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Synthesis of a phenyl β-avobioside derivative of the disaccharide component of avoparcins

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ABSTRACT

The synthesis of the phenyl β-glycoside of avobiose, a disaccharide fragment present in the antibiotic avoparcin, is reported [1]. It is based on glycosylation of phenyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside with 2,3,6-trideoxy-4-*O*-*p*-nitrobenzoyl-3-trifluoroacetamido-L-*ribo*-hex-1-enitol, a fully protected glycal of L-ristosamine, in the presence of trimethylsilyl triflate.

INTRODUCTION

During the past two decades, considerable interest has been devoted to the structural elucidation and synthesis of the glycopeptide-type vancomycin and related antibiotics [1,2]. A common structural feature of many representatives of this group of antibiotics is a 2-*O*-(3-amino-2,3,6-trideoxy-α-L-hexopyranosyl)-β-D-glucopyranosyl side chain attached to the tri- or tetra-cyclic heptapeptide aglycon. However, the aminotrideoxy sugar component (L-acosamine [3], L-ristosamine [4,5], L-vancosamine [6,7] and 4-*epi*-L-vancosamine [8–11]) of the heterodisaccharide unit varies in the individual antibiotics.

Until now, only the synthesis of phenyl β-acobioside [12], present in the vancomycin-type compounds actinoidin A and B, and of the heterotetrasaccharide side-chain (ristotetraose [13]) of ristocetin (ristomycin) A have been accomplished.

The present paper deals with the synthesis of the common heterodisaccharide component (Fig. 1) of avoparcins [4] α and β and helvecardins [5] A and B, which is

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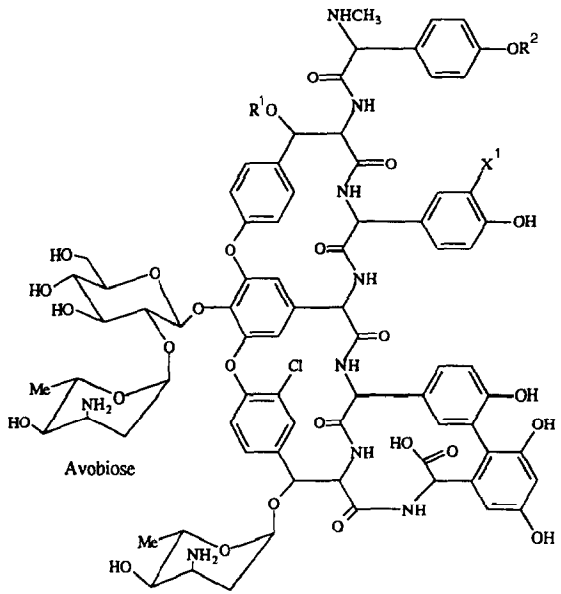


	X^1	R^1	R^2
Avoparcin α	H	α-D-Man*p*	α-L-Rha*p*
Avoparcin β	Cl	α-D-Man*p*	α-L-Rha*p*
Helvecardin A	Cl	α-D-Man*p*	2-O-Me-α-L-Rha*p*
Helvecardin B	Cl	H	2-O-Me-α-L-Rha*p*

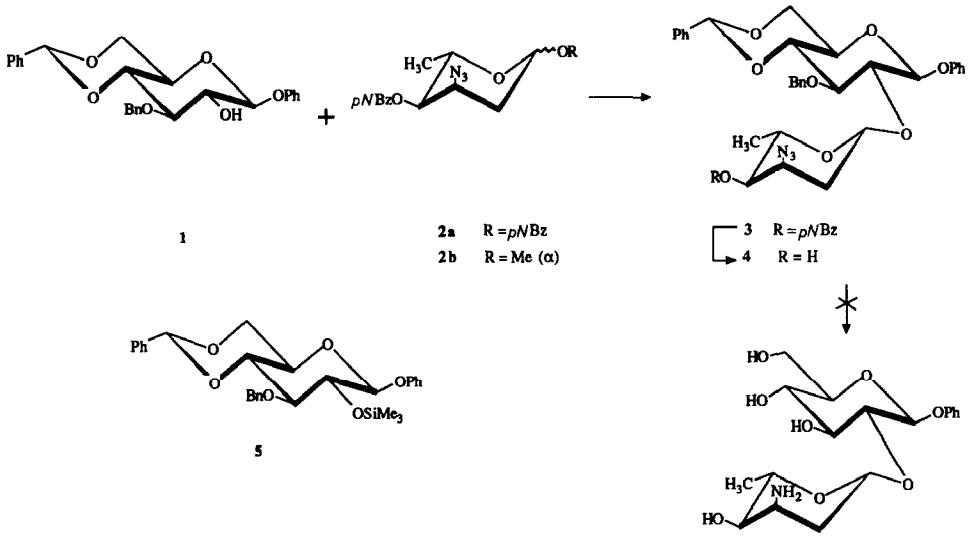
Fig. 1. Structures of avoparcin (α and β) and helvecardin (A and B).

composed of L-ristosamine and D-glucose. Since this disaccharide was first isolated from the avoparcins, we suggest naming it avobiose.

RESULTS AND DISCUSSION

At first, a strategy was attempted analogous to that successfully used [12] for the preparation of phenyl β-acobioside. Thus, phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**1**) as a glycosyl acceptor was to be condensed with 3-azido-2,4,6-trideoxy-1,4-di-*O*-*p*-nitrobenzoyl-D-*ribo*-hexopyranose (**2a**) or with the corresponding methyl α-glycoside **2b** as glycosyl donors (Scheme 1). However, when **1** and methyl 3-azido-2,3,6-trideoxy-4-*O*-*p*-nitrobenzoyl-α-L-*ribo*-hexopyranoside [2] (**2b**) in dichloromethane were treated under N_2 with a catalytic amount of trimethylsilyl triflate in the presence of molecular sieves, phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-trimethylsilyl-β-D-glucopyranoside (**5**) was the only isolable product (besides the starting materials **1** and **2b**); **5** yielded **1** on methanolysis with methanolic sodium methoxide.

When the di-*p*-nitrobenzoate [14] **2a** was used as the glycosylating agent under the same conditions, phenyl 2-*O*-(3-azido-2,3,6-trideoxy-4-*O*-*p*-nitrobenzoyl-β-L-*ribo*-



Scheme 1.

hexopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**3**) was the only isolable compound of disaccharide character. No product with an α-interglycosidic bond was formed. The β anomeric interglycosidic connection in **3** was unequivocally demonstrated by the ^{1}H-NMR spectrum: the signal for H-1′ appeared at 5.36 ppm as a doublet of doublets with coupling constants of 9 and 2.5 Hz, in agreement with 1′,2′*ax* and 1′,2′*eq* relationships, respectively. The remaining $J_{x',y'}$ values (Table I) indicated no change of the $^1C_4$(L) conformation of the azido-deoxy sugar moiety.

Zemplén transesterification of **3** resulted in the azido alcohol **4**, but reduction of the azido group and *O*-deprotection in a single step failed to afford the corresponding amino sugar.

Thus, hydrogenation of **4** in 60% acetic acid or 1,4-dioxane in the presence of Pd-charcoal at room temperature gave only fission products, and no disaccharide could be isolated, and attempted reduction with sodium in liquid ammonia led only to extensive degradation, as revealed by chromatography. Attempts to remove the benzylidene group prior to reduction, by means of trifluoroacetic acid containing 3% water in dichloromethane [14] or with iodine in methanol [15] did not yield the debenzylidenated disaccharide, but only products of decomposition.

In view of these disappointing results, we turned our attention to another route, depicted in Scheme 2, based on glycosidation of an orthoester with phenol and coupling of the resulting phenyl glycoside with a 3-amino- or 3-azido-3-deoxy glycal precursor of the ristosamine moiety.

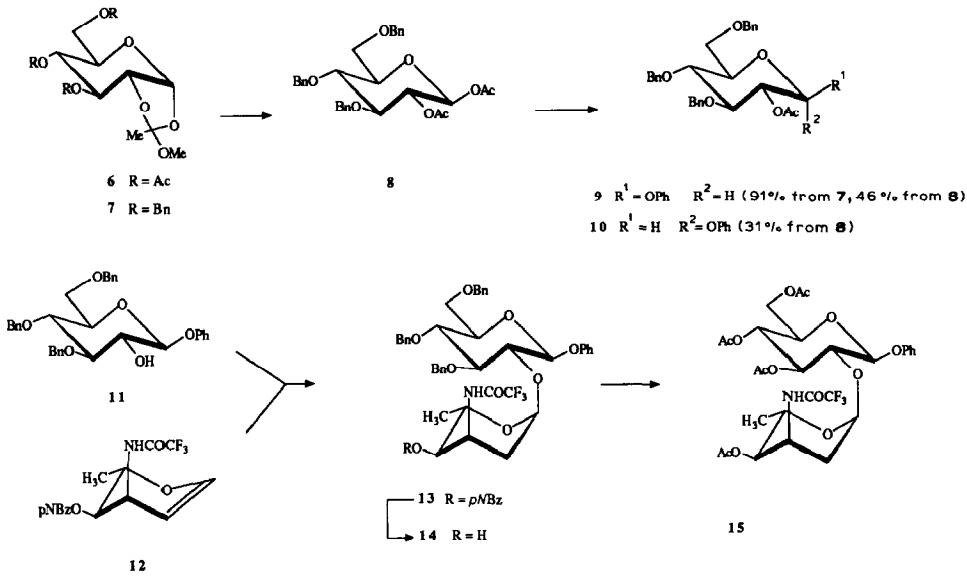
The tri-*O*-acetyl orthoester derivative **6** of D-glucose was readily prepared [16] from tetra-*O*-acetyl-α-D-glucopyranosyl bromide and converted into the corre-

TABLE 1

^{1}H-NMR data for compounds **3–5**, **9–11**, and **13–15**

Compound	H-1	H-2	H-3	H-4	H-5	H-6a	H-6e	H-1′	H-2′a	H-2′a	H-3′	H-4′	H-5′	H-6′	OCH_2Ph	Ph	Others
3	5.04	4.05	3.76	3.83	3.59	4.41	3.78	5.36	2.12	1.89	4.31	5.00	3.59	1.31			
4	5.03	4.03	3.69	3.80	3.57	4.39	3.78	5.27	2.12	1.77	4.08	3.36	3.64	1.33			
5	5.03	←(3.65–3.95)→			3.57	4.38	3.79										
9	4.95	5.38	←(3.78–3.62)→		3.70	(3.78–3.67)	3.80								4.82 and 4.70 4.82 and 4.59 4.60 and 4.53	7.98–6.39 (4 Ph)	2.02 (OAc)
10	5.70	5.02	4.23	3.85	3.94	3.76	3.62								4.90 and 4.83 4.83 and 4.53 4.62 and 4.44	7.48–6.79 (4 Ph)	2.02 (OAc)
11	4.89	3.85	←(3.73–3.66)→		3.64	(3.73–3.64)	3.81								4.97 and 4.89 4.87 and 4.59 4.61 and 4.53	7.41–7.04 (4 Ph)	
13	5.02	4.15	3.85	3.81	3.76	(3.81–3.75)		5.48	2.02	1.72	4.67	4.89	4.82	1.36	5.02 and 4.65 4.84 and 4.75 4.57 and 4.63	8.25 and 8.03 (PNBz)	7.92 (NH)
14	4.94	4.07	←(3.84–3.65)→					5.41	1.70	1.89	4.38	3.51	4.38	1.37	5.01 and 4.72 4.82 and 4.61 4.61 and 4.53	7.30–6.95 (4 Ph)	7.89 (NH)
15	5.12	4.17	5.38	5.10	3.92	4.33	4.17	5.10	2.03	1.79	4.57	4.53	4.40	1.36		7.33, 7.08, 7.03 (1 Ph)	2.09, 2.08, 2.05 2.00, 1.49 (5 Ac)

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6}$	$J_{6a,6b}$	$J_{1',2'a}$	$J_{1,',2'e}$	$J_{2'a,2'e}$	$J_{2'e,3'}$	$J_{2'a,3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'}$
3	8	8	10	9	9	5	10	9	2.5		3	3	5	10	6
4	8	8	9.5	10	10.5	5	11	9	4		2.5	3	3	9	6
5	7.5						10.5								
9	8	9	10	10	5	2	11								
10	3	10	9	9	3	1	11								
11	8	8					11								
13	9	9	10	10				2	0.5	14			4	10	6
14	9	9	10				12	2.5	0.5	14	2	3	4	10	6
15	9	9	9		5.5	2.5	12	2	0.5	14			4	10	6



Scheme 2.

sponding tri-*O*-benzyl analog [17] **7** by base-catalyzed *O*-deacetylation and subsequent benzylation.

Reaction of **7** with phenol in boiling chlorobenzene, i.e., under the conditions reported by Honma and Hamada [18], afforded the crystalline phenyl β-glycoside **9** with excellent stereoselectivity in 91% yield. Since glycosidations of orthoesters often proceed with low stereoselectivity and yield, in contrast to the present instance, we had first examined a different approach to **9**. The orthoester **7** was converted into an alternative glycosyl donor, namely, the corresponding 1,2-*trans*-di-*O*-acetyl derivative **8**. However, coupling of **8** with phenol by use of trimethylsilyl triflate as a condensing agent gave a mixture of anomers **9** and **10** with poor stereoselectivity (1.5 : 1) and in lower total yield (77%). Zemplén deacetylation of **9** gave the desired glycosyl acceptor **11** in 92% yield.

The glycosyl donor, 2,3,6-trideoxy-4-*O*-*p*-nitrobenzoyl-3-trifluoroacetamido-L-*ribo*-hex-1-enitol (**12**) was obtained from di-*O*-acetyl-L-rhamnal in four steps as previously reported [19]: (*i*) allylic azidolysis, (*ii*) LAH reduction, (*iii*) *N*-trifluoroacetylation, and (*iv*) *p*-nitrobenzoylation. Alternatively, it could be prepared via formation of the hex-2-enopyranose, Michael addition of hydrazoic acid, and reduction [20].

Then glycosylation of **11** with the glycal **12** in the presence of trimethylsilyl triflate afforded the disaccharide **13**, isolated in 81% yield after flash chromatography. The α-L linkage was unambiguously deduced from ^{1}H-NMR data, since H-1′ appeared at 5.48 ppm as a doublet of doublets with small coupling constants, $J = 2$ and $J' = 0.5$. Final removal of the *p*-nitrobenzoate ester by alkaline hydrolysis

gave **14** and subsequent removal of the benzyl ethers by sodium in liquid ammonia and oxolane, gave phenyl β-avobioside, isolated as its peracetyl derivative **15**.

EXPERIMENTAL

General Methods.—Melting points were determined on a Kofler hot stage and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker WP 200 SY instrument at 200 and 50.3 MHz, using Me_4Si as internal standard. IR spectra were obtained with a Perkin–Elmer 283B photometer. CI (ammonia)-mass spectra were obtained with a Nermag R10-10 spectrometer. Flash chromatography [21] was performed on Merck Silica Gel (Art. 9385), and TLC on Silica Gel $60F_{254}$ ΔC Alurolle (Merck), the spots being detected by spraying with 5% ethanolic H_2SO_4 and heating.

Phenyl 2-O-(3-azido-2,3,6-trideoxy-4-O-p-nitrobenzoyl-β-L-ribo-hexopyranosyl)-3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (**3**).—A solution of 3-azido-2,3,6-trideoxy-1,4-di-*O*-*p*-nitrobenzoyl-L-*ribo*-hexopyranose (**2a**; 217 mg, 0.46 mmol) and phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**1**; 200 mg, 0.46 mmol) in dry CH_2Cl_2 (25 mL) was stirred overnight with 600 mg of powdered molecular sieves (Fluka, 3A) under N_2 at room temperature. After cooling to −40°, trimethylsilyl triflate (36 μL) was added and the mixture was stirred for 4 h at −15°. The mixture was diluted with CH_2Cl_2 (50 mL), washed with satd $NaHCO_3$ solution, and evaporated. The residue was chromatographed on a Kieselgel 60 column (50 g) with 9:1 toluene–EtOAc as the eluent, to give unreacted **2a** (100 mg, 48%) and **3** (95 mg, 36%; after crystallization from EtOH–water); mp 142–143°; $[\alpha]_D^{25}$ +24.6° (*c* 0.8, $CHCl_3$); ν_{max}^{KBr} 2100 (N_3), 1725 (C=O), 1522 and 1343 (NO_2) cm^{-1}.

Anal. Calcd for $C_{39}H_{38}N_4O_{11}$ (738.76); C, 63.34; H, 5.14; N, 7.58. Found: C, 63.27; H, 5.33; N, 7.56.

Phenyl 2-O-(3-azido-2,3,6-trideoxy-β-L-ribo-hexopyranosyl)-3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (**4**).—A solution of **3** (58 mg; 0.078 mmol) in abs MeOH was treated with 0.1 M methanolic NaOMe, and boiled under reflux for 5 min. After cooling to room temperature, the solution was treated with Amberlite IRA-120 (H^+), and evaporated. After chromatography (30 g of Kieselgel 60) with 9:1 toluene–EtOAc, the product was crystallized from CH_2Cl_2–hexane to give the disaccharide **4** (36.3 mg, 78.4%); mp 180–182°; $[\alpha]_D^{25}$ −67.1° (*c* 0.8, $CHCl_3$); ν_{max}^{KBr} 3465 (O–H), 2101 (N_3) cm^{-1}.

Anal. Calcd for $C_{32}H_{35}N_3O_8$ (589.62): C, 65.18; H, 5.98; N, 7.13. Found: C, 65.03; H, 6.03; N, 7.13.

Phenyl 3-O-benzyl-4,6-O-benzylidene-2-O-trimethylsilyl-β-D-glucopyranoside (**5**).—A solution of phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**1**; 434 mg, 1.0 mmol), and methyl 3-azido-2,3,6-trideoxy-4-*O*-*p*-nitrobenzoyl-α-L-*ribo*-hexopyranoside (**2b**; 336 mg, 1.0 mmol) in anhyd CH_2Cl_2 (30 mL) was stirred with

molecular sieves (100 mg, Fluka, 3A) for 1 h under N_2 at room temperature. After cooling to −40° and addition of trimethylsilyl triflate (100 μL), stirring was continued for 4 h at −15°. Processing as described for **3** yielded 184 mg (69.7%) of compound **5** after recrystallization from CH_2Cl_2; mp 62–63°; $[\alpha]_D^{25}$ +55° (*c* 0.8, $CHCl_3$).

Anal. Calcd for $C_{29}H_{34}O_6Si$ (506.65): C, 68.74; H, 6.96. Found: C, 68.34; H, 6.76.

Phenyl 2-O-acetyl-3,4,6-tri-O-benzyl-β-D-glucopyranoside (**9**) *and its α anomer* (**10**).—*A. From* **7** *and phenol.* A solution of 3,4,6-tri-*O*-benzyl-α-D-glucopyranose 1,2-methyl orthoacetate (**7**, 396 mg, 0.78 mmol) and phenol (96 mg, 1.02 mmol) in chlorobenzene (10 mL) was heated under reflux for 2 h. Evaporation under diminished pressure afforded a residue which was crystallized from EtOH to give **9** (403 mg, 91%).

B. From **8** *and phenol.* A mixture of **8** (ref. 22) (2.7 g, 5 mmol) and phenol (0.6 g, 8 mmol) in anhyd CH_2Cl_2 (8 mL) was stirred in the presence of molecular sieves for 45 min at −40°. Trimethylsilyl triflate (1 mL, 5 mmol) was then added and stirring maintained for 30 min at the same temperature. The reaction mixture was allowed to reach room temperature and Et_3N (0.5 mL) was added. Evaporation under diminished pressure and flash chromatography afforded successively **9** (1.3 g, 46%) and **10** (0.9 g, 31%).

Compound **9** had: mp 83–84°, $[\alpha]_D^{20}$ +3° (*c* 1, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 1749 (C=O ester), 1600 (Ar) cm^{-1}; MS (NH_3): *m/z* 586 $[M + NH_4^+]$, 475 $[M - PhO]^+$, 91 $[PhO]^+$.

Anal. Calcd for $C_{35}H_{36}O_7$ (568.67): C, 73.92; H, 6.38. Found: C, 73.96; H, 6.46.

Compound **10** had: mp 97–98°; $[\alpha]_D^{20}$ +133° (*c* 1, $CHCl_3$); MS (NH_3): *m/z* 586 $[M + NH_4^+]$.

Anal. Calcd for $C_{35}H_{36}O_7$ (568.67); C, 73.92; H, 6.38. Found: C, 73.90; H, 6.36.

Phenyl 3,4,6-tri-O-benzyl-β-D-glucopyranoside (**11**).—A solution of **9** (800 mg, 1.35 mmol) in M NaOMe in MeOH (30 mL) was stirred overnight at room temperature. Neutralization by addition of Amberlite IR 50 (H^+) ion-exchange resin, followed by filtration and concentration of the filtrate under diminished pressure gave **11** (680 mg, 92%) as a crystalline residue, which was recrystallized from hexane–EtOAc; mp 94°; $[\alpha]_D^{20}$ −21.5° (*c* 1, $CHCl_3$); $\nu_{max}^{CHCl_3}$, 3599 (OH), 1600 (Ar) cm^{-1}. MS (NH_3): *m/z* 544 $[M + NH_4]^+$, 454, 91.

Anal. Calcd for $C_{33}H_{34}O_6$ (526.63): C, 75.26; H, 6.51. Found: C, 75.22; H, 6.51. Found: C, 75.22; H, 6.67.

Phenyl 3,4,6-tri-O-benzyl-2-O-(2,3,6-trideoxy-4-O-p-nitrobenzoyl-3-trifluoroacetamido-α-L-ribo-hexopyranosyl)-β-D-glucopyranoside (**13**).—A solution of **11** (304 mg, 0.58 mmol) and glycal (refs. 19 and 20) **12** (216 mg, 0.58 mmol) in a minimum amount of dry CH_2Cl_2 (1 mL) was stirred at room temperature for 1 h in the presence of 4A molecular sieves. The reaction mixture was then cooled to −40° and stirred for 15 min and then trimethylsilyl triflate (121 μL, 0.58 mmol) was added. After the mixture was stirred at −40° for 30 min, and then allowed to reach room temperature gradually overnight, triethylamine (≈ 0.5 mL) was added,

and the resulting solution was subjected to flash chromatography with 6:1 hexane–EtOAc. The isolated material was chromatographed once more, using 19:1 toluene–acetone, to give **13** (425 mg, 81.5%) which crystallized from EtOH; mp 74–75°; $[\alpha]_D^{20}$ −32° (*c* 1, $CHCl_3$), $\nu_{max}^{CHCl_3}$ 1732 (CO ester), 1601 (Ar), 1531 (CO amide), 1349 (NO_2) cm^{-1}; MS (NH_3) *m/z*: 918 $[M + NH_4]^+$, 91.

Anal. Calcd for $C_{48}H_{47}F_3N_2O_{12}$ (900.91): C, 63.99; H, 5.26; N, 3.11. Found: C, 64.06; H, 5.30; N, 3.03.

*Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-(2,3,6-trideoxy-3-trifluoroacetamido-α-*L*-ribo-hexopyranosyl)-β-*D*-glucopyranoside* (**14**).—A solution of **13** (290 mg, 0.32 mmol) in MeOH (25 mL) was stirred at room temperature for 30 min in the presence of aq 0.1 M NaOH (0.7 mL), neutralized with Amberlite 50 (H^+), and concentrated *in vacuo*. The syrupy residue was purified by flash chromatography with 5:1 hexane–EtOAc as eluent to give crystalline **14** (220 mg, 91%); mp 156–158°, $[\alpha]_D^{20}$ −36° (*c* 0.9, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 3619 (OH), 1728 (CO ester), 1600 (Ar) and 1530 cm^{-1} (CO amide). MS (NH_3): *m/z* 769 $[(M + NH_4]^+$, 226 (75%).

Anal. Calcd for $C_{41}H_{44}F_3NO_9$ (751.80): C, 65.50; H, 5.90; N, 1.86. Found: C, 65.70; H, 6.02; N, 2.00.

*Phenyl 3,4,6-tri-*O*-acetyl-2-*O*-(3-trifluoroacetamido-4-*O*-acetyl-2,3,6-trideoxy-α-*L*-ribo-hexopyranosyl)-β-*D*-glucopyranoside* (**15**).—To a solution of **14** (160 mg, 0.18 mmol) in anhyd THF (10 mL) was added liquid NH_3 (≃ 5 mL) and small pieces of sodium until a blue coloration was obtained, and the mixture was stirred overnight at room temperature. Addition of satd, aq NH_4Cl solution, and evaporation, gave a solid residue which was dissolved in pyridine (6 mL). Acetic anhydride (1 mL) was added, and the mixture was stirred overnight. Conventional processing by extraction with CH_2Cl_2 and flash chromatography of the residue with 1:2 hexane–EtOAc gave **15** (70 mg, 65%); $[\alpha]_D^{20}$ −261° (*c* 0.13, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 3696 (NH), 1742 (CO ester), 1676 (CO amide), 1600 (Ar) cm^{-1}; MS (NH_3): *m/z* 613 $[M + NH_4]^+$; 596 $[M + H^+]$.

Anal. Calcd for $C_{28}H_{37}NO_{13}$ (595.61): C, 56.47; H, 6.26; N, 2.35. Found: C, 56.60; H, 6.15; N, 2.22.

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