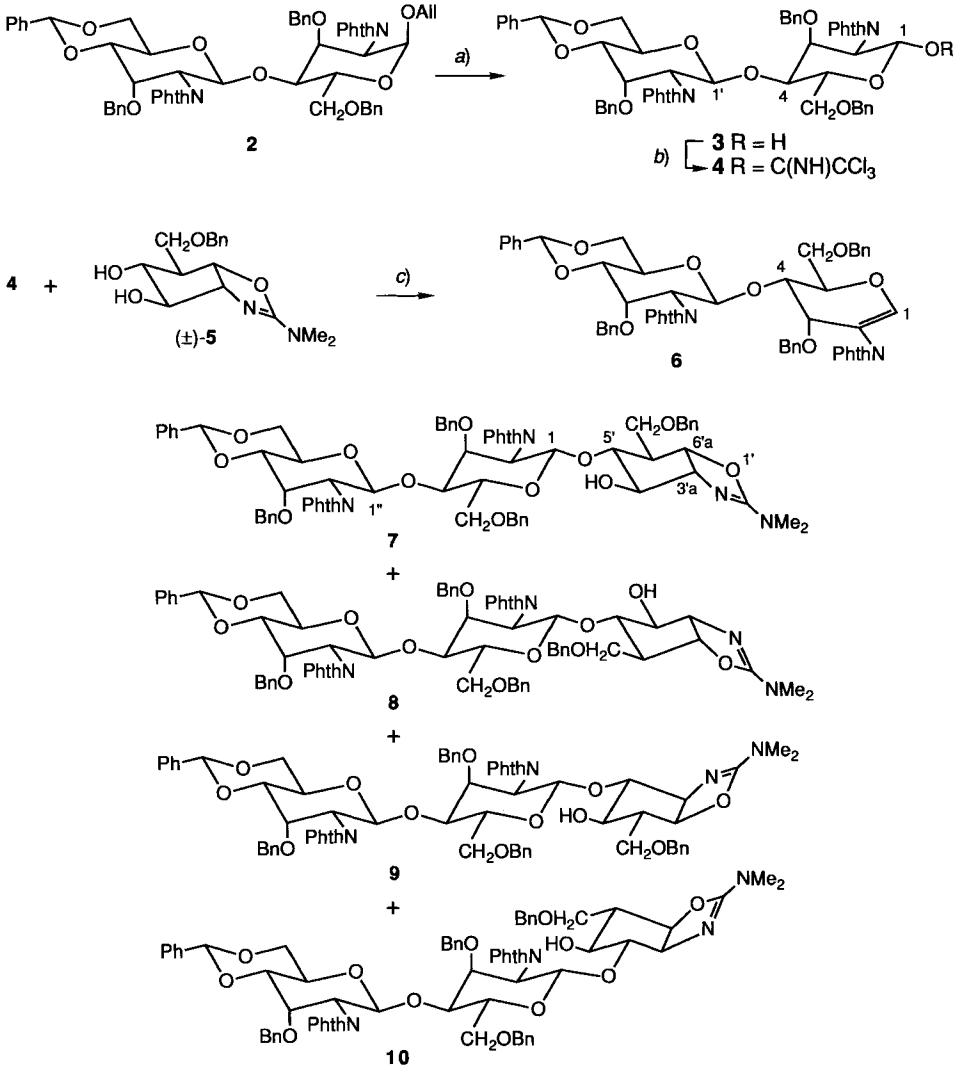
The previously prepared disaccharide **2** was deprotected (→ **3**) and transformed into the trichloroacetimidate **4**. In the presence of Me_3SiOTf, **4** reacted regioselectively with the racemic allosamizoline benzyl ether **5**, to yield (61%) the pseudotrisaccharides **7**–**10** (44:40:9:7) and the elimination product **6** (*Scheme 1*). Selective dephthaloylation ($MeNH_2$, MeOH) of **7** and **8**, followed by acetylation, gave **12** (73%) and **13** (74%), respectively (*Scheme 2*); harsher conditions ($NH_2NH_2 \cdot H_2O$, EtOH, reflux), followed by acetylation, transformed **7** into **11**. Deacetylation of **11**–**13** yielded **14**–**16**, respectively. Allosamidin (**1**) was obtained in high yield by hydrogenation of **15** under acidic conditions (*Scheme 3*). Similarly, **16** and **14** were transformed into **17** and **18**, respectively. Preliminary data on the inhibition of endochitinases by **1** and **17** are reported.

Introduction. – In the preceding paper [1], we have described the synthesis of the protected disaccharide **2** (*Scheme 1*), corresponding to the disaccharide moiety of allosamidin (**1**), the first representative of a new class of endochitinase inhibitors. Here, we report on the synthesis of allosamidin and of two new analogues, **17** and **18** (see *Scheme 3*). The synthesis is based on the regioselective glycosidation of the partially protected racemate (±)-**5** [2], corresponding to allosamizoline, the aglycon of allosamidin.

Results and Discussion. – The best results in the glycosidation leading to **2** had been realized with the trichloroacetimidate method [3]. For this reason, we chose the trichloroacetimidate **4** (*Scheme 1*) as the glycosyl donor which was obtained in high yield from the allyl glycoside **2** after usual deprotection [4] (→ **3**) and reaction with CCl_3CN and K_2CO_3 in CH_2Cl_2. In keeping with previous results [1], we obtained exclusively the β-D-anomers of the hemiacetal **3** and the imidate **4**.

Glycosidation by **4** of the partially protected racemate (±)-**5** [2], promoted by Me_3SiOTf, afforded the four pseudotrisaccharides **7**/**8**/**9**/**10** in an overall yield of 61% and in a ratio of 44:40:9:7. No α-D-glycosides and only traces of pseudopentasaccharides were obtained. The main by-product was the aminoglycal **6**. Similar elimination products have been isolated in the synthesis of **2** [1]. The regioselectivity of the glycosidation (5:1) was as expected, favouring OH–C(5′), which possesses only one vicinal, electronegative substituent, while OH–C(4′) possesses two such neighbours. One of them is part of the dihydro-oxazole moiety, which may react with Me_3SiOTf, leading to a further decrease of electron density at OH–C(4′) and of its nucleophilic character. An attempt to increase the selectivity of the glycosidation by performing it at −30° only lowered the overall yield. Determination of the absolute configuration of the allosamizoline moiety of the pairs of diastereoisomers **7**/**8** and **9**/**10** was impossible at this stage and had to be derived from the conversion of **7** to **1**.

Scheme 1



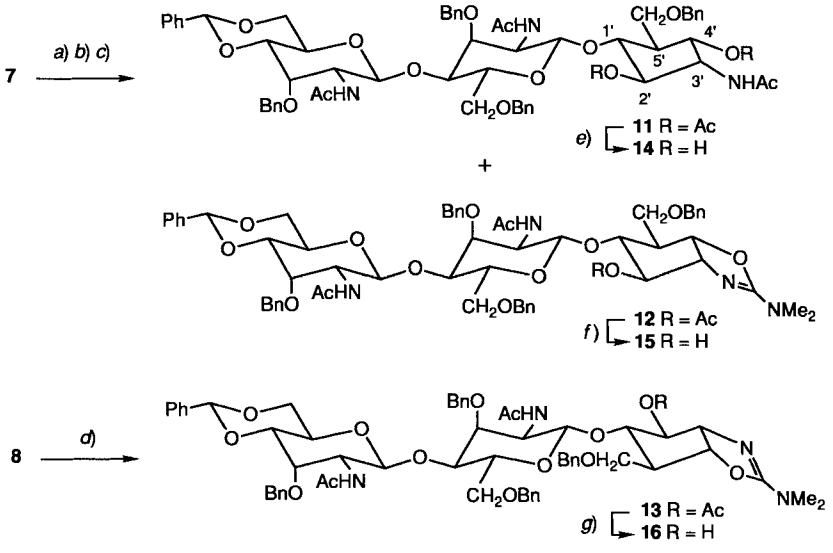
a) 1. (Cycloocta-1,5-diene)bis(methyldiphenylphosphine)iridium hexafluorophosphate, H_2, THF, 3 h, r.t.; 2. HgO, $HgCl_2$, acetone/H_2O 9:1, 1 h, r.t.; 75%. *b*) CCl_3CN, K_2CO_3, CH_2Cl_2, 16 h, r.t.; 90%. *c*) Me_3SiOTf, 4-Å molecular sieves, CH_2Cl_2, 20 min, 0°; **6**, 17%; **7**, 27%; **8**, 24.5%; **9** and **10**, 5.5 and 4.3% (or *vice versa*).

The OH group of the hemiacetal **3** absorbs at 3590 cm^{-1}. In the ^{1}H-NMR spectrum of **3**, H–C(1) resonates at 6.20 ppm as a *dd*(J(1,2) = 8.6 Hz, J(1,OH–C(1)) = 5.3 Hz). The imino group of **4** is characterized by IR bands at 3330 cm^{-1} (NH) and at 1675 cm^{-1} (C=N). NH resonates at 8.66 and H–C(1) at 7.15 ppm (*d*, J(1,2) = 9.1 Hz). H–C(1) of **6** appears as a *s* at 6.59 ppm. The ^{13}C-NMR spectrum of **6** is characterized by the downfield shift of C(1) (*d*, 145.6 ppm) and of C(2) (*s*, 107.8 ppm). The OH group of **7** and of **8** absorbs at 3480 and 3520 cm^{-1}, respectively. The NMR spectra of **7** and **8** both exhibit the characteristic signals of the aminocyclitol (±)-**5**: H–C(6'a) resonates at low field (4.64 ppm for **7**, 4.66 ppm for **8**) and is characterized by a large coupling constant with H–C(3'a)

(J(3'a,6'a) = 9.2 Hz for **7** and **8**); H–C(5') resonates at high field (2.08 ppm for **7**, 2.13 ppm for **8**) as a *m*; the signals of Me_2N appear at 2.84 and 2.80 ppm for **7** and **8**, respectively; C(2') resonates at low field (161.4 ppm for **7**, 161.7 ppm for **8**). In the ^{1}H-NMR spectrum of **7**, H–C(1) resonates at 5.95 ppm as *d* with J(1,2) = 8.7 Hz, typical for a 1,2-*trans*-configurated glycosidic bond. OH–C(4') resonates at 4.54–4.49 ppm and H–C(4') at 3.87 ppm as a *m* which is transformed into a *dd* after exchange with D_2O. In the ^{1}H-NMR spectrum of **8**, the signal of H–C(1) is a *d* at 5.99 ppm (J(1,2) = 8.7 Hz). The signal of OH–C(4') appears at 4.51–4.44 ppm. It disappears upon addition of D_2O, and the signal of H–C(4') is simplified (*ddd* → *dd*). The chemical shifts of H–C(1), H–C(1''), H–C(3), and H–C(3'') of **7** and **8** are in agreement with a conformation of the 2- and 2''-phthalimido group analogous as the one observed for the 2-phthalimido-β-D-allopyranosides [1]. Similarly to **2**, the 2 H–C(6) signals of **8** appear at high field (3.53 and 3.45 ppm). The shielding effect, which may be due to the 2''-phthalimido group, is even stronger for the 2 H–C(6) signals of **7** (3.35 and 3.19 ppm). This indicates a conformation of the disaccharide moiety of **7** and **8** which is similar to the one of **2** [1]. The signals for the 2 CH–C(6') are slightly shifted for **8** (3.64 and 3.48 ppm *vs.* 3.70 and 3.65 ppm in (±)-**5**) and more strongly shifted for **7** (3.41 and 3.33 ppm). An unambiguous determination of the conformation of the glycosidic bond between the disaccharide moiety and the allosamizoline moiety was, however, not possible, as these chemical-shift differences may be due to the 6-*O*-benzyl group, or to the 2-phthalimido group. For **7** and **8**, NOE's between H–C(1'') and H–C(5'') and between H–C(1'') and H–C(4) (same intensity) confirm previous observations [1] and suggest that the torsion angles Ψ(H–C(1'')–O–C(4)) and Ψ(H–C(4)–O–C(1'')) of the glycosidic bond of the disaccharide moiety are *ca.* 0 and −30°, respectively. For both diastereoisomers, no NOE was observed between H–C(1) and any protons of the aminocyclitol moiety.

Dephthaloylation of **7** and **8** was the critical step in the sequence of deprotection and *N*-acetylation, as mild conditions were necessary to avoid concomitant hydrolysis of the dihydro-oxazole group. Moreover, the progression of the reaction was difficult to follow, as the intermediates, the side products, and the desired diamines had similar R_f values. In a first attempt, **7** was treated for 4 h with excess $NH_2NH_2 \cdot H_2O$ in refluxing EtOH [5] and then acetylated. This gave the triacetamide **11** (*Scheme 2*) in 61%. Using only 2 equiv. of

Scheme 2



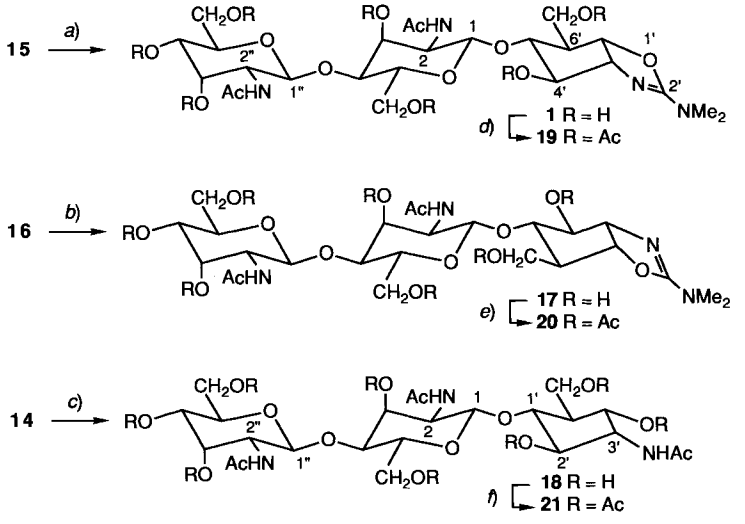
a) 1. $NH_2NH_2 \cdot H_2O$, EtOH, 4 h, reflux; 2. pyridine, Ac_2O, 4-$(Me_2N)C_5H_4N$, 10 h, r.t.; **11**, 61%. *b*) 1. $NH_2NH_2 \cdot H_2O$, EtOH, 45 min, reflux; 2. pyridine, Ac_2O, 4-$(Me_2N)C_5H_4N$, 10 h, r.t.; **11**, 12%; **12**, 17%. *c*) 1. 40% aq. $MeNH_2$, MeOH, 48 h, r.t.; 2. pyridine, Ac_2O, 4-$(Me_2N)C_5H_4N$, 10 h, r.t.; **12**, 73%. *d*) As *c*); **13**, 74%. *e*) NaOMe, MeOH, 10 h, r.t., 97%. *f*) NaOMe, MeOH, 5 h, r.t., 96%. *g*) NaOMe, MeOH, 5 h, r.t., 93%.

$NH_2NH_2 \cdot H_2O$ and shortening the reaction time to 45 min, led, after acetylation, in low yields to the diacetamide **12** and to **11**. The use of hydrazine acetate [6] gave complex mixtures. Treatment of **7** with $BuNH_2$ in refluxing MeOH [7], followed by acetylation, yielded inseparable mixtures of the desired **12** and *N*-butylphthalamide derivatives. The desired bis-acetamide **12** was finally obtained (73%) by effecting the dephthaloylation with aq. $MeNH_2$ in EtOH [8], followed by acetylation. The diastereoisomer **8** was treated similarly to yield 74% of **13**. Deacetylation under *Zemplén* conditions of **11**, **12**, and **13** gave **14**, **15**, and **16**, respectively, in high yields.

The IR spectra of **11**–**13** show the disappearance of the strong phthalimido band at 1720 cm^{-1}. In the ^{1}H-NMR spectrum of **11**, NH–C(3′) appears at 6.01 ppm (J(NH,3′) = 8.8 Hz), while NH–C(2″) and NH–C(2) resonate at 5.82 and 5.51 ppm. The H–C(4′) signal appears at 5.33 ppm (shifted upfield by 1.3 ppm as compared to H–C(3′a) of **7**). The 5 Ac groups give rise to *s* at 2.05, 1.99, 1.96, 1.62, and 1.55 ppm. In the ^{13}C-NMR, there are 5*s* in the typical C=O region, and 5*q* between 23 and 20.8 ppm, characteristic for *Me*CO. The ^{1}H-NMR spectra of **12** and **13** exhibit the typical signal of Me_2N (2.90 ppm for **12** and 2.89 ppm for **13**), the high-field resonance of H–C(4′) (5.26 ppm for **12** and 5.10 ppm for **13**) confirming the regioselectivity of the glycosidation, and 3*s* for the Ac groups. The C(2′) signals of **12** and **13** appear as *s* at 161.7 and 161.9 ppm, respectively, and $(CH_3)_2N$ resonates at 37.6 (**12**) and 37.5 ppm (**13**).

Hydrogenolysis of **15** under acidic conditions yielded allosamidin (**1**) (*Scheme 3*) in 95% yield. Similarly, **16** was deprotected to give the diastereoisomer **17**. Hydrogenolysis of **14**, albeit more sluggish, afforded **18**, equally in high yield. The spectroscopic data of the synthetic allosamidin (**1**) were in agreement with the one reported by *Sakuda et al.* [9] and could not be distinguished from those of an authentic sample[1]). Allosamidin (**1**) and the two analogues **17** and **18** were peracetylated to **19**, **20**, and **21**, respectively. The

Scheme 3



a) H_2 (7 bar), 10% Pd/C, MeOH/AcOH 9:1, 36 h, r.t.; 95%. *b*) As *a*); 95%, *c*) H_2 (7 bar), 10% Pd/C, MeOH/AcOH 9:1, 72 h, r.t.; 92%. *d*) Pyridine, Ac_2O, 4-$(Me_2N)C_5H_4N$, 14 h, r.t.; 97%. *e*) As *d*); 96%. *f*) As *d*); 97%.

[1]) We thank *Lilly* Research Laboratories, *Eli Lilly & Co.*, Indianapolis, Indiana 46285, USA, for providing an authentic sample of allosamidin.

spectroscopic data of **19** could again not be distinguished from those of a similarly prepared acetate of authentic allosamidin. The ^{1}H-NMR data of **1**, **17**, and **18** are collected and assigned in *Table 1*, the ^{1}H-NMR data of their peracetates **19–21** in *Table 2*, and the ^{13}C-NMR data of **1** and **17–21** in *Table 3*.

Table 1. *^{1}H-NMR* (D_2O/0.3% CD_3CO_2D) *Data for* **1**, **17**, *and* **18**. δ in ppm, J in Hz.

	1	**17**	**18**
H–C(6′a)[a]) or –C(4′)[b])	5.44 (*dd*, *J* = 5, 9)	5.45 (*dd*, *J* = 5, 9)	4.02 (*dd*, *J* = 3, 6)
H–C(3′a)[a]) or –C(3′)[b])	4.44 (*dd*, *J* = 4, 9)	4.42 (*dd*, *J* = 4, 9)	3.94 (*dd*, *J* = 6, 10)
H–C(4′)[a]) or –C(2′)[b])	4.35 (*dd*, *J* = 4, 6)	4.2 (*dd*, *J* = 4, 6)	4,17 (*dd*, *J* = 7, 10)
H–C(5′)[a]) or –C(1′)[b])	3.94 (*dd*, *J* = 6, 7)	4.07 (*dd*, *J* = 6, 7)	3.79 (*dd*, *J* = 6, 7)
H–C(6′)[a]) or –C(5′)[b])	2.61 (*m*)	2.65 (*m*)	2.01 (*m*)
CH–C(6′)[a]) or –C(5′)[b])	3.87 (*dd*, *J* = 5, 12);	3.94 (*dd*, *J* = 5, 12);	3.75 (*dd*, *J* = 5, 12);
	3.74 (*dd*, *J* = 7, 12)	3.82 (*dd*, *J* = 7, 12)	3.69 (*dd*, *J* = 6, 12)
Me_2N	3.15, 3.14 (2*s*)	3.15, 3.13 (2*s*)	–
H–C(1)	4.85 (*d*, *J* = 9)	4.85 (*d*, *J* = 9)	4.86 (*d*, *J* = 9)
H–C(2)	3.91 (*dd*, *J* = 3, 9)	3.87 (*dd*, *J* = 3, 9)	3.95 (*dd*, *J* = 3, 9)
H–C(3)	4.41 (*t*, *J* = 3)	4.41 (*t*, *J* = 3)	4.42 (*t*, *J* = 3)
H–C(4)	3.79 (*dd*, *J* = 3, 10)	3.80 (*dd*, *J* = 3, 10)	3.80 (*dd*, *J* = 3, 10)
H–C(5)	3.96 (*ddd*, *J* = 2, 7, 10)	3.91 (*ddd*, *J* = 2, 6, 10)	3.93 (*ddd*, *J* = 2, 7, 10)
H–C(6)	3.88 (*dd*, *J* = 2, 12),	3.86 (*dd*, *J* = 2, 12),	3.85 (*dd*, *J* = 2, 12),
	3.68 (*dd*, *J* = 7, 12)	3.69 (*dd*, *J* = 6, 12)	3.67 (*dd*, *J* = 7, 12)
H–C(1″)	4.87 (*d*, *J* = 9)	4.92 (*d*, *J* = 9)	4.85 (*d*, *J* = 9)
H–C(2″)	3.95 (*dd*, *J* = 3, 9)	3.95 (*dd*, *J* = 3, 9)	3.93 (*dd*, *J* = 3, 9)
H–C(3″)	4.12 (*t*, *J* = 3)	4.11 (*t*, *J* = 3)	4.10 (*t*, *J* = 3)
H–C(4″)	3.75 (*dd*, *J* = 3, 10)	3.75 (*dd*, *J* = 3, 10)	3.74 (*dd*, *J* = 3, 10)
H–C(5″)	3.83 (*ddd*, *J* = 2, 5, 10)	3.83 (*ddd*, *J* = 2, 5, 10)	3.83 (*ddd*, *J* = 2, 5, 10)
H–C(6″)	3.92 (*dd*, *J* = 2, 12),	3.92 (*dd*, *J* = 2, 12),	3.91 (*dd*, *J* = 2, 12),
	3.80 (*dd*, *J* = 5, 12)	3.79 (*dd*, *J* = 5, 12)	3.79 (*dd*, *J* = 5, 12)
Ac	2.15, 2.13 (2*s*)	2.13, 2.11 (2*s*)	2.12 (*s*); 2.10 (2*s*)

[a]) For **1** and **17**. [b]) For **18**.

Table 2. *^{1}H-NMR* ($CDCl_3$) *Data for* **19–21**. δ in ppm, J in Hz.

	19	**20**	**21**
H–C(6′a)[a]) or –C(4′)[b])	4.76 (*dd*, *J* = 6, 9)	4.82 (*dd*, *J* = 5, 9)	4.96 (*dd*, *J* = 3, 6)
H–C(3′a)[a]) or –C(3′)[b])	4.27 (*dd*, *J* = 4, 9)	4.39 (*dd*, *J* = 3, 9)	4.37 (*td*, *J* = 6, 9)
H–C(4′)[a]) or –C(2′)[b])	5.23 (*dd*, *J* = 4, 7)	5.18 (*dd*, *J* = 3, 5)	5.38 (*dd*, *J* = 7, 9)
H–C(5′)[a]) or –C(1′)[b])	3.81 (*dd*, *J* = 7, 9)	4.03–3.94 (*m*)	3.82 (*t*, *J* = 7)
H–C(6′)[a]) or –C(5′)[b])	2.5 (*m*)	2.54 (*m*)	2.28 (*m*)
CH–(6′)[a]) or –C(5′)[b])	4.41 (*dd*, *J* = 5, 12);	4.26 (*dd*, *J* = 5, 12);	4.42 (*dd*, *J* = 5, 11);
	4.23–4.17 (*m*)	4.19–4.05 (*m*)	4.23–4.07 (*m*)
NH–C(3′)	–	–	5.96 (*d*, *J* = 9)
Me_2N	2.92 (*s*)	2.91 (*s*)	–
H–C(1)	4.75 (*d*, *J* = 8)	4.66 (*d*, *J* = 9)	4.62 (*d*, *J* = 8)
H–C(2)	4.09–4.01 (*m*)	3.89 (*td*, *J* = 8, 3)	4.23–4.07 (*m*)
H–C(3)	5.65 (*t*, *J* = 3)	5.77 (*t*, *J* = 3)	5.63 (br. *s*)
H–C(4)	3.62 (*dd*, *J* = 3, 8)	3.53 (*dd*, *J* = 3, 10)	3.59 (*dd*, *J* = 3, 9)
H–C(5)	3.99–3.92 (*m*)	3.86 (*td*, *J* = 3, 10)	3.89 (*td*, *J* = 3, 9)
H–C(6)	4.58 (*dd*, *J* = 4, 12);	4.62 (*dd*, *J* = 3, 12);	4.66 (*dd*, *J* = 3, 12);
	4.09–4.01 (*m*)	4.03–3.94 (*m*)	3.99–3.94 (*m*)

Table 2 (cont.)

	19	**20**	**21**
NH–C(2)	6.35 (*d*, *J* = 8)	6.80 (*d*, *J* = 7)	6.14 (*d*, *J* = 9)
H–C(1″)	4.53 (*d*, *J* = 9)	4.56 (*d*, *J* = 9)	4.51 (*d*, *J* = 8)
H–C(2″)	4.23–4.17 (*m*)	3.95 (*dd*, *J* = 3, 9)	4.23–4.07 (*m*)
H–C(3″)	5.53 (*t*, *J* = 3)	5.62 (*t*, *J* = 3)	5.53 (*t*, *J* = 3)
H–C(4″)	4.85 (*dd*, *J* = 3, 10)	4.84 (*dd*, *J* = 3, 10)	4.87 (*dd*, *J* = 3, 10)
H–C(5″)	3.99–3.92 (*m*)	4.03–3.94 (*m*)	3.99–3.94 (*m*)
H–C(6″)	4.13 (*dd*, *J* = 5, 12); 4.09–4.01 (*m*)	4.19–4.05 (*m*); 4.19–4.05 (*m*)	4.23–4.07 (*m*); 4.23–4.07 (*m*)
NH–C(2″)	6.27 (*d*, *J* = 9)	6.33 (*d*, *J* = 9)	6.29 (*d*, *J* = 8)
Ac	2.18, 2.15, 2.12, 2.11, 2.09, 2.07, 1.97, 1.96, 1.93 (9*s*)	2.17, 2.15, 2.11, 2.10, 2.09, 2.07, 1.96, 1.95, 1.91 (9*s*)	2.18, 2.17, 2.15, 2.11, 2.10, 2.09 (6 H), 1.98, 1.97 (6 H), 1.96 (9*s*)

[a]) For **19** and **20**. [b]) For **21**.

Table 3. *^{13}C-NMR Assignments of* **1** *and* **17**–**21**. δ in ppm.

	1[c])	**17**[c])	**18**[c])	**19**[d])	**20**[d])	**21**[d])
C(6′a)[a]) or C(4′)[b])	87.7 (*d*)	88.5 (*d*)	69.9 (*d*)	80.3 (*d*)	81.8 (*d*)	72.6 (*d*)
C(3′a)[a]) or C(3′)[b])	65.1 (*d*)	65.5 (*d*)	56.7 (*d*)	71.5 (*d*)	71.9 (*d*)	59.2 (*d*)
C(4′)[a]) or C(2′)[b])	81.3 (*d*)	81.9 (*d*)	78.2 (*d*)	81.7 (*d*)	84.9 (*d*)	78.2 (*d*)
C(5′)[a]) or C(1′)[b])	85.9 (*d*)	84.5 (*d*)	85.3 (*d*)	81.1 (*d*)	80.9 (*d*)	80.8 (*d*)
C(6′)[a]) or C(5′)[b])	52.3 (*d*)	52.0 (*d*)	52.8 (*d*)	48.9 (*d*)	48.8 (*d*)	48.8 (*d*)
CH_2–C(6′)[a]) or –C(5′)[b])	60.1 (*t*)	60.1 (*t*)	61.7 (*t*)	61.1 (*t*)	61.5 (*t*)	62.4 (*t*)
C(2′)[a])	161.4 (*s*)	161.5 (*s*)	–	161.8 (*s*)	161.7 (*s*)	–
Me_2N	38.4, 38.2 (2*q*)	38.6, 38.4 (2*q*)	–	37.7 (2*q*)	37.8 (2*q*)	–
C(1)	100.7 (*d*)	100.4 (*d*)	100.2 (*d*)	97.7 (*d*)	97.6 (*d*)	99.9 (*d*)
C(2)	53.4 (*d*)	53.5 (*d*)	53.4 (*d*)	51.4 (*d*)	52.1 (*d*)	50.9 (*d*)
C(3)	69.8 (*d*)	69.9 (*d*)	69.8 (*d*)	69.3 (*d*)	69.7 (*d*)	69.8 (*d*)
C(4)	77.7 (*d*)	77.5 (*d*)	75.8 (*d*)	74.2 (*d*)	74.3 (*d*)	73.9 (*d*)
C(5)	73.4 (*d*)	73.6 (*d*)	73.3 (*d*)	71.9 (*d*)	71.7 (*d*)	72.2 (*d*)
C(6)	61.8 (*t*)	61.8 (*t*)	61.8 (*t*)	62.6 (*t*)	62.5 (*t*)	62.4 (*t*)
C(1″)	101.4 (*d*)	101.4 (*d*)	101.4 (*d*)	100.1 (*d*)	99.9 (*d*)	100.2 (*d*)
C(2″)	53.7 (*d*)	53.8 (*d*)	53.7 (*d*)	50.7 (*d*)	50.9 (*d*)	50.7 (*d*)
C(3″)	70.9 (*d*)	71.0 (*d*)	70.9 (*d*)	70.0 (*d*)	70.0 (*d*)	69.9 (*d*)
C(4″)	67.2 (*d*)	67.3 (*d*)	67.2 (*d*)	66.5 (*d*)	66.5 (*d*)	66.5 (*d*)
C(5″)	74.4 (*d*)	74.4 (*d*)	74.4 (*d*)	70.1 (*d*)	70.2 (*d*)	70.1 (*d*)
C(6″)	61.8 (*t*)	61.8 (*t*)	61.7 (*t*)	62.6 (*t*)	62.0 (*t*)	62.2 (*t*)
Me*C*O	174.8 174.6 (2*s*)	174.9, 174.7 (2*s*)	175.1, 174.8, 174.6 (3*s*)	171.5, 171.1, 171.0, 170.2, 170.0, 169.8 169.6, 169.2, 169.1 (9*s*)	[e])	[e])
*Me*CO	22.8 (*q*)	23.0, 22.9 (2*q*)	22.9, 22.8, 22.7 (3*q*)	23.0, 22.9, 21.2, 21.1 21.0, 20.9, 20.8, 20.7, 20.5 (9*q*)	23.0 (2*q*); 21.1–20.5 (several *q*)	23.0 (2*q*); 21.1–20.5 (several *q*)

[a]) For **1**, **17**, **19**, and **20**. [b]) For **18** and **21**. [c]) In D_2O/0.3% CD_3CO_2. [d]) In $CDCl_3$. [e]) Not measured.

Allosamidin (**1**) inhibited *Artemia salina* endochitinase to 84% (0.25 μM final conc.) and the *Streptomyces* enzyme to about the same extent as determined by *Koga et al.* [10]. The diastereoisomer **17** inhibited *Artemia salina* endochitinase to 62% (0.25 μM final conc.), but had no effect on the *Streptomyces* enzyme [11].

We thank Prof. Dr. *K. D. Spindler* and Dr. *M. Spindler-Barth* for the inhibition studies, Mr. *M. Vöhler*, Mr. *D. Nanz*, and Dr. *H. Bircher* for their help with the NMR experiments, Dr. *A. Schäfer* for the mass spectra with electrospray ionisation, and the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, for generous support.

Experimental Part

General. See [1]. TLC: imidate **4** was detected by spraying the plates with a 2% 4-(4-nitrobenzyl)pyridine soln. in acetone and heating at 100° [12]. ^{1}H-NMR Spectra: in D_2O, DHO (δ 4.8 ppm) as internal standard; in ambiguous cases, assignments by selective homonuclear decoupling experiments, 1D-TOCSY [13], or ^{1}H,^{1}H-TOCSY (^{1}H, 400 or 600 MHz) with various mixing times; coupling constants J(H,H) of **1**, **17**, and **18** from J-resolved 2D spectra. ^{13}C-NMR Spectra: in D_2O, dioxane (δ 67.4 ppm) as external reference; assignments by ^{1}H,^{13}C-HMQC spectra (^{1}H, 400 or 600 MHz) [14]. Mass spectra: FAB on a *Varian-711* spectrometer, ESI (electrospray ionization [15]) on a *Finnigan MAT TSQ 700* spectrometer.

3,6-Di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-allopyranosyl)-2-deoxy-2-phthalimido-β-D-allopyranose (**3**). [Ir(cyclooctа-1,5-diene)(PMePh$_2$)$_2$]PF$_6$ (0.1 equiv.) was added under N_2 to a stirred soln. of **2** (3.618 g, 3.62 mmol) in dry THF (500 ml). The orange soln. was degassed and left under H_2 until the colour turned yellow (*ca.* 1 min). The soln. was then degassed again and left under N_2 for 3 h. Evaporation gave a foam which was dissolved in acetone (360 ml) and H_2O (40 ml). HgO (1.49 g, 6.88 mmol) and $HgCl_2$ (1.67 g, 6.14 mmol) were added. The mixture was stirred for 1 h and then filtered through *Celite*. The acetone was evaporated to give a suspension which was extracted with AcOEt. The org. layer was washed with sat. aq. KI soln. (2×) and H_2O, dried, and evaporated. FC (toluene/AcOEt 3:1) afforded **3** (2.61 g, 75%). White foam. R_f(toluene/AcOEt 4:1) 0.16. $[\alpha]_D^{25} = -127.8$ ($c = 0.8$, $CHCl_3$). IR ($CHCl_3$): 3590*w*, 3570*w* (sh), 3090*w* (sh), 3060*w* (sh), 3040*w*, 3000*w*, 1755*m*, 1720*m* (sh), 1710*s*, 1685*w* (sh), 1610*w*, 1490*w*, 1465*w* (sh), 1450*w*, 1380*s*, 1360*m* (sh), 1310*m*, 1260*w*, 1160*m* (sh), 1135*m*, 1005*s* (sh), 1075*s* (br.), 1040*s*, 1025*s*, 1010*s* (sh), 970*m* (sh), 915*w*, 895*w*, 860*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.78–7.63 (*m*, 8 arom. H); 7.53–7.50 (*m*, 2 arom. H); 7.43–7.38 (*m*, 3 arom. H); 7.29–7.19 (*m*, 5 arom. H); 7.09–7.06 (*m*, 4 arom. H); 6.99–6.76 (*m*, 5 arom. H); 6.27 (*d*, $J = 8.5$, H–C(1′)); 6.20 (*dd*, $J = 8.6$, 5.3, with D_2O *d*, $J = 8.6$, H–C(1)); 5.56 (*s*, PhC*H*); 4.85 (*d*, $J = 12.2$, PhC*H*); 4.65 (*d*, $J = 11.9$, PhC*H*); 4.54–4.47 (*m*, 2 PhC*H*, H_{eq}–C(6′)); 4.38 (*d*, $J = 11.7$, PhC*H*); 4.34 (*t*, $J = 2.6$, H–C(3′)); 4.32 (*ddd* (= '*td*'), $J = 10.0$, 5.1, H–C(5′)); 4.21–4.12 (*m*, PhC*H*, H–C(3), H–C(5), H–C(2′)); 3.96 (*dd*, $J = 10.0$, 2.5, H–C(4)); 3.92 (*dd*, $J = 8.7$, 2.6, H–C(2)); 3.84 (*dd*, $J = 9.4$, 2.3, H–C(4′)); 3.81 (*t*, $J = 10.0$, H_{ax}–C(6′)); 3.55 (*dd*, $J = 10.5$, 6.6, H–C(6)); 3.49 (*dd*, $J = 10.5$, 2.0, H–C(6)); 3.26 (*d*, $J = 5.3$, exchange with D_2O, OH–C(1)). ^{13}C-NMR (50 MHz, $CDCl_3$): 167.9 (*s*, 2 CO); 167.7 (*s*, CO); 167.5 (*s*, CO); 138.2 (*s*); 137.9 (*s*); 137.4 (*s*); 137.3 (*s*); 134.0 (*d*); 133.7 (*d*); 133.4 (*d*); 132.2 (*s*); 131.7 (*s*); 131 (*s*); 129.1–122.9 (*m*, arom. C); 102 (*d*, PhCH); 98.0 (*d*, C(1′)); 90.4 (*d*, C(1)); 79.9 (*d*, C(4′)); 76.8 (*d*); 76.5 (*d*); 74.1 (*d*, *t*, 2 C); 74.0 (*t*, PhCH_2); 72.9 (*t*, PhCH_2); 72.4 (*d*, C(5)); 70 (*t*, C(6)); 69.1 (*t*, C(6′)); 64 (*d*, C(5′)); 57.8 (*d*, C(2′)); 56.8 (*d*, C(2)). Anal. calc. for $C_{56}H_{50}N_2O_{13}$ (959.017): C 70.14, H 5.26, N 2.92; found: C 70.36, H 4.99, N 2.82.

3,6-Di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-allopyranosyl)-2-deoxy-2-phthalimido-β-D-allopyranosyl Trichloroacetimidate (**4**). CCl_3CN (1.37 ml, 13.61 mmol) and powdered anh. K_2CO_3 (1.81 g, 13.1 mmol) were added to a stirred soln. of **3** (2.61 g, 2.72 mmol) in CH_2Cl_2 (80 ml). After 16 h, the mixture was filtered through *Celite* and the filtrate evaporated. FC (AcOEt/hexane 2:5) gave **4** (2.7 g, 90%). Colourless oil. R_f(AcOEt/hexane 1:2) 0.22. IR ($CHCl_3$): 3330*w*, 3090*w* (sh), 3060*w* (sh), 3000*w*, 2920*w*, 2855*w*, 1775*w*, 1720*m* (sh), 1710*s*, 1675*m*, 1650*w* (sh), 1645*w* (sh), 1635*w* (sh), 1605*w*, 1585*w*, 1555*w*, 1490*w*, 1465*w* (sh), 1450*w*, 1380*m*, 1360*m* (sh), 1310*m*, 1260*w*, 1160*m* (sh), 1130*m*, 1095*s* (sh), 1065*s* (br.), 1040*s* (sh), 1000*m* (sh), 965*m* (sh), 910*w*, 890*w*, 870*w*, 830*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 8.66 (*s*, NH); 7.79–7.63 (*m*, 8 arom. H); 7.55–7.50 (*m*, 2 arom. H); 7.43–7.38 (*m*, 3 arom. H); 7.29–7.19 (*m*, 5 arom. H); 7.15 (*d*, $J = 9.1$, H–C(1)); 7.12–7.04 (*m*, 4 arom. H); 6.92–6.80 (*m*, 6 arom. H); 6.32 (*d*, $J = 8.4$, H–C(1′)); 5.58 (*s*, PhC*H*); 4.87 (*d*, $J = 12.1$, PhC*H*); 4.70 (*d*, $J = 11.9$, PhC*H*); 4.57–4.49 (*m*, 3 PhC*H*, H_{eq}–C(6′)); 4.41 (*dd* (= '*t*'), $J \approx 2.6$, H–C(3′)); 4.39 (*d*, $J = 11.9$, PhC*H*); 4.32 (*ddd* (= '*td*'), $J = 10.1$, 5.1, PhC*H*, H–C(5)); 4.28 (*dd*, $J = 9.1$, 2.6, H–C(2)); 4.28–4.24 (*m*, H–C(2′), H–C(5′)); 4.21

(*dd* (= '*t*'), J = 2.6, H–C(3)); 4.19–4.16 (*m*, H–C(2'), H–C(4)); 3.86 (*dd*, J = 9.6, 2.3, H–C(4')); 3.83 (*t*, J = 10.3, H_{ax}–C(6')); 3.60 (*m*, 2 H–C(6)).

*Glycosidation of (±)-***5** *by* **4**. A mixture of (±)-**5** (586 mg, 1.9 mmol), **4** (2.1 g, 1.9 mmol), and 4-Å molecular sieves (500 mg) in CH_2Cl_2 (30 ml) was stirred at r.t. for 20 min. The suspension was cooled to 0° and treated with a soln. of Me_3Si-OTf (345 µl, 1.9 mmol) in CH_2Cl_2 (1 ml). After stirring for 20 min at 0°, TLC showed that **4** had disappeared. After addition of Et_3N (0.9 ml), the mixture was left for 10 min, filtered through *Celite*, and evaporated. The residue was dissolved in a minimum of $CHCl_3$ and adsorbed on silica gel. FC ($CHCl_3$/MeOH 99:1→90:10) gave **6** (304 mg, 17%), partially purified mixtures **9**/**7** (436 mg), **7**/**10** (458 mg), **10**/**8** (629 mg), and unreacted (±)-**5** (70 mg, 12%). MPLC ($CHCl_3$/MeOH 97:3) of the mixtures of pseudotrisaccharides, yielded **9** (135 mg, 5.7%), **7** (640 mg, 27%), **10** (102 mg, 4.3%), and **8** (576 mg, 24.3%).

*1,5-Anhydro-3,6-di-*O*-benzyl-4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-*D*-allopyranosyl)-2-deoxy-2-phthalimido-*D*-ribo-hex-1-enitol* (**6**). R_f(toluene/AcOEt 10:1) 0.18. $[\alpha]_D^{25} = -28.4$ (c = 0.8, $CHCl_3$). IR ($CHCl_3$): 3080*w* (sh), 3060*w* (sh), 3000*w*, 2920*w*, 2860*w*, 1755*w*, 1715*s*, 1665*w* (sh), 1650*w* (sh), 1640*w*, 1600*w*, 1575*w* (sh), 1490*w*, 1465*w* (sh), 1450*w*, 1375*m* (br.), 1360*m* (sh), 1320*w* (sh), 1305*w*, 1280*w*, 1160*w* (sh), 1135*m* (sh), 1100*s*, 1075*s* (br.), 1035*m*, 1025*m*, 1000*m*, 965*w* (sh), 910*w*, 895*w*, 870*w*, 840*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.80–7.67 (*m*, 9 arom. H); 7.55–7.52 (*m*, 2 arom. H); 7.44–7.38 (*m*, 3 arom. H); 7.29–7.19 (*m*, 4 arom. H); 7.11–7.06 (*m*, 4 arom. H); 6.91–6.83 (*m*, 5 arom. H); 6.74–6.70 (*m*, 1 arom. H); 6.59 (*s*, H–C(1)); 6.36 (*d*, J = 8.4, H–C(1')); 5.60 (*s*, PhC*H*); 4.87 (*d*, J = 12.1, PhC*H*); 4.65 (*d*, J = 12.5, PhC*H*); 4.56–4.49 (*m*, 3 PhC*H*, H_{eq}–C(6')); 4.47 (*d*, J = 11.8, PhC*H*); 4.39–4.36 (*m*, 2 H); 4.33 (*td*, J = 9.9, 5.0, H–C(5')); 4.24–4.20 (*m*, 3 H); 3.89 (*dd*, J = 9.4, 2.2, H–C(4')); 3.86 (*t*, J = 10.2, H_{ax}–C(6')); 3.65 (*dd*, J = 10.3, 5.3, H–C(6)); 3.58 (*dd*, J = 10.3, 1.8, H–C(6)). ^{13}C-NMR (50 MHz, $CDCl_3$): 167.6 (*s*, CO); 167.4 (*s*, CO); 167.2 (*s*, 2 CO); 145.6 (*d*, C(1)); 139.6 (*s*); 139.0 (*s*); 138.6 (*s*); 137.3 (*s*); 134–124 (*m*, arom. C); 107.8 (*s*, C(2)); 101.9 (*d*, PhCH); 97.9 (*d*, C(1')); 79.8 (*d*, C(4')); 75.3 (*d*); 74.1 (*d*, C(3')); 74 (*t*, PhCH_2); 73.1 (*t*, PhCH_2); 72.8 (*t*, PhCH_2); 72.7 (*d*); 70.6 (*d*, C(5)); 69.0, 68.9 (2 *t*, C(6), C(6')); 64.0 (*d*, C(5')); 56.7 (*d*, C(2')). Anal. calc. for $C_{56}H_{48}N_2O_{12}$ (941.002): C 71.48, H 5.14, N 2.98; found: C 71.27, H 5.26, N 2.99.

*(3aR,4R,5R,6S,6aS)-6-[(Benzyloxy)methyl]-2-(dimethylamino)-3a,5,6,6a-tetrahydro-4-hydroxy-4*H*-cyclopentoxazol-5-yl 3,6-Di-*O*-benzyl-4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-*D*-allopyranosyl)-2-deoxy-2-phthalimido-β-*D*-allopyranoside* (**7**). R_f ($CHCl_3$/MeOH 92.5:7.5) 0.37. $[\alpha]_D^{25} = -89$ (c = 0.6, $CHCl_3$). IR ($CHCl_3$): 3480*w* (br.), 3090*w*, 3070*w*, 3040*w*, 3000*w*, 2920*m*, 2860*w*, 1775*m*, 1715*s*, 1685*w* (sh), 1655*m* (sh), 1650*m*, 1620*w*, 1495*w*, 1470*w*, 1455*w*, 1385*s*, 1365*m* (sh), 1320*w*, 1160*m*, 1135*m*, 1105*s*, 1085*s*, 1075*s*, 1040*s*, 1025*s*,1015*s* (sh), 1005*m* (sh), 970*m*, 890*w*, 870*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.74–7.59 (*m*, 8 arom. H); 7.52–7.49 (*m*, 2 arom. H); 7.43–7.38 (*m*, 3 arom. H); 7.31–7.18 (*m*, 8 arom. H); 7.09–7.04 (*m*, 6 arom. H); 6.92–6.84 (*m*, 5 arom. H); 6.81–6.77 (*m*, 1 arom. H); 6.24 (*d*, J = 8.6, H–C(1")); 5.95 (*d*, J = 8.7, H–C(1)); 5.55 (*s*, PhC*H*); 4.84 (*d*, J = 12.2, PhC*H*); 4.65 (*d*, J = 11.7, PhC*H*); 4.64 (*dd*, J = 9.2, 6.5, H–C(6'a)); 4.54–4.49 (*m*, exchange with D_2O (1 H), PhC*H*, H_{eq}–C(6"), OH–C(4')); 4.46 (*d*, J = 12.2, PhC*H*); 4.37–4.31 (*m*, 2 PhC*H*, H–C(5"), H–C(3)); 4.29–4.21 (*m*, H–C(5), PhC*H*); 4.19 (*t*, J = 2.5, H–C(3")); 4.09 (*dd*, J = 8.6, 2.9, H–C(2")); 4.04 (*dd*, J = 9.2, 5.8, H–C(3'a)); 4.03 (*d*, J = 12.3, PhC*H*); 3.98 (*dd*, J = 8.7, 2.7, H–C(2)); 3.87 (*m*, with D_2O *dd*, J = 7.4, 5.6, H–C(4')); 3.83–3.77 (*m*, H_{ax}–C(6"), H–C(4), H–C(4")); 3.69 (*dd*, J = 10.7, 7.4, H–C(5')); 3.41 (*dd* (= '*t*'), J = 9.6, CH–C(6')); 3.35 (*dd*, J = 11.6, 3.5, H–C(6)); 3.33 (*dd*, J = 9.7, 2.4, CH–C(6')); 3.19 (*dd*, J = 11.6, 5.6, H–C(6)); 2.84 (*s*, Me_2N); 2.08 (*m*, H–C(6')). ^{13}C-NMR (50 MHz, $CDCl_3$): 167.8 (*s*, CO); 167.5 (*s*, CO); 167.4 (*s*, CO); 167.3 (*s*, CO); 161.4 (*s*, C(2')); 138.8–122.6 (several *d* and *s*, arom. C); 101.8 (*d*, PhCH); 98.4 (*d*, C(1")); 96.7 (*d*, C(1)); 85.4 (*d*, C(5')); 84.2 (*d*, C(4')); 80.6 (*d*, C(6'a)); 79.6 (*d*, C(4")); 78.4 (*d*, C(4)); 76.1 (*d*, C(3)); 74.0 (*t*, PhCH_2); 73.8 (*t*, *d*, PHCH_2, C(3")); 72.9 (*t*, PhCH_2); 72.7 (*d*, C(3'a)); 72.6 (*t*, PhCH_2); 71.4 (*d*, C(5)); 69.8 (*t*, C(6)); 68.9 (*t*, C(6")); 68.0 (*t*, CH_2–C(6')); 63.9 (*d*, C(5")); 56.6 (*d*, C(2")); 56.4 (*d*, C(2)); 49.2 (*d*, C(6')); 37.5 (*q*, Me_2N). ESI-MS: 1248 ([M + 1]$^+$).

*(3aS,4S,5S,6R,6aR)-6-[(Benzyloxy)methyl]-2-(dimethylamino)-3a,5,6,6a-tetrahydro-4-hydroxy-4*H*-cyclopentoxazol-5-yl 3,6-Di-*O*-benzyl-4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-*D*-allopyranosyl)-2-deoxy-2-phthalimido-β-*D*-allopyranoside* (**8**). R_f ($CHCl_3$/MeOH 92.5:7.5) 0.3. $[\alpha]_D^{25} = -73.8$ (c = 0.8, $CHCl_3$). IR ($CHCl_3$): 3540*w* (sh), 3520*w* (br.), 3090*w*, 3070*w*, 3040*w*, 3000*w*, 2920*m*, 2870*w*, 1775*w*, 1715*s*, 1685*w* (sh), 1655*m* (sh), 1650*m*, 1620*w* (sh), 1495*w*, 1465*w*, 1450*w*, 1380*s*, 1365*m* (sh), 1310*w*, 1260*m*, 1160*m*, 1135*m* (sh), 1105*s*, 1085*s*, 1040*s*, 1025*s*, 1015*s* (sh), 970*m*, 915*w*, 890*w*, 870*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.77–7.60 (*m*, 8 arom. H); 7.53–7.51 (*m*, 2 arom. H); 7.42–7.38 (*m*, 3 arom. H); 7.30–7.20 (*m*, 9 arom. H); 7.1–7.03 (*m*, 5 arom. H); 6.91–6.83 (*m*, 5 arom. H); 6.78–6.74 (*m*, 1 arom. H); 6.25 (*d*, J = 8.5, H–C(1")); 5.99 (*d*, J = 8.7, H–C(1)); 5.56 (*s*, PhC*H*); 4.85 (*d*, J = 12.1, PhC*H*); 4.66 (*dd*, J = 9.2, 6.0, H–C(6'a)); 4.61 (*d*, J = 12.0, PhC*H*); 4.51–4.44 (*m*, exchange with D_2O (1 H), 3 PhC*H*, H_{eq}–C(6"), OH–C(4')); 4.37–4.31 (*AB*, 2 PhC*H*); 4.28 (*ddd* (= '*td*'), J = 10.1, 5.3, H–C(5")); 4.26 (*t*, J = 2.6, H–C(3)); 4.22 (*d*, J = 11.7, PhC*H*); 4.18 (*t*, J = 2.6, H–C(3")); 4.13 (*dd*, J = 8.5, 2.7, H–C(2"));

4.06 (*dd*, J = 10.0, 2.5, H–C(4)); **4**.01 (*dd*, J = 9.2, 5.8, H–C(3'a)); 3.98 (*ddd*, J = 10.0, 5.0, 1.8, H–C(5)); 3.94 (*dd*, J = 8.7, 2.7, H–C(2)); 3.88 (*dd*, J = 10.1, 7.6, H–C(5')); 3.84 (*m*, H–C(4")); 3.80 (*t*, J = 10.3, H–C(6")); 3.69 (*m*, with D_2O *dd*, J = 7.5, 5.8, H–C(4')); 3.64 (*dd*, J = 9.8, 3.3, CH–C(6')); 3.53 (*dd*, J = 10.6, 5, H–C(6)); 3.48 (*dd*, J = 9.8, 5.6, CH–C(6')); 3.45 (*dd*, J = 10.6, 1.8, H–C(6)); 2.80 (*s*, Me_2N); 2.13 (*m*, H–C(6')). ^{13}C-NMR (50 MHz, $CDCl_3$): 168.1 (*s*, CO); 167.8 (*s*, CO); 167.7 (*s*, CO); 167.4 (*s*, CO); 161.7 (*s*, C(2')); 138.5–122.3 (several *d* and *s*, arom. C); 102.1 (*d*, PhCH); 97.7 (*d*, C(1")); 95.7 (*d*, C(1)); 84.2 (*d*, C(5')); 82 (*d*, C(4')); 81.9 (*d*, C(6'a)); 80.0 (*d*, C(4")); 76.6 (*d*, C(4)); 75.8 (*d*, C(3)); 74.2 (2*t*, 1*d*, 2 PhCH_2, C(3")); 72.9 (*t*, PhCH_2); 72.7 (*t*, PhCH_2); 72.2 (*d*, C(3'a)); 71.9 (*d*, C(5)); 69.6 (*t*, C(6)); 69.1 (*t*, C(6")); 68.0 (*t*, CH_2–C(6')); 64.0 (*d*, C(5")); 56.9 (*d*, C(2")); 56.6 (*d*, C(2)); 49.1 (*d*, C(6')); 37.6 (2*q*, Me_2N). ESI-MS: 1248 ([M + 1]$^+$). FAB-MS: 1248 (100, [M + 1]$^+$), 1249 (89, M + 2]$^+$).

(3aR,4S*,5S*,6S*,6aR*)-6-[(Benzyloxy)methyl]-2-(dimethylamino)-3a,5,6,6a-tetrahydro-5-hydroxy-4H-cyclopentoxazol-4-yl 3,6-Di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-allopyranosyl)-2-deoxy-2-phthalimido-β-D-allopyranoside* (**9**). R_f ($CHCl_3$/MeOH 92.5:7.5) 0.40. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.79–7.64 (*m*, 8 arom. H); 7.53–7.51 (*m*, 2 arom. H); 7.43–7.37 (*m*, 3 arom. H); 7.30–7.20 (*m*, 8 arom. H); 7.18–7.15 (*m*, 2 arom. H); 7.11–7.03 (*m*, 4 arom. H); 6.93–6.84 (*m*, 5 arom. H); 6.80–6.84 (*m*, 1 arom. H); 6.27 (*d*, J = 8.5, H–C(1")); 5.99 (*d*, J = 8.6, H–C(1)); 5.56 (*s*, PhC*H*); 4.96 (*dd*, J = 2.9, 7.9, H–C(6'a)); 4.86 (*d*, J = 12.2, PhC*H*); 4.63 (*d*, J = 11.9, PhC*H*); 4.52–4.48 (*m*, 3 PhC*H*, H_{eq}–C(6")); 4.45–4.38 (*m*, H–C(3'a), H–C(4')); 4.31 (*d*, J = 11.7, PhC*H*); 4.30 (*m*, H–C(5")); 4.28 (*dd* (= '*t*'), J = 2.5, H–C(3)); 4.25 (*m*, 2 PhC*H*); 4.19 (*dd* (= '*t*'), J = 2.5, H–C(3")); 4.13 (*dd*, J = 8.5, 2.9, H–C(2")); 4.14 (*m*, exchange with D_2O (1 H), H–C(5), OH–C(5')); 4 (*dd*, J = 9.9, 2.4, H–C(4)); 3.94 (*dd*, J = 8.6, 2.5, H–C(2)); 3.84 (*dd*, J = 9.7, 2.3, H–C(4")); 3.83–3.78 (*m*, H–C(6"), H–C(5')); 3.60–3.54 (*m*, 2 H–C(6)); 3.38 (*dd*, J = 9.5, 4.1, CH–C(6')); 3.29 (*dd* (= '*t*'), J = 8.9, CH–C(6')); 2.88 (*s*, Me_2N); 2.38 (*m*, H–C(6')).

(3aS,4R*,5R*,6R*,6aS*)-6-[(Benzyloxy)methyl]-2-(dimethylamino)-3a,5,6,6a-tetrahydro-5-hydroxy-4H-cyclopentoxazol-4-yl 3,6-Di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-allopyranosyl)-2-deoxy-2-phthalimido-β-D-allopyranoside* (**10**). R_f ($CHCl_3$/MeOH 92.5:7.5) 0.34. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.78–7.57 (*m*, 8 arom. H); 7.52–7.49 (*m*, 2 arom. H); 7.43–7.38 (*m*, 3 arom. H); 7.31–7.14 (*m*, 10 arom. H); 7.09–7.05 (*m*, 5 arom. H); 6.92–6.84 (*m*, 4 arom. H); 6.81–6.77 (*m*, 1 arom. H); 6.25 (*d*, J = 8.5, H–C(1")); 5.97 (*d*, J = 8.7, H–C(1)); 5.56 (*s*, PhC*H*); 4.99 (*dd*, J = 8.7, 4.3, H–C(6'a)); 4.84 (*d*, J = 12.0, PhC*H*); 4.62 (*d*, J = 12.0, PhC*H*); 4.48 (*d*, J = 12.0, PhC*H*); 4.48 (*d*, J = 10.3, 5.1, H_{eq}–C(6")); 4.38 (*d*, J = 12.2, PhC*H*); 4.36–4.19 (*m*, 9 H); **4**.14 (*dd*, J = 8.5, 2.9, H–C(2")); 4.11–3.99 (*m*, exchange with D_2O (1 H), H–C(5'), H–C(5), OH–C(5')); 3.93 (*dd*, J = 5.7, 4.3, H–C(4')); 3.87 (*dd*, J = 8.7, 2.7, H–C(2)); 3.83 (*dd*, J = 9.8, 2.4, H–C(4")); 3.80 (*t*, J = 10.4, H_{ax}–C(6")); 3.57 (*m*, 2 CH–C(6')); 3.51 (*dd*, J = 10.5, 4.6, H–C(6)); 3.43 (br. *d*, J = 10.1, H–C(6)); 2.9 (*s*, Me_2N); 2.61 (*m*, H–C(6')).

Deprotection of **7** *and* **8**. *a*) A soln. of **7** (200 mg, 0.16 mmol) and $NH_2NH_2 \cdot H_2O$ (2 ml) in EtOH (5 ml) was heated at 80° for 4 h. The mixture was evaporated, co-evaporated with toluene (3 × 20 ml), and dried under h.v. The residue was treated with pyridine (8 ml) and Ac_2O (4 ml) for 14 h under Ar at r.t., workup as usual and FC ($CHCl_3$/MeOH 99:1→95:5) yielded **11** (112 mg, 61%). White foam.

b) A soln. of **7** (50 mg, 0.04 mmol) and $NH_2NH_2 \cdot H_2O$ (3.8 µl, 0.08 mmol) in EtOH (2 ml) was kept for 45 min at 80°. Workup as described in *a*); treatment with pyridine (4 ml) and Ac_2O (1 ml) for 14 h, and FC ($CHCl_3$/MeOH 99:1→95:5) afforded **11** (5.5 mg, 12%) and **12** (7.6 mg, 17%) as a colourless oil.

c) A soln. of **7** (250 mg, 0.2 mmol) and 40% aq. $MeNH_2$ soln. (5 ml) in EtOH (8 ml) was stirred at r.t. for 48 h. The mixture was evaporated, co-evaporated with toluene (2 × 30 ml), and dried under h.v. The residue was treated with pyridine (10 ml) and Ac_2O (5 ml) for 14 h under Ar. Workup as usual and FC ($CHCl_3$/MeOH 99:1→95:5) yielded **12** (163 mg, 73%).

(1R,2R,3S,4S,5S)-3-Acetamido-2,4-diacetoxy-5-[(benzyloxy)methyl]cyclopentyl 2-Acetamido-4-O-(2-acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-β-D-allopyranosyl)-3,6-di-O-benzyl-2-deoxy-β-D-allopyranoside (**11**). R_f ($CHCl_3$/MeOH 9:1) 0.49. $[\alpha]_D^{25} = -60.6$ (c = 0.4, $CHCl_3$). IR ($CHCl_3$): 3420*m*, 3350*w*, 3090*w*, 2860*w*, 1745*s*, 1720*m* (sh), 1665*s*, 1655*s* (sh), 1635*m* (sh), 1510*m* (sh), 1495*m*, 1450*m*, 1435*w*, 1420*w*, 1365*m*, 1325*w*, 1260*m* (sh), 1240*w*, 1160*m*, 1145*m* (sh), 1115*s*, 1090*s*, 1040*s*, 1025*s*, 1005*s* (sh), 960*w*, 940*w*, 910*w*, 880*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.52–7.47 (*m*, 2 arom. H); 7.42–7.24 (*m*, 23 arom. H); 6.01 (*d*, J = 8.8, NH–C(3')); 5.82 (*d*, J = 8.7, NH–C(2")); 5.54 (*s*, PhC*H*); 5.51 (br. *s*, NH–C(2)); 5.33 (*dd*, J = 8.2, 5.5, H–C(2')); 4.97 (*d*, J = 11.8, PhC*H*); 4.91 (*dd*, J = 5.8, 3.3, H–C(4')); 4.88 (*dd*, J = 13.1, PhC*H*); 4.76 (*dd*, J = 8.4, H–C(1")); 4.74 (*d*, J = 11.3, PhC*H*); 4.60 (*d*, J = 12.1, PhC*H*); 4.55 (*d*, J = 11.8, PhC*H*); 4.54–4.40 (*m*, 3 PhC*H*, H–C(1), H–C(3'), H_{eq}–C(6")); 4.19–4.12 (*m*, H–C(3), H–C(5")); 4.08–4.02 (*m*, H–C(3"), H–C(2")); 3.98 (*t*, J = 5.3, H–C(1')); 3.91–3.84 (*m*, H–C(2), H–C(5)); 3.80 (*m*, H–C(4)); 3.79 (*t*, J = 10.2, H_{ax}–C(6")); 3.73 (*dd*, J = 9.5, 2.0, H–C(4")); 3.69 (*dd*, J = 11.6, 3.0, H–C(6)); 3.53–3.45 (*m*, H–C(6), 2 CH–C(5')); 2.11 (*m*, H–C(5')); 2.05 (*s*, Ac); 1.99 (*s*, Ac); 1.96 (*s*,

Ac); 1.62 (*s*, Ac); 1.55 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.4 (*s*, CO); 170.0 (*s*, CO); 169.9 (*s*, CO); 169.3 (*s*, CO); 169.2 (*s*, CO); 138.5 (*s*, arom. C); 138.1 (2*s*, arom. C); 137.7 (*s*, arom. C); 137.2 (*s*, arom. C); 129.1–126.1 (several *d*, arom. C); 102.4 (*d*, C(1″)); 102.0 (*d*, PhCH); 100.5 (*d*, C(1)); 82.3 (*d*, C(1′)); 80.0 (*d*, C(4″)); 79.3 (*d*, C(2′)); 78.1 (*d*, C(4)); 76.8 (*d*, C(3″)); 75.1 (*d*, C(3)); 74.6 (*t*, PhCH$_2$); 74.2 (*t*, PhCH$_2$); 74.0 (*t*, PhCH$_2$); 73.7 (*d*, C(4′)); 73.1 (*t*, PhCH$_2$); 72.5 (*d*, C(5)); 69.1 (*t*, C(6″)); 68.7 (2*t*, C(6), CH$_2$–C(5′)); 63.8 (*d*, C(5″)); 53.6 (*d*, C(3′)); 52.7 (*d*, C(2″)); 51.4 (*d*, C(2)); 49.8 (*d*, C(5′)); 23.0 (*q*, Me); 22.8 (*q*, Me); 20.9 (*q*, Me); 20.8 (2 *q*, 2 Me). ESI-MS: 1145 ([*M* + 1]$^+$).

*(3a*S*,4*R*,5*R*,6*S*,6a*S*)-4-Acetoxy-6-[(benzyloxy)methyl]-2-(dimethylamino)-3a,5,6,6a-tetrahydro-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-*O*-(2-acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-*D*-allopyranosyl)-3,6-di-*O*-benzyl-2-deoxy-β-*D*-allopyranoside* (**12**). R_f ($CHCl_3$/MeOH 92.5:7.5) 0.44. $[\alpha]_D^{25} = -50.5$ (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3420*w*, 3370*w*, 3090*w*, 3060*w*, 2980*w* (sh), 2950*w* (sh), 2920*m*, 2800*m*, 1730*m*, 1720*m*, 1650*s* (br.), 1635*m* (sh), 1510*w* (sh), 1490*m*, 1450*m*, 1410*w*, 1365*m*, 1315*w*, 1240*m* (br.), 1155*m*, 1115*s* (sh), 1080*s* (br.), 1040*s*, 1025*s*, 970*m*, 915*w*, 885*w*, 865*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.50–7.48 (*m*, 2 arom. H); 7.40–7.24 (*m*, 23 arom. H); 6.09–5.94 (br. *s*, NH–C(2)); 5.91 (*d*, *J* = 8.5, NH–C(2″)); 5.53 (*s*, PhC*H*); 5.26 (*m*, H–C(4′)); 4.98 (*d*, *J* = 11.7, PhC*H*); 4.9 (*dd*, *J* = 8.2, 4.1, H–C(6′a)); 4.87 (*d*, *J* = 11.8, PhC*H*); 4.75 (*d*, *J* = 8.7, H–C(1)); 4.72 (*d*, *J* = 12.2, PhC*H*); 4.59–4.43 (*m*, H$_{eq}$–C(6″), H–C(1″), 5 PhC*H*); 4.26 (*dd*, *J* = 8.3, 2.6, H–C(3′a)); 4.13 (*ddd* (= '*td*'), *J* = 10.0, 5.3, H–C(5″)); 4.11 (*m*, H–C(3)); 4.06–4.04 (*m*, H–C(3″), H–C(2)); 3.96–3.85 (*m*, H–C(5′), H–C(2″), H–C(4), H–C(5)); 3.78 (*t*, *J* = 10.3, H$_{ax}$–C(6″)); 3.74–3.71 (*m*, H–C(4″), H–C(6)); 3.62 (*dd*, *J* = 11.3, 2.5, H–C(6)); 3.50 (*d*, *J* = 5.4, 2 CH–C(6′)); 2.90 (*s*, Me$_2$N); 2.43 (*m*, H–C(6′)); 2.02 (*s*, Ac); 1.99 (*s*, Ac); 1.64 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.5 (*s*, CO); 169.4 (*s*, 2 CO); 161.7 (*s*, C(2′)); 138.6 (*s*, arom. C); 138.2 (*s*, arom. C); 138.1 (*s*, arom. C); 138.0 (*s*, arom. C); 137.3 (*s*, arom. C); 129.0–126.1 (several *d*, arom. C); 102.2 (*d*, C(1)); 102.0 (*d*, PhCH); 99.5 (*d*, C(1″)); 83.4 (*d*, C(4′)); 81,9 (*d*, C(5′)); 81.6 (*d*); 80.0 (*d*, C(4″)); 77.2 (*d*); 75.1 (*d*); 74.5 (*t*, PhCH$_2$); 73.9 (*t*, PhCH$_2$); 73.1 (2*t*, 1*d*); 72.6 (*d*); 69.3, 69.1 (*t*, C(6), C(6″)); 52.6 (*d*, C(2)); 51.6 (*d*, C(2″)); 50.0 (*d*, CH$_2$–C(6′)); 37.6 (*q*, Me$_2$N); 22.9 (*q*, Me); 22.8 (*q*, Me); 21.1 (*q*, Me).

*(3a*R*,4*S*,5*S*,6*R*,6a*R*)-4-Acetoxy-6-[(benzyloxy)methyl]-2-(dimethylamino)-3a,5,6,6a-tetrahydro-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-*O*-(2-acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-*D*-allopyranosyl)-3,6-di-*O*-benzyl-2-deoxy-β-*D*-allopyranoside* (**13**). Similarly as for the preparation of **11** from **7**, a soln. of **8** (310 mg, 0.249 mmol) in EtOH (8 ml) and 40% aq. MeNH$_2$ soln. (5 ml) was stirred at r.t. for 48 h. Evaporation, treatment of the residue with pyridine/Ac$_2$O 2:1 (6 ml), normal workup, and FC ($CHCl_3$/MeOH 99:1 → 95:5) gave **13** (205 mg, 74%). Colourless oil. R_f ($CHCl_3$/MeOH 92.5:7.5) 0.48. $[\alpha]_D^{25} = -69.6$ (*c* = 0.8, $CHCl_3$). IR ($CHCl_3$): 3410*w*, 3380*w* (br.), 2980*w*, 2920*m*, 2860*m*, 1725*m*, 1655*s*, 1645*s*, 1620*m* (sh), 1545*w*, 1530*w*, 1510*w*, 1495*w*, 1450*w*, 1410*w*, 1315*m*, 1245*w*, 1155*m* (sh), 1165*s*, 1080*s*, 1040*s*, 1025*s*, 970*m*, 950*w*, 910*w*, 885*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.50–7.47 (*m*, 2 arom. H); 7.39–7.20 (*m*, 23 arom. H); 6.28 (*d*, *J* = 4.4, NH–C(2)); 5.77 (*d*, *J* = 8.6, NH–C(2″)); 5.10 (*dd*, *J* = 7.2, 5.1, H–C(4′)); 4.98 (*d*, *J* = 11.8, PhC*H*); 4.87 (*d*, *J* = 11.4, PhC*H*); 4.82 (*dd*, *J* = 9.1, 6.4, H–C(6′a)); 4.75 (*d*, *J* = 8.5, H–C(1)); 4.54–4.46 (*m*, 7 H); 4.27 (*d*, *J* = 11.9, PhC*H*); 4.21 (br. *s*, H–C(3)); 4.18 (*dd*, *J* = 9.1, 5.1, H–C(3′a)); 4.15–4.1 (*m*, H–C(3″), H–C(5″)); 4.03 (*dd*, *J* = 10.1, 7.2, H–C(5′)); 4.02 (*m*, H–C(5)); 3.84–3.8 (*m*, 3 H); 3.75 (*t*, *J* = 10.4, H$_{ax}$–C(6″)); 3.72–3.64 (*m*, 3 H); 3.63 (*dd*, *J* = 9.6, 4.2, CH–C(6′)); 3.48 (br. *d*, *J* = 11.3, H–C(6)); 2.89 (*s*, Me$_2$N); 2.28 (*m*, H–C(6′)); 1.92 (*s*, Ac); 1.84 (*s*, Ac); 1.6 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 171.0 (*s*, CO); 170 (*s*, 2 CO); 161.9 (*s*, C(2′)); 138.8 (*s*, arom. C); 138.3 (*s*, arom. C); 138.1 (*s*, arom. C); 137.9 (*s*, arom. C); 137.2 (*s*, arom. C); 128.9–126.0 (several *d*, arom. C); 101.9 (2*d*, C(1), PhCH); 98.6 (*d*, C(1″)); 85.6 (*d*); 80.1 (*d*, C(4″)); 79.9 (*d*); 79.4 (*d*); 77.7 (*d*); 77.2 (*d*); 75.1 (*d*); 74.4 (*t*, PhCH$_2$); 73.8 (*t*, 2 PhCH$_2$); 72.9 (*t*, PhCH$_2$); 72.8 (*d*); 71.3 (*d*); 69.0 (*t*, C(6), C(6″)); 67.3 (*t*, CH$_2$–C(6′)); 63.6 (*d*); 52.7, 52.5 (2 *d*, C(2), C(2″)); 49.6 (*d*, C(6′)); 37.5 (*q*, Me$_2$N); 22.9 (*q*, Me); 22.7 (*q*, Me); 20.9 (*q*, Me).

*(1*R*,2*R*,3*S*,4*S*,5*S*)-3-Acetamido-5-[(benzyloxy)methyl]-2,4-dihydroxycyclopentyl 2-Acetamido-4-*O*-(2-acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-*D*-allopyranosyl)-3,6-di-*O*-benzyl-2-deoxy-β-*D*-allopyranoside* (**14**). A soln. of **11** (90 mg, 0.079 mmol) in MeOH (10 ml) was treated at r.t. with 1 mM NaOMe in MeOH (3 ml). After stirring 5 h and addition of *Dowex-1* (H$^+$), filtration and evaporation left a residue which upon FC ($CHCl_3$/MeOH 97:3) yielded **14** (80.8 mg, 97%). Colourless glass. R_f ($CHCl_3$/MeOH 9:1) 0.33. IR ($CHCl_3$): 3595*w*, 3500*w* (sh), 3400*m*, 3350*w* (br.), 3090*w*, 3070*w*, 2995*w*, 2940*w*, 2870*m*, 1670*s*, 1655*s* (sh), 1610*w*, 1585*w*, 1545*w* (sh), 1510*m* (sh), 1500*m*, 1455*m*, 1370*m*, 1320*m*, 1165*m*, 1110*s*, 1090*s* (br.), 1040*s*, 1025*s*, 1010*s* (sh), 965*w*, 945*w*, 915*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.48–7.45 (*m*, 2 arom. H); 7.40–7.45 (*m*, 23 arom. H); 6.26 (*d*, *J* = 4.5, NH–C(3′)); 5.90 (*d*, *J* = 9, NH–C(2″)); 5.54–5.51 (br. *s*, NH–C(2)); 5.51 (*s*, PhC*H*); 4.97 (*d*, *J* = 11.8, PhC*H*); 4.92 (*d*, *J* = 11.9, PhC*H*); 4.70 (*d*, *J* = 8.5, H–C(1″)); 4.64 (*d*, *J* = 12.2, PhC*H*); 4.59 (*d*, *J* = 12.0, PhC*H*); 4.53 (*d*, *J* = 11.8, PhC*H*); 4.52 (*d*, *J* = 12.3, PhC*H*); 4.47 (*d*, *J* = 8.3, H–C(1)); 4.46 (*d*, *J* = 12.2, PhC*H*); 4.43 (*dd*, *J* = 10.3, 5.1, H$_{eq}$–C(6″)); 4.38 (*d*, *J* = 12.3, PhC*H*); 4.31 (br. *s*, exchange with D$_2$O, OH–C(2′)); 4.15–3.90 (*m*, 9 H); 3.76 (*t*, *J* = 10.3, H$_{ax}$–C(6″)); 3.72 (*dd*, *J* = 9.8, 2.1, H–C(4″)); 3.69 (*dd*, *J* = 9.8, 1.7, H–C(4)); 3.64–3.54 (*m*,

H–C(4′), 2 H–C(6)); 3.43 (*dd*, J = 9.2, 5.2, CH–C(5′)); 3.36 (*dd*, J = 9.2, 5.4, CH–C(5′)); 2.90 (br. *s*, exchange with D_2O, OH–C(4′)); 2.06 (*m*, H–C(5′)); 1.98 (*s*, Ac); 1.59 (*s*, Ac); 1.47 (*s*, Ac).

*(3a*R,*4*R,*5*R,*6*S,*6a*S*)-6-[(Benzyloxy)methyl]-2-(dimethylamino)-3a,5,6,6a-tetrahydro-4-hydroxy-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-*O*-(2-acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-*D*-allopyranosyl)-3,6-di-*O*-benzyl-2-deoxy-β-*D*-allopyranoside* (**15**). As described for **14**, with **12** (120 mg, 0.108 mmol) in MeOH (10 ml) and 1 mM NaOMe in MeOH (2 ml; 10 h). FC ($CHCl_3$/MeOH 98:2→95:5) yielded **15** (110 mg, 96%). Colourless glass. R_f ($CHCl_3$/MeOH 9:1) 0.35. $[\alpha]_D^{25} = -35$ (*c* = 0.9, $CHCl_3$). IR ($CHCl_3$): 3590*w*, 3540*w*, 3495*w*, 3430*m*, 2990*w*, 2970*w*, 2960*m*, 2950*m*, 2920*m*, 2875*m*, 1670*s* (sh), 1655*s*, 1510*w* (sh), 1495*m*, 1470*w*, 1450*w*, 1405*w*, 1365*m*, 1320*w*, 1310*w*, 1260*w*, 1160*m*, 1140*m* (sh), 1115*s* (sh), 1095*s* (br.), 1040*s*, 1025*s*, 970*m*, 940*w*, 915*w*, 885*w*, 860*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.50–7.47 (*m*, 2 arom. H); 7.42–7.2 (*m*, 22 arom. H); 7.17–7.13 (*m*, 1 arom. H); 5.61 (*d*, J = 9.1, NH–C(2″)); 5.52 (*s*, PhC*H*); 5.30 (br. *d*, J = 8.2, NH–C(2)); 5.00 (*d*, J = 11.7, PhC*H*); 4.95 (*d*, J = 11.8, PhC*H*); 4.78 (*dd*, J = 9.2, 6.8, H–C(6′a)); 4.70–4.61 (*m*, PhC*H*, H–C(1″)); 4.57 (*d*, J = 11.8, PhC*H*); 4.53 (*d*, J = 11.7, PhC*H*); 4.51 (*d*, J = 12.3, PhC*H*); 4.47 (*dd*, J = 10.3, 5.1, H_{eq}–C(6″)); 4.42 (*d*, J = 8.3, H–C(1)); 4.34 (*d*, J = 12.7, PhC*H*); 4.21 (br. *s*, exchange with D_2O, OH–C(4′)); 4.14–4.04 (*m*, 6 H); 3.98 (*dd* (= '*td*'), J = 8.8, 2.6, H–C(2)); 3.89 (*m*, after D_2O exchange *dd*, J = 7.4, 5.9, H–C(4′)); 3.75 (*t*, J = 10.4, H_{ax}–C(6″)); 3.71 (*dd*, J = 9.5, 1.9, H–C(4″)); 3.66 (*dd*, J = 9.8, 2.1, H–C(4)); 3.61–3.55 (*m*, H–C(5′), 2 H–C(6)); 3.53 (*dd*, J = 9.4, 3.1, CH–C(6′)); 3.36 (*dd*, J = 3.4, 9.4, CH–C(6′)); 2.87 (*s*, Me_2N); 2.19 (*m*, H–C(6′)); 1.53 (*s*, Ac); 1.43 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.2 (*s*, CO); 169.1 (*s*, CO); 161.7 (*s*, C(2′)); 138.6 (*s*, arom. C); 138.5 (*s*, arom. C); 138.0 (*s*, arom. C); 137.7 (*s*, arom. C); 137.2 (*s*, arom. C); 129.2–126.1 (several *d*, arom. C); 102.4 (*d*, C(1″)); 102.1 (*d*, PhCH); 100.9 (*d*, C(1)); 85.7 (*d*, C(5′)); 84.0 (*d*, C(4′)); 80.1 (*d*, C(4″)); 79.8 (*d*, C(6′a)); 78.6 (*d*, C(4)); 77.3 (*d*); 75.3 (*d*); 74.7 (*t*, 2 PhCH_2); 74.1 (*t*, PhCH_2); 72.7 (*t*, PhCH_2); 72.2, 71.8 (2*d*, C(5), C(5″)); 69.3 (*t*, C(6)); 69.1 (*t*, C(6″)); 66.2 (*t*, CH_2–C(6′)); 63.8 (*d*, C(3′a)); 52.3 (*d*, C(2″)); 51.4 (*d*, C(2)); 49.4 (*d*, C(6′)); 37.7 (*q*, Me_2N); 22.8 (*q*, Me); 22.7 (*q*, Me).

*(3a*S,*4*S,*5*S,*6*R,*6a*R*)-6-[(Benzyloxy)methyl]-2-(dimethylamino)-3a,5,6,6a-tetrahydro-4-hydroxy-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-*O*-(2-acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-*D*-allopyranosyl)-3,6-di-*O*-benzyl-2-deoxy-β-*D*-allopyranoside* (**16**). As described for **14**, with **13** (135 mg, 0.121 mmol) in MeOH (10 ml) and 1mM NaOMe in MeOH (2 ml; 10 h). FC ($CHCl_3$/MeOH 98:2→95:5) yielded **16** (121 mg, 93%). Colourless glass. R_f ($CHCl_3$/MeOH 9:1) 0.26. $[\alpha]_D^{25} = -64$ (*c* = 0.7, $CHCl_3$). IR ($CHCl_3$): 3680*w*, 3580*w*, 3490*w* (sh), 3430*w*, 3360*w* (br.), 3090*w*, 3070*w*, 2990*w*, 2920*m*, 2855*m*, 2800*w*, 1685*w* (sh), 1650*s* (br.), 1545*w*, 1530*w*, 1510*w* (sh), 1490*w*, 1450*w*, 1410*w*, 1360*m*, 1315*w*, 1155*m* (sh), 1115*m*, 1070*s*, 1040*s*, 1025*s*, 1010*m* (sh), 970*m*, 945*w*, 915*w*, 890*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.52–7.46 (*m*, 2 arom. H); 7.41–7.22 (*m*, 23 arom. H); 5.93–5.91 (br. *s*, NH); 5.76 (*d*, J = 8.8, NH–C(2″)); 5.53 (*s*, PhC*H*); 4.99 (*d*, J = 11.7, PhC*H*); 4.85 (*d*, J = 12.4, PhC*H*); 4.78–4.76 (*m*, 2 H); 4.75 (*dd*, J = 9.1, 5.9, H–C(6′a)); 4.69 (*d*, J = 12.1, PhC*H*); 4.56 (*d*, J = 12.0, PhC*H*); 4.54 (*d*, J = 11.7, PhC*H*); 4.50–4.43 (*m*, 3 H); 4.34 (*d*, J = 12.1, PhC*H*); 4.16–4.11 (*m*, 4 H, exchange with D_2O (1 H)); 4.08–3.95 (*m*, 3 H); 3.90 (*ddd* (= '*dt*'), J = 8.9, 2.6, H–C(5)); 3.87–3.81 (*m*, 3 H); 3.77 (*t*, J = 10.4, H_{ax}–C(6″)); 3.72 (*dd*, J = 9.5, 3.3, H–C(4″)); 3.67 (*dd*, J = 9.5, 3.3, H–C(6)); 3.63–3.58 (*m*, CH–C(6′), H–C(6)); 3.45 (*dd*, J = 11.2, 1.4, CH–C(6′)); 2.85 (*m*, Me_2N); 2.23 (*m*, H–C(6′)); 1.75 (*s*, Ac); 1.59 (*s*, Ac). ^{13}C-NMR (50 MHz, $CDCl_3$): 169.4 (*s*, CO); 169.2 (*s*, CO); 161.8 (*s*, C(2′)); 138.8 (*s*, arom. C); 138.3 (*s*, arom. C); 138.1 (*s*, arom. C); 138 (*s*, arom. C); 137.2 (*s*, arom. C); 129–126 (several *d*, arom. C); 102.1 (*d*, C(1″)); 101.9 (*d*, PhCH); 100.1 (*d*, C(1)); 83.9 (*d*); 82.1 (*d*); 81.7 (*d*); 80.6 (*d*); 79.9 (*d*); 78.1 (*d*); 77.2 (*d*); 75.1 (*d*); 74.5 (*t*, PhCH_2); 73.8 (*t*, PhCH_2); 72.9 (*t*, 2 PhCH_2); 72.5 (*d*); 71.7 (*d*); 69.0 (*t*, C(6), C(6″)); 67.4 (*t*, CH_2–C(6′)); 63.7 (*d*, C(3′a)); 52.7, 52.4 (2*d*, C(2), C(2″)); 48.7 (*d*, C(6′)); 37.5 (2*q*, Me_2N); 23 (*q*, Me); 22.7 (*q*, Me).

*(3a*R,*4*R,*5*R,*6*S,*6a*S*)-2-(Dimethylamino)-3a,5,6,6a-tetrahydro-4-hydroxy-6-(hydroxymethyl)-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-*O*-(2-acetamido-3-deoxy-β-*D*-allopyranosyl)-2-deoxy-β-*D*-allopyranoside* (**1**). A mixture of **15** (45 mg, 0.042 mmol) and 10% Pd/C (80 mg) in MeOH/AcOH 9:1 (18 ml) was stirred for 36 h at r.t. under 7 bar of H_2. The solids were then removed by centrifugation (2000 r.p.m., 5 min), and the pellet was washed with MeOH/AcOH 9:1 (3 × 20 ml). The combined supernatants were collected and evaporated. The white solid residue was dissolved in a minimum of a 3% aq. AcOH soln. and chromatographed on *Sephadex G 10*: **1** (25 mg, 95%). White powder. R_f (AcOEt/pyridine/AcOH/H_2O 5:5:1:3) 0.40. $[\alpha]_D^{25} = -21.4$ (*c* = 0.3, H_2O). ^{1}H-NMR (600 MHz, D_2O/0.3% CD_3CO_2D[2]): *Table 1*. ^{13}C-NMR (150 MHz, D_2O/0.3% CD_3CO_2D): *Table 3*. ESI-MS: 623 (100 $[M + H]^+$).

*(3a*S,*4*S,*5*S,*6*R,*6a*R*)-2-(Dimethylamino)-3a,5,6,6a-tetrahydro-4-hydroxy-6-(hydroxymethyl)-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-*O*-(2-acetamido-3-deoxy-β-*D*-allopyranosyl)-2-deoxy-β-*D*-allopyranoside* (**17**). As de-

[2]) The values of the coupling constants of the signals between 3.95 and 3.65 ppm were determined from the *J*-resolved 2D spectra.

scribed for **1**, with 10% Pd/C (90 mg), 7 bar of H_2, **16** (72 mg, 0.067 mmol), and MeOH/AcOH 9:1 (18 ml): **17** (39.7 mg, 95%). White powder. R_f (AcOEt/pyridine/AcOH/H_2O 5:5:1:3) 0.40. $[\alpha]_D^{25} = -12.3$ ($c = 0.26$, H_2O). ^{1}H-NMR (600 MHz, D_2O/0.3% CD_3CO_2D)[2]): *Table 1.* ^{13}C-NMR (50 MHz, D_2O/0.3% CD_3CO_2D): *Table 3.* ESI-MS: 623 (100, $[M + H]^+$).

*(1*R*,2*R*,3*S*,4*S*,5*S*)-3-Acetamido-2,4-dihydroxy-5-(hydroxymethyl)cyclopentyl 2-Acetamido-4-*O*-(2-acetamido-2-deoxy-β-*D*-allopyranosyl)-2-deoxy-β-*D*-allopyranoside* (**18**). As described for **1**, with **14** (58 mg, 0.055 mmol), 10% Pd/C (80 mg), MeOH/AcOH 9:1 (18 ml), and 7 bar of H_2 (72 h): **18** (30.8 mg, 92%). White powder. R_f ($CHCl_3$/MeOH/H_2O/NH_3 10:10:1.75:0.25) 0.2. $[\alpha]_D^{25} = -18.3$ ($c = 0.5$, 0.1M aq. AcOH). ^{1}H-NMR (600 MHz, D_2O/0.3% CD_3CO_2D)[2]): *Table 1.* ^{13}C-NMR (50 MHz, D_2O/0.3% CD_3CO_2D): *Table 3.* ESI-MS: 612 (100, $[M + H]^+$).

*(3a*S*,4*R*,5*R*,6*S*,6a*S*)-4-Acetoxy-6-(acetoxymethyl)-2-(dimethylamino)-3a,5,6,6a-tetrahydro-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-allopyranosyl)-3,6-di-*O*-acetyl-2-deoxy-β-*D*-allopyranoside* (**19**). A soln. of **1** (9 mg, 0.014 mmol) and 4-(Me_2N)C_5H_4N (0.5 mg) in pyridine (2 ml) was cooled to 0°, treated with Ac_2O (1 ml), and stirred for 14 h at r.t. The solvents were co-evaporated with toluene (4 × 10 ml). FC ($CHCl_3$/MeOH 95:5) of the residue yielded **19** (12.7 mg, 97%). Oil. R_f ($CHCl_3$/MeOH 9:1) 0.23. $[\alpha]_D^{25} = -41.5$ ($c = 0.2$, $CHCl_3$). IR ($CHCl_3$): 3450*w*, 3390*w*, 1740*s* (br.), 1675*m* (sh), 1655*s*, 1550*w*, 1530*w*, 1415*w*, 1370*m*, 1280*m* (sh), 1240*s*, 1165*m*, 1125*w*, 1090*m*, 1040*s*, 975*w*, 950*w*. ^{1}H-NMR (600 MHz, $CDCl_3$): *Table 2.* ^{13}C-NMR (150 MHz, $CDCl_3$): *Table 3.* ESI-MS: 623 (100, $[M + H]^+$).

*(3a*R*,4*S*,5*S*,6*R*,6a*R*)-4-Acetoxy-6-(acetoxymethyl)-2-(dimethylamino)-3a,5,6,6a-tetrahydro-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-allopyranosyl)-3,6-di-*O*-acetyl-2-deoxy-β-*D*-allopyranoside* (**20**). As described for **19**, with **17** (12 mg, 0.019 mmol), pyridine (2 ml), Ac_2O (1 ml), and 4-(Me_2N)C_5H_4N (0.5 mg): **20** (16.9 mg, 96%). Oil. R_f($CHCl_3$/MeOH 9:1) 0.27. $[\alpha]_D^{25} = -55.4$ ($c = 0.1$, $CHCl_3$). IR ($CHCl_3$): 3450*w*, 3390*w*, 1740*s* (br.), 1675*m* (sh), 1655*s*, 1550*w*, 1530*w*, 1415*w*, 1370*m*, 1280*m* (sh), 1240*s*, 1165*m*, 1125*w*, 1090*m*, 1040*s*, 975*w*, 950*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 2.* ^{13}C-NMR (HMQC 100 MHz, $CDCl_3$): *Table 3.*

*(1*R*,2*R*,3*S*,4*S*,5*S*)-3-Acetamido-2,4-diacetoxy-5-(acetoxymethyl)cyclopentyl 2-Acetamido-4-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-allopyranosyl)-3,6-di-*O*-acetyl-2-deoxy-β-*D*-allopyranoside* (**21**). As described for **19**, with **18** (8 mg, 0.013 mmol), pyridine (2 ml), Ac_2O (1 ml), and 4-(Me_2N)C_5H_4N (0.5 mg): **21** (11.9 mg, 97%). Oil. R_f ($CHCl_3$/MeOH 9:1) 0.29. $[\alpha]_D^{25} = -36.7$ ($c = 0.7$, $CHCl_3$). IR ($CHCl_3$): 3440*w*, 3390*w*, 3040*w*, 2990*w*, 2980*w*, 2900*w*, 1735*s* (br.), 1685*s* (sh), 1675*s*, 1655*m* (sh), 1620*w*, 1565*w*, 1545*w*, 1525*m* (sh), 1510*m*, 1500*m*, 1475*w*, 1370*s*, 1270*m*, 1160*s*, 1130*s* (sh), 1090*s*, 1045*s*, 995*m*, 950*m*, 935*w* (sh), 900*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): *Table 2.* ^{13}C-NMR (HMQC 100 MHz, $CDCl_3$): *Table 3.* ESI-MS: 948 (50, $[M + H]^+$), 970 (100, $[M + Na]^+$), 986 (50, $[M + K]^+$).

REFERENCES

[1] J.-L. Maloisel, A. Vasella, *Helv. Chim. Acta* **1992,** *75,* 1491.
[2] B. M. Trost, D. L. van Vranken, *J. Am. Chem. Soc.* **1990,** *112,* 1261.
[3] R. R. Schmidt, *Angew. Chem.* **1986,** *98,* 213.
[4] C. D. Warren, R. W. Jeanloz, *Carbohydr. Res.* **1977,** *53,* 67.
[5] R. U. Lemieux, M. T. Takeda, B. Y. Chung, *ACS Symp. Ser.* **1976,** *39,* 90.
[6] H.-H. Lee, D. A. Schwartz, J. F. Harris, J. P. Carter, J. J. Krepinsky, *Can. J. Chem.* **1986,** *64,* 1912.
[7] P. L. Durette, E. P. Meitzner, T. Y. Shen, *Carbohydr. Res.* **1979,** *77,* Cl.
[8] S. Wolfe, S. K. Hasan, *Can. J. Chem.* **1970,** *48,* 3572.
[9] S. Sakuda, A. Isogai, T. Makita, S. Matsumoto, K. Koseki, H. Kodama, A. Suzuki, *Agric. Biol. Chem.* **1987,** *51,* 3251.
[10] D. Koga, A. Isogai, S. Sakuda, S. Matsumoto, A. Suzuki, S. Kimura, *Agric. Biol. Chem.* **1987,** *51,* 471.
[11] K. D. Spindler, M. Spindler-Barth, unpublished results.
[12] G. W. Fischer, *Anal. Chim. Acta* **1977,** *92,* 149.
[13] S. Subramanian, A. Bax, *J. Magn. Reson.* **1987,** *71,* 325.
[14] A. Bax. M. Ikura, L. E. Kay, D. A. Torchia, R. Tschudin, *J. Magn. Reson.* **1990,** *86,* 304; A. Bax, R. H. Griffey, B. L. Hawkins, *ibid.* **1983,** *55,* 301.
[15] J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong, C. N. Whitehouse, *Science* **1989,** *246,* 64.