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SYNTHESIS OF PHENYL β-ACOBIOSIDE, A DERIVATIVE OF THE DISACCHARIDE COMPONENT OF ACTINOIDINS*

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ABSTRACT

The title glycoside [phenyl 2-*O*-(3-amino-2,3,6-trideoxy-α-L-*arabino*-hexopyranosyl)-β-D-glucopyranoside] was prepared from phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside and 3-azido-2,3,6-trideoxy-1,4-di-*O*-*p*-nitrobenzoyl-L-*arabino*-hexopyranose or 3-azido-2,3,6-trideoxy-4-*O*-*p*-nitrobenzoyl-L-*arabino*-hexopyranosyl chloride.

INTRODUCTION

A common structural feature of the vancomycin group of antibiotics (actinoidin, avoparcin, vancomycin) is the heterodisaccharide side-chain which is attached[1] to ring B of the vancomycinic acid or monodechlorovancomycinic acid unit of the tricyclic heptapeptide aglycons. Most of these disaccharides are of the 2-*O*-(3-amino-2,3,6-trideoxy-α-L-hexopyranosyl)-β-D-glucopyranosyl type with different stereochemistry in the individual antibiotics.

The disaccharide moiety acobiose is present in actinoidins A and B (**1a** and **1b**). Formulae **1a** and **1b** were first suggested by Sztaricskai *et al.*[2] and later supported by Berdnikova *et al.*[3] on the basis of ^{1}H-n.m.r. data, but the configuration of the glycosidic linkages was not established.

No syntheses of the heterodisaccharide components or their derivatives have been reported and we now describe a synthesis of phenyl β-acobioside (**2a**), which, in principle, could be of general use for the heterodisaccharide units of the other vancomycin-type antibiotics. The phenyl group was chosen as the aglycon since the phenyl glycosides could be model compounds suitable for comparative studies.

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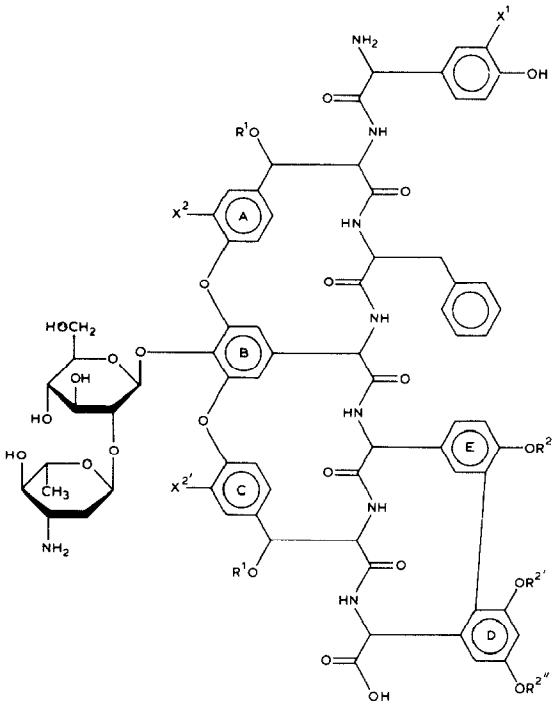
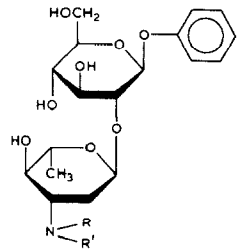
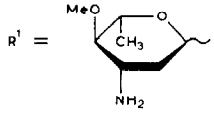
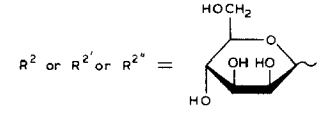


1a $X^1 = X^2 = R^1 = H$, $X^{2'} = Cl$
1b $X^1 = X^{2'} = Cl$, $R^1 = X^2 = H$



2a R = R′ = H
2b R = R′ = Et

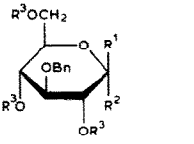




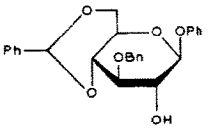
RESULTS AND DISCUSSION

The protective groups of the key intermediates **5, 9**, and **10** were selected so that they could be removed readily after preparation of the protected disaccharide. Acetylation of 3-*O*-benzyl-D-glucose[4] gave 1,2,4,6-tetra-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranose, which was converted into phenyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-α- (**3a**) and -β-D-glucopyranoside (**3b**) using the Coleman method[5]. *O*-Deacetylation of **3a** and **3b** gave phenyl 3-*O*-benzyl-α- (**4a**) and -β-D-glucopyranoside (**4b**), respectively. Benzylidenation of **4b** afforded phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**5**) which has HO-2 unsubstituted. In the vancomycin group of antibiotics[1], HO-2 of the glucose unit is glycosylated by different deoxy-amino sugars. Several methods have been elaborated for the synthesis of acosamine[6], of which that reported by Gupta[7] is the most suitable. Thus, methyl

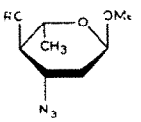
3-azido-2,3,6-trideoxy-α-L-*arabino*-hexopyranoside (**6**) was converted into the 4-*p*-nitrobenzoate **7**. Acid hydrolysis of **7** gave 3-azido-2,3,6-trideoxy-4-*O*-*p*-nitrobenzoyl-L-*arabino*-hexopyranose (**8**), which was converted into the 1,4-di-*p*-nitrobenzoate **9** in good yield. Treatment of **9** with dry hydrogen chloride in dichloromethane gave 80–90% of the glycosyl chloride **10**, which was used without further purification for the glycosylation of **5**.



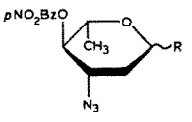
3a R^1 = H, R^2 = PhO, R^3 = Ac
3b R^1 = PhO, R^2 = H, R^3 = Ac
4a R^1 = H, R^2 = PhO, R^3 = H
4b R^1 = PhO, R^2 = H, R^3 = H



5

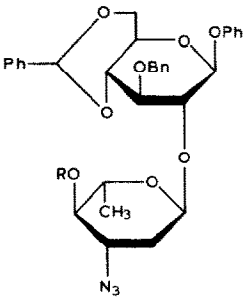


6 R = H
7 R = *p*NO_2Bz

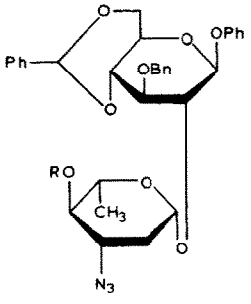


8 R = OH
9 R = *p*NO_2BzO
10 R = Cl

Condensation of **5** and **10** in the presence[8] of silver trifluoromethanesulfonate and *N,N,N',N'*-tetramethylurea gave a 4:1 mixture of the disaccharide derivatives **11a** and **11b**, which was resolved by column chromatography to give the crystalline compounds in 46% overall yield. Reaction of **5** and **9** in the presence of trimethylsilyl triflate[9] was stereospecific and gave **11a**. The structure of these compounds was indicated by the n.m.r. data (Tables I and II). Zemplén saponification of **11a** and **11b** gave **12a** and **12b**, respectively.



11a R = *p*NO_2Bz
12a R = H



11b R = *p*NO_2Bz
12b R = H

The glycosidic linkages characteristic of the disaccharide components[1] of the antibiotics of the vancomycin group are present in **12a**. Catalytic hydrogenation (ethanol, Pd/C) of **12a** reduced the azide group, and continuation of the reaction, after the addition of acetic acid[11], under more vigorous conditions (20–70 atm., 20°, 54 h) gave the *N,N*-diethyl derivative **2b** of phenyl β-acobioside. The presence of the diethylamino group in **2b** was indicated by elemental analysis and n.m.r. and mass spectra data (see Experimental, and Tables I and II).

TABLE I

^{1}H-NMR DATA (δ, J Hz)

Compound	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	H-1'	H-2'a	H-2'b	H-3'	H-4'	H-5'	H-6',6',6'	Others
3a[a]	5.74	5.01	4.21	5.17	4.18	4.06	4.01								
3b[a]	4.99	5 34	3.80	5.20	3.77	4.15	4.25								2.00, 2.02, 2.08 (3 OAc), 4.62 (OCH_2Ph) 6.95–7.37 (Ph)
4a[b]	5.39			(3.25–3.75)											4 53 (HO-6), 5.23 (OH), 5.29 (OH), 4.85 (OCH_2Ph), 6.95–7.50 (Ph)
4b[b]	4.93			(3.68–3.72)											4.63 (OH), 4.85 (OCH_2Ph), 5.29 (OH), 5.59 (OH), 6.94–7.48 (Ph)
5[a]	5.01	(3.68–3.91)			3.56	3.80	4.37								2.63 (OH), 4.82, 5.02 (OCH_2Ph), 5.58 (H-7), 7.00–7.75 (Ph)
7[a]								4.83	1.85	2.27	4.02	4.94	3.96	1.24	3.40 (OMe), 8.23–8.35 (pNO$_2$-C$_6$H$_4$CO)
11a[a]	5.17	4.01	3.93	3.83	3.61	3.81	4.41	5.50	1.70	2.01	3.86	4.88	4.36	1.23	5.02, 4.74 (OCH_2Ph), 5.61 (H-7), 7.0–7.6 (Ph), 8.05–8.3 (pNO$_2$-C$_6$H$_4$CO)
11b[a]	5.08	4.07	3.81	3.80	3.56	3.82	4.39	5.12	1.79	2.34	3.74	4.97	3.67	1.27	4 89, 4.98 (OCH_2Ph), 5.58 (H-7), 7.0–7.6 (Ph), 8.15-8.37 (pNO$_2$-C$_6$H$_4$CO)
12a[a]	5.09	3.91	3.88	3.80	3.65	3.79	4.38	5.38	1.55	1.91	3.58	3.05	4.02	1.26	2.16 (OH), 4.68, 5.00 (OCH_2Ph), 5.60 (H-7), 6.90–7.60 (Ph)
12b[a]	5.07	4.04	3.76	3.76	3 54	3.80	4.38	4.99	1.62	2.22	3.39	3.14	3.36	1.35	2.38 (OH), 4.84, 4.94 (OCH_2Ph), 5.58 (H-7), 7.0–7.62 (Ph)
2b[c]	5 36		(3.53–3.82)			3.90	3.90	5.50	2.02	2.35	(3.53	3.82)	4.06	1.28	1.31 (CH_2CH_3), 3.08, 3.41 (CH_2CH_3), 7.1–7.47 (Ph)
2a[c]	5.35		(3.50–3.80)				3.91	5 41	1.96	2.40	3.46	3.31	4 04	1.25	7.05–7.45 (Ph)

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$	$J_{1,2b}$	$J_{1,2a}$	$J_{2b,3}$	$J_{2a,3}$	$J_{2a,2b}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$
3a	3.6	10.0	9.5	10.0											
3b	7.8	9.2	9.2	9.7	2.7	5.7	12.0								
4a	4.0														
4b	6.6														
5	7.0						10.5								
8								1.2	3.4	5.0	12.5	12.5	9.7	9.7	6.1
11a	7.5	8.5	9.0	9.8	8.5	4.7	10.5	1.4	3.2	5.0	12.8	13.0	9.7	9.7	6 2
11b	7.5	7.5				4.7	10.5	2.0	9.5	5.0	12.5	12.5	9.5	9.5	6.1
12a	7.2					4.7	10.2	1.2	3.7	4.8	12.0	13.0	9.0	9.0	6.1
12b	7.7	8.5				4.7	10.2	2.0	9.6	5.0	12.5	12.5	9.0	9 0	6.1
2b	7.5							1.4	3.5	3.4	12.5	12.5			
2a	7.5							1.3	3.8	4.2	12.5	13.0	10.0	9.0	6.2

[a]In $CDCl_3$. [b]In Me_2SO. [c]In D_2O.

TABLE II

^{13}C-N.M R CHEMICAL SHIFTS[a] *(P P.M.)*

Compound	*1*	*2*	*3*	*4*	*5*	*6*	*1'*	*2'*	*3'*	*4'*	*5'*	*6'*	*Others*
3a[b]	94.41	(72.71)	77.09	(69.42)	68.25	61.73							170.22, 169.76, 169.16, 156.02, 137.96, 129.36, 128.18, 127.50, 122.74, 116.60, 74.75, 20.43, 20.34
3b[b]	99.29	(72.21)	79.86	(72.21)	69.54	62.27							129.43, 128.38, 127.73, 123.06, 116.83
4a[c]	98.16	(73.75)	82.19	(71.50)	(69.52)	60.58							157.20, 139.73, 129.47, 127.97, 127.48, 127.07, 122.04, 117.10, 73.90
4b[c]	100.57	(73.90)	85.11	(73.24)	(69.49)	60.71							157.52, 139.57, 129.45, 128.00, 127.55, 127.13, 121.95, 116.42, 77.01
5b[b]	101.32	74.04	(80.25)	(81.09)	66.54	68.63							156.95, 138.29, 137.18, 129.51, 128.97, 128.39, 128.20, 127.98, 127.77, 126.02, 123.11, 117.05, 101.40, 74.62
7b[b]							97.36	35.09	54.85	76.88	65.67	17.53	57.73 OMe, 130.94, 123.66
11a[b]	99.87	76.05	(81.86)	(81.71)	66.36	68.69	96.74	34.84	54.47	76.85	65.98	17.42	163.59, 156.92, 137.18, 138.80, 129.71, 129.06, 126.00, 123.55, 123.07, 116.39, 101.40, 74.92
11b[b]	101.94	80.20	(79.61)	(80.74)	66.54	68.68	99.74	36.55	59.97	76.36	70.98	17.72	130.89, 129.82, 128.98, 128.21, 128.13, 128.00, 127.57, 126.06, 123.67, 123.46, 116.94, 101.39, 74.99
12a[b]	99.54	76.28	81.81	81.54	66.06	68.61	97.09	34.67	60.05	75.83	67.88	17.55	156.68, 137.89, 137.11, 129.63, 129.00, 128.45, 128.23, 128.18, 127.94, 125.93, 122.82, 116.24, 101.19, 74.89
12b[b]	101.88	79.92	(79.73)	(80.71)	66.49	68.73	99.76	36.36	62.71	75.71	72.70	17.84	129.78, 128.96, 128.21, 128.10, 127.99, 127.50, 126.09,123.33, 116.87, 101.37, 74.83
2b[d]	98.38	(78.44)	(76.61)	(69.15)	(76.12)	60.70	97.07	28.08	58.83	69.52	69.63	16.65	130.17, 123.35, 116.24, 45.99, 9.72
2a[d]	98.24	(78.80)	(76.51)	(69.43)	(76.08)	60.66	97.03	33.44	49.55	72.34	68.78	16.55	156.19, 130.13, 123.33, 116.28

[a]The assignments given in parentheses were made by analogy with data[10] in the literature. [b]In $CDCl_3$. [c]In Me_2SO. [d]In D_2O.

When the catalytic hydrogenation of **12a** was performed in aqueous 60% acetic acid at atmospheric pressure (115 h, 20°), phenyl β-acobioside (**2a**, 43%) was obtained. The structure of **2a** was established unequivocally on the basis of elemental analyses, ^{1}H- and ^{13}C-n.m.r. data, and the mass spectrum.

The ^{1}H- and ^{13}C-n.m.r. data are summarised in Tables I and II. The ^{1}H assignments (Table I) were made with the aid of spin decoupling and two-dimensional (2D) chemical shift correlation[12] (COSY-45) experiments, and ^{13}C assignments were performed by the 2D chemical shift correlation method[13]. The anomeric configurations assigned to the various synthetic compounds were based on the $J_{1,2}$ values. On the basis of these and the other $^3J_{H,H}$ values, the favoured conformation of the D-glucopyranose and the L-deoxy sugar residues is $^4C_1$(D) and $^1C_4$(L), respectively. The ^{13}C chemical shifts of the signals of the anomeric carbons of the α anomers are at higher field in each case (Table II). The ^{13}C chemical shift value for C-1 of the β-D-glucopyranosyl residue of the disaccharide derivatives **11ab** and **12ab** is ~2 p.p.m. higher when the second structural unit is α. Also, the chemical shift of the signal of C-5′ of the disaccharides having a β-interglycosidic linkage is higher by ~5 p.p.m. than that of the corresponding α-linked compound.

EXPERIMENTAL

General methods. — Melting points (uncorrected) were determined on a Kofler hot-stage apparatus and in capillary tubes. Optical rotations were measured with a Perkin–Elmer 241 automatic polarimeter. The ^{1}H- (200 MHz) and ^{13}C-n.m.r. spectra (50.3 MHz) were recorded with a Bruker WP 200 SY spectrometer (internal or external Me_4Si). I.r. spectra (KBr) were recorded with a Perkin–Elmer 283 B spectrophotometer. Mass spectra were recorded with a VG-7035 spectrometer (direct insertion, 70 eV, ion-source temp. 150°). T.l.c. was performed on Kieselgel 60 F_{254} (Merck) with (*A*) light petroleum–acetone (7:3), (*B*) benzene–methanol (85:15), (*C*) benzene–methanol (97:3), (*D*) benzene–ethyl acetate (9:1), (*E*) 2-propanol–conc. ammonia–water (60:5:5), (*F*) 2-propanol–conc. ammonia–water (60:7:3), and detection by charring with sulphuric acid.

*Phenyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-α-* (**3a**) *and -β-*D*-glucopyranoside* (**3b**). — A solution of 1,2,4,6-tetra-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranose[14] (9.0 g, 20.5 mmol) in phenol (7.9 g, 83.7 mmol) was distilled *in vacuo*[5] in the presence of toluene-*p*-sulfonic acid, to give a mixture of **3a** and **3b**. Crystallisation from 2:1 ether–light petroleum gave **3b** (3.90 g, 40%), m.p. 112–113°, $[\alpha]_D^{23}$ −28° (*c* 0.7, chloroform).

Anal. Calc. for $C_{25}H_{28}O_9$: C, 63.55; H, 5.97. Found: C, 63.51; H, 5.89.

The mother liquor was concentrated, and the residue was treated with light petroleum and then crystallised from dry ethanol to give **3a**, m.p. 119–120°, $[\alpha]_D^{23}$ +113° (*c* 0.7, chloroform).

Anal. Calc. for $C_{25}H_{28}O_9$: C, 63.55; H, 5.97. Found: C, 63.63; H, 5.88.

*Phenyl 3-*O*-benzyl-α- and -β-*D*-glucopyranoside* (**4a** *and* **4b**). — A solution of

3b (3.3 g, 6.98 mmol) in dry methanol (20 mL) containing a catalytic amount of sodium methoxide was boiled under reflux for 3 h, then cooled, neutralised with acetic acid to pH ~6.0, and concentrated. The residue was crystallised from dry benzene to yield **4b** (2.06 g, 86%), m.p. 106–107°, $[\alpha]_D^{23}$ −52° (*c* 1.2, chloroform).

Anal. Calc. for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found: C, 65.95; H, 6.47.

O-Deacetylation of **3a** and crystallisation of the product were carried out as described above for the preparation of **4b**, to give **4a** (87%), m.p. 113–115°, $[\alpha]_D^{23}$ +135° (*c* 0.55, chloroform).

Anal. Calc. for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found: C, 65.36; H, 6.36.

*Phenyl 3-O-benzyl-4,6-O-benzylidene-β-*D*-glucopyranoside* (**5**). — A mixture of **4b** (2.0 g, 5.77 mmol), freshly fused zinc chloride (8.0 g, 59.0 mmol), and benzaldehyde (40 mL) was shaken at room temperature for 24 h, and then poured into a mixture of ice–water (50 mL) and light petroleum (150 mL). The crystals were collected, washed with water and light petroleum, and crystallised from ethanol to give **5** (1.61 g, 64.1%), m.p. 176–177° (crystallisation from dry benzene gives a 95% yield; m.p. 178–179°), $[\alpha]_D^{23}$ −33° (*c* 1.1, chloroform), R_F (solvent *A*) 0.53. Mass spectrum: *m/z* 435.0962 (0.05%) $M^+ + 1$, 434.1824 (2) M^+, 341.1067 (19) $M^+ - PhO$.

Anal. Calc. for $C_{26}H_{26}O_6$: C, 71.88; H, 6.03. Found: C, 71.52; H, 5.91.

*Methyl 3-azido-2,3,6-trideoxy-4-*O-p-*nitrobenzoyl-α-*L-arabino-*hexopyranoside* (**7**). — Conventional treatment of methyl 3-azido-2,3,6-trideoxy-α-L-*arabino*-hexopyranoside[7] (**6**; 0.68 g, 3.63 mmol) with pyridine (4.0 mL) and *p*-nitrobenzoyl chloride (1.30 g, 6.99 mmol), with crystallisation of the product from 2:1 ethanol–water, gave **7** (1.23 g, 68.7%), m.p. 66–67°, $[\alpha]_D^{23}$ −44° (*c* 0.8, chloroform); ν_{max}^{KBr} 2098 (C–N azide), 1725 (C=O ester), 1529 and 1349 cm^{-1} (NO_2). Mass spectrum: *m/z* 321 (6%) $M^+ - Me$, 305 (37) $M^+ - OMe$, 290 (10) $M^+ - Me - OMe$, 150 (78) $[C_6H_4NO_2CO]^+$.

Anal. Calc. for $C_{14}H_{16}N_4O_6$: C, 50.00; H, 4.80; N, 16.66. Found: C, 50.64; H, 4.87; N, 16.66.

*3-Azido-2,3,6-trideoxy-4-*O-p-*nitrobenzoyl-*L-arabino-*hexopyranose* (**8**). — Compound **7** (0.40 g, 1.19 mmol) was hydrolysed with 1:2 M hydrochloric acid–acetic acid (7.2 mL) at 80° for 2.5 h. The mixture was then concentrated. A solution of the syrupy residue in chloroform (30 mL) was washed with saturated aqueous $NaHCO_3$ and water, dried ($CaCl_2$), and concentrated. The residue (375 mg, 97%) was dried over wax *in vacuo* and then crystallised from light petroleum to give **8** (260 mg, 68%), m.p. 109–111°, $[\alpha]_D^{27}$ +8→+10° (*c* 1.6, chloroform; 24 h), R_F (solvent *B*) 0.75; ν_{max}^{KBr} 2095 (C–N azide), 1734 cm^{-1} (C=O ester). Mass spectrum (c.i.-ammonia): *m/z* 323 (28%) $M^+ + 1$, 280 (5) $M^+ + 1 - NH_3$.

Anal. Calc. for $C_{13}H_{14}N_4O_6$: N, 17.39. Found: N, 17.03.

*3-Azido-2,3,6-trideoxy-1,4-di-*O-p-*nitrobenzoyl-*L-arabino-*hexopyranose* (**9**). — Conventional *p*-nitrobenzoylation of **8** (485 mg, 1.5 mmol), with crystallisation of the product from 2:1 ether–light petroleum, gave **9** (525 mg, 74%), m.p. 71–73°, $[\alpha]_D^{27}$ +5° (*c* 0.75, chloroform), R_F (solvent *C*) 0.80; ν_{max}^{KBr} 2098 (C–N azide), 1734 (C=O ester), 1526 and 1319 cm^{-1} (NO_2).

Anal. Calc. for $C_{20}H_{17}N_5O_9$: N, 14.86. Found: N, 14.78.

*Phenyl 2-O-(3-azido-2,3,6-trideoxy-4-O-p-nitrobenzoyl-α- and -β-*L*-arabino-hexopyranosyl)-3-O-benzyl-4,6-O-benzylidene-β-*D*-glucopyranoside* (**11a** *and* **11b**). — (*a*) Dry hydrogen chloride was bubbled into a cold solution of **9** (236 mg, 0.5 mmol) in dry dichloromethane (10 mL) for 1 h. The separated *p*-nitrobenzoic acid was quickly removed and the solvent was evaporated *in vacuo*. Dry dichloromethane was evaporated several times from the residue to give the glycosyl chloride **10** (80–90%) which was used without further purification.

Compound **5** (217 mg, 0.50 mmol) was glycosylated[8] with freshly prepared **10** (236 mg, 0.50 mmol) in dry dichloromethane in the presence of *N,N,N',N'*-tetramethylurea and silver trifluoromethanesulfonate for 45 h. The mixture was then diluted with dichloromethane, filtered through Celite, washed successively with aqueous 10% $NaHCO_3$ and water, dried ($MgSO_4$), filtered, and concentrated. The residue was subjected to column chromatography (Kieselgel 60, 98:2 benzene–ethyl acetate) to give **11a** as colourless prisms (138.1 mg, 37.1%) from dry methanol; m.p. 165.5–166.5°, $[\alpha]_D^{20}$ −21° (*c* 0.5, chloroform), R_F (solvent *D*) 0.69; ν_{max}^{KBr} 2096 (C–N azide), 1727 (C=O ester), 1529 and 1347 cm^{-1} (NO_2). Mass spectrum (c.i.-ammonia): *m/z* 740 (3.2%) $M^+ + 1$, 739 (2.6) M^+. After mixing the sample with NH_4Cl (1:10), an e.i. mass spectrum of excellent quality was obtained: 739 (2%) M^+, 710 (6), 647 (12), 619 (14), 434 (8), 361 (12), 341 (24), 279 (44), and 167 (100).

Anal. Calc. for $C_{39}H_{38}N_4O_{11}$: C, 63.40; H, 5.18; N, 7.57. Found: C, 63.33; H, 5.34; N, 7.50.

Compound **11b** crystallised as colourless needles from dry methanol; m.p. 194–195°, $[\alpha]_D^{20}$ +23° (*c* 1, chloroform), R_F (solvent *D*) 0.62; ν_{max}^{KBr} 2093 (C–N azide), 1736 (C=O ester), 1527 and 1346 cm^{-1} (NO_2). Mass spectrum: *m/z* 667 (1%), 637 (2), 524 (4), 435 (8), 417 (19), and 361 (27).

Anal. Calc. for $C_{39}H_{38}N_4O_{11}$: C, 63.40; H, 5.18; N, 7.57. Found: C, 63.76; H, 5.42; N, 7.22.

(*b*) A mixture of **5** (165 mg, 0.38 mmol), **9** (180 mg, 0.38 mmol), and powdered Molecular sieve Type 3A (300 mg) in dry dichloromethane was stirred at room temperature for 1 h and then cooled to −40°. Trimethylsilyl triflate[9] (30 μL) was added and stirring was continued for 4 h at −15°. The mixture was diluted with dichloromethane (100 mL), washed with aqueous 10% $NaHCO_3$ (2 × 10 mL) and water (3 × 10 mL), dried (Na_2SO_4), and concentrated. Column chromatography of the crystalline residue, as described in (*a*), gave **11a** (95 mg, 34%). Recrystallisation from dry methanol gave a product that was identical with **11a** in (*a*).

*Phenyl 2-O-(3-azido-2,3,6-trideoxy-α- and -β-*L*-arabino-hexopyranosyl)-3-O-benzyl-4,6-O-benzylidene-β-*D*-glucopyranoside* (**12a** *and* **12b**). — A solution of **11a** (106 mg; 0.18 mmol) or **11b** (30 mg, 0.05 mmol) in dry methanol containing a catalytic amount of sodium methoxide was boiled under reflux for 3 min, then cooled, neutralised with Serdolit-Rot^R (H^+) resin, and concentrated. Column chromatography (99:1 benzene–ethyl acetate) of the residue removed the methyl

p-nitrobenzoate and gave **12a** as a syrup (84.3 mg, 99.5%), $[\alpha]_D^{20}$ −55° (*c* 1, chloroform), R_F (solvent *D*) 0.37; ν_{max}^{KBr} 2094 (C–N azide). Mas spectrum: *m/z* 590 (3%) $M^+ + 1$, 589 (4) M^+, 497 (1.6) M − PhO, 435 (14), 341 (27), 156 (32), 91 (100) $C_7H_7^+$.

Compound **12b** was crystallised from dry ethanol to give material (23 mg, 96%) having m.p. 175–176°, $[\alpha]_D^{20}$ −17° (*c* 0.3, chloroform). Mass spectrum: *m/z* 590 (2%) $M^+ + 1$, 497 (11) M^+ − PhO, 434 (14), 341 (52), 340 (48), 268 (100), and 91 (62).

Anal. Calc. for $C_{32}H_{35}N_3O_8$: C, 65.18; H, 5.98; N, 7.13. Found: C, 64.99; H, 6.00; N, 7.10.

*Phenyl 2-O-(2,3,6-trideoxy-3-diethylamino-α-*L-arabino-*hexopyranosyl)-β-*D-*glucopyranoside* (**2b**). — A solution of **12a** (60 mg, 0.10 mmol) in dry ethanol (12 mL) was hydrogenated in the presence of 10% Pd/C (30 mg) for 4 h (1.2 atm., 20°). The product did not show i.r. absorption for azide (~2100 cm^{-1}). After the addition of acetic acid (2 mL), hydrogenation was continued at 20–70 atm. (20°, 54 h). T.l.c. then revealed only one compound. The mixture was filtered through Celite and concentrated, and the residue was subjected to column chromatography (2:1 benzene–methanol) to give **2b** (27 mg, 59.2%) as a colourless gum, $[\alpha]_D^{20}$ −32° (*c* 0.7, methanol), R_F (solvent *E*) 0.55. Mass spectrum: *m/z* 441 (5%) M^+, 426 (4) M^+ −15, 284 (7) M^+ − 58 + 1, 369 (2) M^+ − NEt_2, 348 (14) M^+ − OPh, 186 (65) $C_{10}H_{20}NO_2^+$, 71 (58) $C_4H_9N^+$.

Anal. Calc. for $C_{22}H_{35}NO_8$: C, 59.84; H, 7.99; N, 3.17. Found: C, 59.63; H, 7.94; N, 2.90.

Phenyl β-acobioside (**2a**). — A mixture of **12a** (95 mg, 0.16 mmol), aqueous 60% acetic acid (6 mL), and 10% Pd/C (30 mg) was hydrogenated for 115 h (room temp., 1 atm.). The catalyst was removed, the filtrate was concentrated, and toluene was evaporated from the residue *in vacuo* at 30° (bath). A solution of the residue in water (5 mL) was neutralised with Dowex 2-X4 (HO^-) resin and concentrated to dryness, and the syrupy residue was eluted from a column (25 × 1 cm) of Silica Gel 40 with a benzene–methanol gradient (1:1→1:2) at 2 mL/30 min (2-mL fractions). Concentration of fractions 16–22 gave **2a** (23.7 mg, 43%), $[\alpha]_D^{20}$ −75° (*c* 1, water), R_F (solvent *F*) 0.35. Mass spectrum: e.i., *m/z* 339 (3%) M^+ − Me − CH_2OH, 292 (6) M^+ − PhO; c.i.-isobutane, *m/z* 386 $M^+ + 1$.

Anal. Calc. for $C_{18}H_{27}NO_8$: C, 56.09; H, 7.06; N, 3.63. Found: C, 56.12; H, 6.71; N, 3.63.

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