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A NEW SYNTHESIS OF 1,2-*trans*-2-ACETAMIDO-2-DEOXYGLYCOPYRANOSIDES *via* 1,2-*trans*-2-DEOXY-2-IODOGLYCOSYL AZIDES

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ABSTRACT

Trans-addition of iodoazide to the double bond of 3,4,6-tri-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol yielded 2-deoxy-2-iodoglycosyl azides, which are precursors of 1,2-*trans*-2-amino-2-deoxyglycopyranosides when treated by an alcohol in the presence of triphenylphosphine.

INTRODUCTION

Trans-addition of iodoazide to the double bond of glycals has recently been described and led to 1,2-*trans*-2-deoxy-2-iodoglycosyl azides in good yields[1]. Staudinger's reaction of these intermediates with trimethylphosphite gave the corresponding 1,2-*trans*-2-deoxy-2-iodoglycosyl phosphoramidates, which are precursors of 1,2-*trans*-2-deoxy-2-phosphoramidoglycosides β[2] *via* a proposed aziridine intermediate[3]. However, this method required the use of protecting groups stable under basic conditions and was mainly utilized for the preparation of 1,2-*trans*-alkyl 2-amino-2-deoxyglycosides. By replacing trimethylphosphite with triphenylphosphine, it was possible to prepare a sugar phosphinimine at C-1, as the nitrogen atom became sufficiently nucleophilic to substitute the iodo group at C-2 to lead to an aziridine opened by the alcohol present in the medium. Cleavage of the N–P bond of the aminophosphonium iodide salt thus obtained was easily carried out under basic conditions. Subsequent acetylation yielded 1,2-*trans*-2-acetamido-2-deoxyglycopyranosides. This new method uses very inexpensive reagents and is complementary to the methods of preparation of 1,2-*trans*-aminoglycosides from 1,5-anhydro-D-*arabino*-hex-1-enitol[4,5] or from 2-amino-2-deoxy-D-glucose by the "oxazoline"[6], "phtalimide"[7], and "allyl carbamate"[8] methods.

RESULTS AND DISCUSSION

Addition of iodoazide onto 3,4,6-tri-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**1**) led to two separable 2-deoxy-2-iodoglycosyl azides, **3** (58%) and **19** (35%), having an α-D-*manno* and a β-D-*gluco* configuration, respectively. The same

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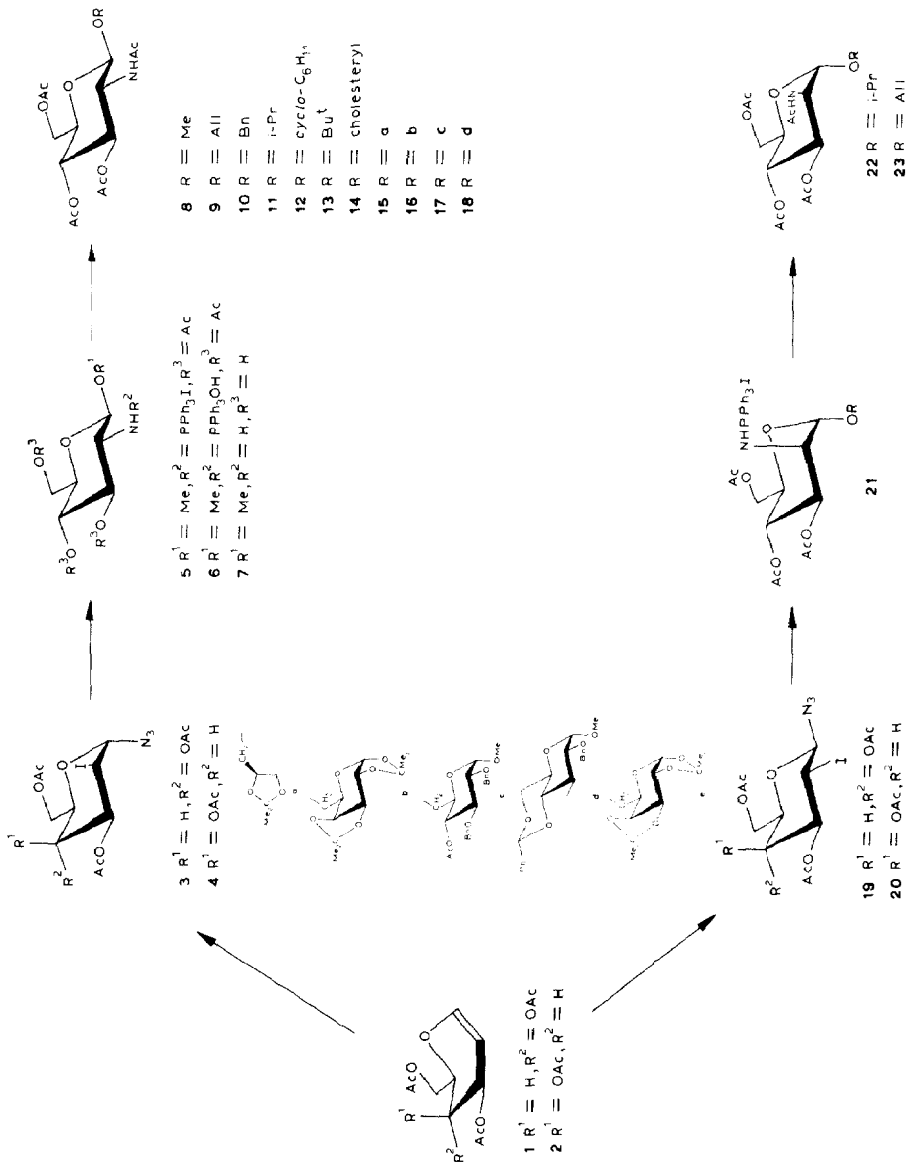
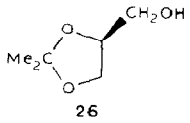

1 R¹ = H, R² = OAc
2 R¹ = OAc, R² = H
3 R¹ = H, R² = OAc
4 R¹ = OAc, R² = H
5 R¹ = Me, R² = PPh3I, R³ = Ac
6 R¹ = Me, R² = PPh3OH, R³ = Ac
7 R¹ = Me, R² = H, R³ = H
8 R = Me
9 R = All
10 R = Bn
11 R = i-Pr
12 R = cyclo-C6H11
13 R = But
14 R = cholesteryl
15 R = a
16 R = b
17 R = c
18 R = d
19 R¹ = H, R² = OAc
20 R¹ = OAc, R² = H
21
22 R = i-Pr
23 R = All
24 R = Bn
25 R = e

reaction with 3,4,6-tri-*O*-acetyl-1,5-anhydro-D-*lyxo*-hex-1-enitol (**2**) led to compounds **4** and **20**. The stereoselectivity was in favor of the α-D-*talo* configuration (62 *vs.* 16%) (Ref. 1). Assignment of configuration for compounds **3, 4, 19,** and **20** was carried out by ^{1}H-n.m.r. and ^{13}C-n.m.r. spectroscopy (see Experimental part). Chemical shifts (^{1}H-n.m.r. $\delta_{H\text{-}1}$ 5.72 for **3** and 5.81 for **4**) and coupling constants ($J_{1,2}$ 1.3 and $J_{2,3}$ 4.3 for **3** and $J_{1,2}$ 2.4 and $J_{2,3}$ 4.7 Hz for **4**) unambiguously suggested an α-D-*manno* configuration for **3** and an α-D-*talo* configuration for **4**. For compounds **19** and **20**, the coupling constants ($J_{1,2}$ 9.8–9.9, $J_{2,3}$ 11.0–11.6 Hz) revealed a β-D-*gluco* and a β-D-*galacto* configuration, respectively. ^{13}C-N.m.r. spectroscopy proved the presence of an iodo group at C-2 ($\delta_{C\text{-}2}$ 26–28 for **3, 19,** and **20**). The C-2 signal of **4** exhibited a highfield shift ($\delta_{C\text{-}2}$ 20.7) characteristic of 2-deoxy-2-iodotalopyranosides having an α-D configuration[1,9] at C-1.

Treatment of 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl azide (**3**) with triphenylphosphine and methanol in dichloromethane afforded methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-triphenylphosphonioamino-β-D-glucopyranoside iodide (**5**) in high yield (90%) after column chromatography. Structural analysis of **5** by ^{1}H-n.m.r. spectroscopy showed coupling constants of 9–10 Hz for $J_{1,2}$ and $J_{2,3}$, indicating a β-D-*gluco* configuration. The ^{13}C-n.m.r. chemical shifts proved the migration of the nitrogen atom from C-1 to C-2 ($\delta_{C\text{-}2}$ 56.6) and the creation of a glycosidic bond ($\delta_{C\text{-}1}$ 101.3). Phosphonium salt formation was evidenced by the chemical shifts and couplings $J_{C,P}$ for C-*ipso*, C-*ortho*, C-*meta*, and C-*para* of the triphenylphosphonium residue (see Experimental section), and also from the ^{31}P-n.m.r. chemical shift (δ_P 40.6), which were compared with literature data[10–12]. The formation of an aziridine intermediate was not surprising, since it was already found by Hassner and Galle[3] in linear series with the reaction of triphenylphosphine and the *trans*-iodoazide adduct of a double bond, and also by Pintér *et al.*[13] in the cyclic series starting from 2,3-*trans*-2-azido-2-deoxy-3-*O*-tosyl-sugar derivatives.

The aminophosphonium salt **5** was transformed into the acetamido compound **8** by elution from a Dowex (OH^--column) with methanol and treated with a catalytic amount of sodium methylate in the same solvent, followed by reacetylation. A mechanism involving the formation of an aminohydroxyphosphorane intermediate **6** (^{31}P-n.m.r., δ 29.2), which was transformed into methyl 2-amino-2-deoxy-β-D-glucopyranoside (**7**) seemed plausible. However, direct acetylation of **6** did not only give the expected acetamido compound **8**, but also compounds having a triphenylphosphinyl group, which suggests that pyridine was not sufficiently basic to transform the aminohydroxyphosphorane into the free amine.

Glycosylation reactions were performed with other simple alcohols, such as 2-propanol, 2-propenol, 2-methyl-2-propanol, cyclohexanol, and benzyl alcohol; with cholesterol; and with sugar derivatives, such as 1,2-*O*-isopropylidene-(*S*)-glycerol (**26**), 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**27**), methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (**28**), and methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**29**), prepared by known methods[14–17]. As indicated in Table I, yields obtained from the α-D-*manno* compound **3** were high with the use of



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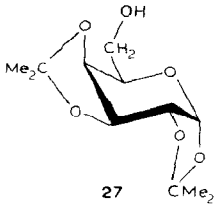

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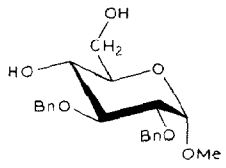

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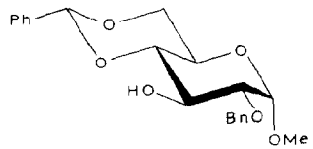

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methanol and 2-propanol, and good with the use of other simple alcohols, except with 2,2-dimethylpropanol. This last-named result may be compared with that similarly found by Kiso and Anderson[18] with the "oxazoline" method.

When sugar alcohols were used as glycosylating agents, yields were lower, except with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose. In the case of methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside, glycosylation occurred only at O-6 with a yield of 55% when 1.1 equiv. of alcohol was used. Even with 0.5 equiv. of alcohol, no glycosylation at O-4 was observed, and the yield decreased to 35% in relation to compound **3** or to 70% in relation to the alcohol. Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside also reacted with **3** under the same conditions to give disaccharide **18** with a 42% yield. However, glycosylation reaction with the 3-*O*-benzyl-2-hydroxy analog failed, and no disaccharide formation was observed. The β-D-*gluco* structure for compounds **8–18** was demonstrated by ^{1}H-n.m.r. ($\delta_{H\text{-}1}$ 4.88–4.36, $J_{1,2}$ 8.5–8 Hz, and $J_{2,3}$ 10.2–8.8 Hz), and ^{13}C-n.m.r. spectroscopy ($\delta_{C\text{-}1}$ 101.5–99.5 and $\delta_{C\text{-}2}$ 54.6–54.1), or by comparison with literature data for known compounds (Refs. 18–26).

Application of the same reaction to 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-β-D-glucopyranosyl azide (**19**) led to the expected α-D-glycosides with lower yields (Table I). Isolation and characterization (^{1}H-, ^{13}C-, and ^{31}P-n.m.r. spectroscopy) of the intermediate **21**, obtained by reaction of the iodoazide adduct **19** with 2-propanol and triphenylphosphine in dichloromethane, enabled us to justify the mechanism proposed previously. For glycosides **23–25**, intermediates were not isolated and the final acetamido compounds were purified by column chromatography. An α-D-*manno* structure for glycosides **22–25** was shown by ^{1}H-n.m.r. ($\delta_{H\text{-}1}$ 4.83–4.62, $J_{1,2}$ 1.2–1.5 Hz; $\delta_{H\text{-}2}$ 4.68–4.48, $J_{2,3}$ 4.1–4.2 Hz) and ^{13}C-n.m.r. spectroscopy ($\delta_{C\text{-}1}$ 99.5–97.5 and $\delta_{C\text{-}2}$ 50.9–50.2). Attempts to prepare the corresponding methyl 2-acetamido 2-deoxy-α-D-mannopyranoside were unsuccessful; glycosylation reactions with methanol gave mixtures of compounds which were not isolated.

TABLE I

GLYCOSYLATION REACTION OF IODOAZIDE ADDUCTS **3** AND **19**

Precursor	*Alcohol*	*Glycoside formed*	*Yield (%)*	*Ref.*
3	Methanol	**8**	80	19
	2-Propenol	**9**	73	18, 20
	Benzyl alcohol	**10**	70	18, 21
	2-Propanol	**11**	81	18, 22
	Cyclohexanol	**12**	74	23
	2-Methyl-2-propanol	**13**	55	18, 24
	Cholesterol	**14**	53	25
	26	**15**	63	
	27	**16**	72	26
	28	**17**	55, 35[a]	
	29	**18**	42	
19	Methanol			
	2-Propanol	**22**	70	
	2-Propenol	**23**	49	
	Benzyl alcohol	**24**	48	
	27	**25**	50	

[a]Ratio of **3** to alcohol 1:2.

The iodoazide adducts **4** and **20** of the per-*O*-acetylated-D-galactal **2** also did not react with alcohols in the presence of triphenylphosphine. This could be due to difficulties of substitution by nucleophiles at C-2 in the *talo* and *galacto* series[27,28], eventually leading to ring-contraction products. In conclusion, our results demonstrated the facile preparation of 1,2-*trans*-glycosides of 2-acetamido-2-deoxy-D-glucose and -D-mannose from iodoazide adducts of the per-*O*-acetyl-D-glucal **1**. As compared to the "phosphoramidate" method previously described[2], the present method has the advantages of being compatible with basic, unstable protecting groups, such as the acetate group, and of using only a slight excess of alcohol in the glycosylation step. Furthermore, the triphenylphosphonio group of the aminophosphonium intermediates can be readily removed, without the use of strongly basic conditions as in the "phthalimide" method[7], and the 2-acetamido-2-deoxy-β-D-glucopyranosides are obtained from **3** in overall yields very close to those obtained with the "oxazoline" method[6]. Nevertheless, this procedure showed two limitations: (*a*) the iodoazide adducts of the per-*O*-acetylated-D-glucal **1** or -D-galactal **2** could not be separated without column chromatography; and (*b*) the glycosylation reaction could not be applied to the iodoazide adducts of the per-*O*-acetyl-D-galactal **2**.

EXPERIMENTAL

General methods. — Melting points were determined with a Büchi melting-

point apparatus. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. I.r. spectra were recorded with a Perkin–Elmer 681 spectrophotometer, and n.m.r. spectra with Bruker W.P. 80 CW, Bruker AM 300, or Cameca 350 spectrometers for solutions in (^{2}H)chloroform and tetramethylsilane as internal standard. T.l.c. was performed on silica gel (Kieselgel 60 F_{254} Merck), and column chromatography on Silica Gel Amicon. Elemental analyses were performed by the C.N.R.S. (Solaize).

*3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-α-*D*-mannopyranosyl azide* (**3**) *and 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-β-*D*-glucopyranosyl azide* (**19**). — To a cold solution (0°) of IN_3 in acetonitrile, prepared by stirring ICl (1.22 g, 7.5 mmol) and NaN_3 (0.62 g, 9.5 mmol) in acetonitrile (25 mL), was added 3,4,6-tri-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**1**) (1.36 g, 5 mmol; Janssen). Stirring was maintained for 2 h. The solution was poured into ice–water, and the products were extracted with dichloromethane (3 × 50 mL). The organic phase was washed first with saturated $Na_2S_2O_3$ solution (10 mL), and then with water (2 × 10 mL), dried and concentrated to give a mixture of **3** and **19** which was applied to a column of silica gel (8:1:3 dichloromethane–ethyl acetate–hexane) to give pure **3** (58%) and **19** (35%).

Compound **3** showed m.p. 50°, $[\alpha]_D^{20}$ +80.4° (*c* 3, chloroform); R_F (1:1:8 ethyl acetate–hexane–dichloromethane) 0.60; ^{1}H-n.m.r. (350 MHz, $CDCl_3$): δ 5.72 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1), 5.36 (dd, 1 H, $J_{3,4}$ 8.6, $J_{4,5}$ 9.5 Hz, H-4), 4.52 (dd, 1 H, $J_{3,2}$ 4.3 Hz, H-3), 4.44 (dd, 1 H, H-2), 4.26 (dd, 1 H, $J_{6a,5}$ 5.1, $J_{6a,6b}$ 12.4 Hz, H-6a), 4.20 (ddd, 1 H, $J_{5,6b}$ 6.9 Hz, H-5), 4.20 (dd, 1 H, H-6b), and 2.26, 2.12, 2.09 (3 s, 3 OAc); ^{13}C-n.m.r. (25.2 MHz): δ 170.2, 169.3, 169.0 (3 C=O), 90.9 (C-1), 71.3, 68.6, 67.0 (C-3,4,5), 61.7 (C-6), 28.0 (C-2), 20.8, 20.6, and 20.5 (3 OAc).

Anal. Calc. for $C_{12}H_{16}IN_3O_7$: C, 32.67; H, 3.66; N, 9.53. Found: C, 32.51; H, 3.64; N, 9.54.

Compound **19** showed m.p. 94–95° (2-propanol), $[\alpha]_D^{20}$ +38.3° (*c* 1.0, chloroform); R_F (1:1:8 ethyl acetate–hexane–dichloromethane) 0.54; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 5.26 (dd, 1 H, $J_{3,2}$ 11.0, $J_{3,4}$ 9.0 Hz, H-3), 4.92 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.89 (d, 1 H, $J_{1,2}$ 9.8 Hz, H-1), 4.27 (dd, 1 H, $J_{6a,6b}$ 12.0, $J_{6a,5}$ 4.5 Hz, H-6a), 4.08 (dd, 1 H, $J_{6b,5}$ 2.4 Hz, H-6b), 3.80 (ddd, 1 H, H-5), 3.74 (dd, 1 H, H-2), 2.05, 2.05, and 1.98 (3s, 3 OAc); ^{13}C-n.m.r. (25.2 MHz): δ 170.1, 169.1, 169.0 (3 C=O), 90.9 (C-1), 75.1, 74.0, 68.5 (C-3,4,5), 61.6 (C-6), 26.8 (C-2), 20.5, 20.5, and 20.5 (3 OAc).

Anal. Calc. for $C_{12}H_{16}IN_3O_7$: C, 32.67; H, 3.66; N, 9.53. Found: C, 32.59; H, 3.66; N, 9.50.

*3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-α-*D*-talopyranosyl azide* (**4**) *and 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-β-*D*-galactopyranosyl azide* (**20**). — Compounds **4** and **20** were prepared as described above, by starting from 3,4,6-tri-*O*-acetyl-1,5-anhydro-D-*lyxo*-hex-1-enitol[29] (**2**), with yields of 62 and 16%, respectively.

Compound **4** showed m.p. 84° (2-propanol), $[\alpha]_D^{20}$ +88° (*c* 1.0, chloroform); R_F (1:1:8 ethyl acetate–hexane–dichloromethane) 0.62; ^{1}H-n.m.r. (350 MHz,

$CDCl_3$): δ 5.81 (d, 1 H, $J_{1,2}$ 2.4 Hz, H-1), 5.38 (dd, 1 H, $J_{4,3}$ 3.3, $J_{4,5}$ 3.0 Hz, H-4), 4.91 (dd, 1 H, $J_{3,2}$ 4.7 Hz, H-3), 4.45 (ddd, 1 H, $J_{5,6a}$ 7.7, $J_{5,6b}$ 4.7 Hz, H-5), 4.37 (dd, 1 H, $J_{6a,6b}$ 11.6 Hz, H-6a), 4.18 (dd, 1 H, H-2), 4.17 (dd, 1 H, H-6b), 2.16, 2.10, and 2.08 (3s, 3 OAc); ^{13}C-n.m.r. (25.2 MHz): δ 170.2, 169.4, 168.9 (3 C=O), 90.9 (C-1), 69.8, 65.5, 65.2 (C-3,4,5), 61.3 (C-6), 20.7 (C-2), 20.6, 20.6, and 20.6 (3 OAc).

Anal. Calc. for $C_{12}H_{16}IN_3O_7$: C, 32.67; H, 3.66; N, 9.53. Found: C, 32.71; H, 3.53; N, 9.43.

Compound **20** showed m.p. 104° (2-propanol), $[\alpha]_D^{20}$ −1.9° (*c* 1.5, chloroform); R_F (1:1:8 ethyl acetate–hexane–dichloromethane) 0.54; ^{1}H-n.m.r. (350 MHz, $CDCl_3$): δ 5.24 (dd, 1 H, $J_{4,3}$ 3.0, $J_{4,5}$ <0.5 Hz, H-4), 5.09 (dd, 1 H, $J_{3,2}$ 11.6 Hz, H-3), 4.99 (d, 1 H, $J_{1,2}$ 9.9 Hz, H-1), 4.18 (dd, 1 H, $J_{6a,5}$ 9.5, $J_{6a,6b}$ 11.2 Hz, H-6a), 4.13 (dd, 1 H, $J_{6b,5}$ 6.0 Hz, H-6b), 4.06 (ddd, 1 H, H-5), 3.95 (dd, 1 H, H-2), 2.15, 2.07, and 2.06 (3s, 3 OAc); ^{13}C-n.m.r. (25.2 MHz): δ 169.8, 169.5, 168.9 (3 C=O), 91.6 (C-1), 73.8, 73.4, 67.0 (C-3,4,5), 61.3 (C-6), 26.1 (C-2), 20.6, 20.5, and 20.4 (3 OAc).

Anal. Calc. for $C_{12}H_{16}IN_3O_7$: C, 32.67; H, 3.66; N, 9.53. Found: C, 32.64; H, 3.72; N, 9.36.

*General procedure for the preparation of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosides* (**8–18**) *and of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-mannopyranosides* (**22–25**). — Compound **3** (or **19**) (0.22–0.30 g, 0.50–0.68 mmol) and the appropriate alcohol (1.1 equiv.) were dissolved in dry dichloromethane (2–3 mL). Triphenylphosphine (1.08 equiv.) was then added and the flask was mounted with a septum and molecular sieve 4A. When all the azido group had reacted (15 min), the flask was closed and the mixture stirred overnight. After concentration, the residue was dissolved in methanol (2 mL) and allowed to migrate on a column packed with Dowex 2 X8 (OH^-) resin in methanol. Concentration of the methanolic solution to 10 mL, followed by addition of a catalytic amount of Na, and stirring for 8 h led, after a new concentration, to a crude compound which was acetylated with 2:1 pyridine–acetic anhydride (75 mL) overnight. Evaporation gave a crude mixture of glycoside, triphenylphosphine oxide, acetylated alcohol, and byproducts which was purified by column chromatography on silica gel to give the desired glycoside.

*Methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranoside* (**8**). — A mixture of **3** (0.3 g, 0.68 mmol), methanol (0.024 g, 0.75 mmol), and triphenylphosphine (0.192 g, 0.735 mmol) was stirred overnight in dichloromethane (3 mL) as described above. After evaporation, the residue was subjected to flash chromatography (eluent, 5:1 ethyl acetate–methanol) to give **5** as an amorphous, orange solid (0.430 g, 90% yield), $[\alpha]_D^{20}$ +11.5° (*c* 1.0, chloroform); R_F (5:1 ethyl acetate–methanol) 0.60; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 7.90–7.40 (m, 15 H, 3 C_6H_5), 5.81 (dd, 1 H, $J_{3,4}$ 9.2, $J_{3,2}$ 9.2 Hz, H-3), 5.55 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 4.73 (dd, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 4.20 (dd, 1 H, $J_{6a,5}$ 4.6, $J_{6a,6b}$ 12.0 Hz, H-6a), 3.92 (m, 2 H, H-5,6b), 3.28 (s, 3 H, CH_3O), 2,95 (m, 1 H, H-2), 1.97, 1.93, and 1.60 (3s, 3 OAc);

^{13}C-n.m.r. (25.2 MHz): δ 170.0, 169.3, 168.9 (3 C=O), 134.9 (C-*p*), 133.6 (d, $J_{C,P}$ 10.8 Hz, C-*o*), 129.7 (d, $J_{C,P}$ 12.8 Hz, C-*m*), 120.8 (d, $J_{C,P}$ 104.1 Hz, C-*ipso*), 101.3 (C-1), 73.9, 70.8, 69.0 (C-3,4,5), 61.6 (C-6), 57.8 (d, $J_{2,P}$ 1.3, C-2), 56.6 (CH_3O), 20.6, 20.6, and 20.6 (3 OAc); ^{31}P-n.m.r. (32.4 MHz): δ 40.6. Compound **5** was then eluted with methanol from a Dowex 2 X8 (OH^-) resin to give **6** as an oil, ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 7.90–7.40 (m, 15 H, 3 C_6H_5), 5.39 (dd, 1 H, $J_{3,2}$ 9.2, $J_{3,4}$ 9.2 Hz, H-3), 4.88 (dd, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 4.52 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.38 (dd, 1 H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 11.8 Hz, H-6a), 4.05 (dd, 1 H, H-6b), 3.83 (m, 1 H, H-5), 3.30 (s, 3 H, CH_3O), 2.92 (ddd, 1 H, $J_{2,P}$ 20 Hz, H-2), 2.02, 2.00, and 1.67 (3s, 3 OAc); ^{31}P-n.m.r. (32.4 MHz): δ 29.2.

Treatment of **6** with a catalytic amount of sodium methylate in methanol gave **7** which was directly acetylated into crude **8**, purified by column chromatography on silica gel (9:1 diethyl ether–methanol) (yield 80%), m.p. 162° (ethanol), $[\alpha]_D^{20}$ +11.9° (*c* 1.0, chloroform); lit.[2,19] m.p. 163°, $[\alpha]_D^{20}$ +12.0° (*c* 1.0, chloroform); R_F (9:1 diethyl ether–methanol) 0.54; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 5.90 (d, 1 H, $J_{NH,2}$ 8.5 Hz, NH), 5.25 (dd, 1 H, $J_{2,3}$ 8.8, $J_{3,4}$ 8.8 Hz, H-3), 4.98 (dd, 1 H, $J_{4,5}$ 8.8 Hz, H-4), 4.56 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.25 (dd, 1 H, $J_{6a,5}$ 4.3 Hz, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.05 (dd, 1 H, $J_{6b,5}$ 2.0 Hz, H-6b), 3.82 (ddd, 1 H, H-2), 3.65 (ddd, 1 H, H-5), 3.44 (s, 3 H, CH_3O), 2.04, 2.00, 2.00 (3 s, 3 OAc), and 1.91 (s, NAc).

*Allyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranoside* (**9**). — This compound was prepared as described in the general procedure from **3** and allylic alcohol in a 73% yield after purification by column chromatography (7:1 ethyl acetate–acetone), m.p. 165–166° (ethanol), $[\alpha]_D^{20}$ −17.5° (*c* 1.0, chloroform); lit.[18,20] m.p. 164–167°, $[\alpha]_D^{23}$ −15.1° (*c* 2.06, chloroform); R_F (7:1 ethyl acetate–acetone) 0.53; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 5.88 (m, 1 H, =CH–), 5.80 (d, 1 H, $J_{NH,2}$ 8.7 Hz, NH), 5.33 (dd, 1 H, $J_{3,2}$ 9.2, $J_{3,4}$ 9.2 Hz, H-3), 5.30–5.10 (m, 2 H, CH_2=Cl), 5.05 (dd, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 4.73 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1), 4.35 (dd, 1 H, $J_{6a,5}$ 4.7, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.25–3.65 (m, 5 H, H-2,5,6b, –CH_2O–), 2.08, 2.03, 2.02 (3s, 3 OAc), and 1.95 (s, NAc).

*Benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranoside* (**10**). — This was prepared in a 70% yield from **3** and benzylic alcohol, after purification by column chromatography (7:1 ethyl acetate–acetone), m.p. 168° (ethanol), $[\alpha]_D^{20}$ −53° (*c* 1.0, chloroform); lit.[18,21] m.p. 164–165°, $[\alpha]_D^{25}$ −54.4° (*c* 0.5, chloroform); R_F (7:1 ethyl acetate–acetone) 0.71; ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 7.35–7.25 (m, 5 H, C_6H_5), 5.76 (d, 1 H, $J_{NH,2}$ 8.9 Hz, NH), 5.22 (dd, 1 H, $J_{3,2}$ 10.3, $J_{3,4}$ 9.4 Hz, H-3), 5.08 (dd, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 4.88 (d, 1 H, *J* 12.2 Hz, –C*H*-C_6H_5), 4.65 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.59 (d, 1 H, *J* 12.2 Hz, –C*H*-C_6H_5), 4.27 (dd, 1 H, $J_{6a,5}$ 4.7, $J_{6a,6b}$ 12.3 Hz, H-6a), 4.15 (dd, 1 H, $J_{6b,5}$ 2.5 Hz, H-6b), 3.98 (ddd, 1 H, H-2), 3.69 (ddd, 1 H, H-5), 2.10, 2.02, 2.01 (3a, 3 OAc), and 1.90 (s, NAc).

*2-Propyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranoside* (**11**). — This compound was prepared from **3** and 2-propanol in a 81% yield after purification by column chromatography (3:1 ethyl acetate–acetone), m.p. 171–172° (ethyl acetate–petroleum ether), $[\alpha]_D^{20}$ −9.8° (*c* 1.0, chloroform); lit.[18,22] m.p. 174–175°,

$[\alpha]_D^{25}$ −6.4° (*c* 0.5, chloroform); R_F (3:1 ethyl acetate–acetone); ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 6.49 (d, 1 H, $J_{NH,2}$ 8.3 Hz, NH), 5.37 (dd, 1 H, $J_{3,2}$ 9.8, $J_{3,4}$ 9.5 Hz, H-3), 4.95 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.82 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.25 (dd, 1 H, $J_{6,5}$ 4.9 Hz, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.20–3.70 [m, 4 H, H-2,5,6b, –C*H*$(CH_3)_2$], 2.03, 2.98, 1.98 (3s, 3 OAc), 1.90 (s, NAc), 1.15 (d, 3 H, *J* 6.2 Hz, C*H*$_3$CH), and 1.09 (d, 3 H, *J* 6.2 Hz, C*H*$_3$CH).

Cyclohexyl 2-acetamido-3,4,6-tri-O-*acetyl-2-deoxy-β*-D-*glucopyranoside* (**12**). — This compound was prepared from **3** and cyclohexanol in a 74% yield after purification by column chromatography (3:1 ethyl acetate–acetone) 0.64, m.p. 182° (ethanol), $[\alpha]_D^{20}$ −10.4° (*c* 1.0, chloroform); lit.[23] m.p. 181–182°; R_F (3:1 ethyl acetate–acetone) 0.64; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 5.82 (d, 1 H, $J_{NH,2}$ 8.5 Hz, NH), 5.32 (dd, 1 H, $J_{3,2}$ 9.2, $J_{3,4}$ 9.8 Hz, H-3), 4.99 (dd, 1 H, $J_{4,5}$ 9 Hz, H-4), 4.82 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.26 (dd, 1 H, $J_{6a,5}$ 4.8, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.05 (dd, 1 H, $J_{6b,5}$ 2.7 Hz, H-6b), 3.83–3.49 (m, 3 H, H-2,5, –CH), 2.04, 1.98, 1.98 (3s, 3 OAc), 1.90 (s, NAc), and 1.77–1.10 (m, 10 H, C_6H_{11}).

2-Methyl-2-propyl 2-acetamido-3,4,6-tri-O-*acetyl-2-deoxy-β*-D-*glucopyranoside* (**13**). — This compound was prepared from **3** and 2-methyl-2-propanol in a 55% yield after purification by column chromatography (3:1 ethyl acetate–acetone), m.p. 204–206° (ethanol), $[\alpha]_D^{20}$ +3.3° (*c* 1.2, chloroform); lit.[18,24] m.p. 206–207°, $[\alpha]_D^{25}$ +2° (*c* 0.5, chloroform); R_F (3:1 ethyl acetate–acetone) 0.64; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 5.64 (d, 1 H, $J_{NH,2}$ 8.2 Hz, NH), 5.43 (dd, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 9.5 Hz, H-3), 4.91 (dd, 1 H, $J_{4,5}$ 9.0 Hz, H-4), 4.88 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.20 (dd, 1 H, $J_{6a,5}$ 5.9 Hz, $J_{6a,6b}$ 12.1 Hz, H-6a), 3.99 (dd, 1 H, $J_{6b,5}$ 2.1 Hz, H-6b), 3.66 (ddd, 1 H, H-5), 3.53 (ddd, 1 H, H-2), 1.98, 1.98, 1.95 (3s, 3 OAc), 1.85 (s, NAc), and 1.16 [s, 9 H, $(CH_3)_3C$].

Cholest-5-3-β-yl 2-acetamido-3,4,6-tri-O-*acetyl-2-deoxy-β*-D-*glucopyranoside* (**14**). — This compound was prepared from **3** and commercially available cholesterol (Aldrich), in a 53% yield after purification by column chromatography (ethyl acetate), m.p. 206°. $[\alpha]_D^{20}$ −22.1° (*c* 1.0, chloroform); lit.[25] m.p. 199–202°, $[\alpha]_D^{20}$ −20.0° (*c* 0.1 chloroform), R_F (ethyl acetate) 0.68; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 5.72 (d, 1 H, $J_{NH,2}$ 8.3 Hz, NH), 5.39 (dd, 1 H, $J_{3,2}$ 9.5, $J_{3,4}$ 9.5 Hz, H-3), 5.33 (m, 1 H, –CH, 5.02 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.85 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.29 (dd, 1 H, $J_{6a,5}$ 5.1, $J_{6a,6'b}$ 12.4 Hz, H-6), 4.06 (dd, 1 H, $J_{6'b,5}$ 2.5 Hz, H6'b), 3.86–3.25 (m, 3 H, H-2,5,3-cholesteryl), 2.06, 2.01, 2.01 (3 s, 3 OAc), 1.94 (s, NAc), and 2.27–0.67 (m, 43 H, cholesteryl).

3-O-*(2-Acetamido-3,4,6-tri*-O-*acetyl-2-deoxy-β*-D-*glucopyranosyl)-1,2*-O-*isopropylidene*-(S)-*glycerol* (**15**). — This compound was prepared from **3** and 1,2-*O*-isopropylidene-(*S*)-glycerol[14] (**26**) in a 63% yield after column chromatography (7:1 ethyl acetate–acetone), m.p. 135° (ethyl acetate–petroleum ether), $[\alpha]_D^{20}$ −13.8° (*c* 1.0, chloroform); R_F (7:1 ethyl acetate–acetone) 0.58; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 5.79 (d, 1 H, $J_{NH,2}$ 8.5 Hz, NH), 5.28 (dd, 1 H, $J_{3',2'}$ 8.3, $J_{3',4'}$ 9.2 Hz, H-3'), 5.09 (dd, 1 H, $J_{4',5'}$ 9.3 Hz, H-4'), 4.76 (d, 1 H, $J_{1',2'}$ 8.3 Hz, H-1'), 4.40–3.50 (m, 9 H, H-1a,1b,2,3a,3b,2',5',6'a,6'b), 2.08, 2.02, 2.02 (3s, 3 OAc), 1.94 (s, NAc), 1.41

and 1.34 [2s, $(CH_3)_2C$]; ^{13}C-n.m.r. (75.5 MHz, $CDCl_3$): δ 170.8, 170.7, 170.5, 169.4 (4 C=O), 109.3 [$C(CH_3)_2$], 100.9 (C-1'), 74.3 (C-2), 72.5, 71.8 (C-5',3'), 69.5 (C-1), 68.8 (C-4'), 66.2 (C-3), 62.2 (C-6'), 54.4 (C-2'), 26.7, 25.1 [$C(CH_3)_2$], 23.2 (NAc), 20.8, 20.7, and 20.6 (3 OAc).

Anal. Calc. for $C_{20}H_{31}NO_{11}$: C, 52.05; H, 6.77; N, 3.04. Found: C, 51.83; H, 6.83; N, 3.02.

6-O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**16**). — This compound was prepared from **3** and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[15] (**27**) in a 72% yield after purification by column chromatography (8:1 dichloromethane–acetone), m.p. 108–110° (diethyl ether), $[\alpha]_D^{20}$ −64° (*c* 1.0, chloroform); lit.[26,30] m.p. 99–102°, $[\alpha]_D^{20}$ −66° (*c* 1.0, chloroform); R_F (ethyl acetate) 0.40; ^1H-n.m.r. (80 MHz, $CDCl_3$): δ 5.75 (d, 1 H, $J_{NH,2'}$ 8.6 Hz, NH), 5.48 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.25–4.90 (m, 2 H, H-3',4'), 4.65 (d, 1 H, $J_{1',2'}$ 8.5 Hz, H-1'), 4.52 (dd, 1 H, $J_{2,3}$ 7.8, $J_{3,4}$ 1.9 Hz, H-3), 4.25 (dd, 1 H, H-2), 4.20–3.55 (m, 8 H, H-4,5,6a,6b,2',5',6'a,6'b), 2.04, 1.99, 1.99 (3s, 3 OAc), 1.91 (s, NAc), 1.46, 1.39, 1.27, and 1.27 [4s, 2 $C(CH_3)_2$].

Methyl 6-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-4-O-acetyl-2,3-di-O-benzyl-α-D-glucopyranoside (**17**). — This compound was prepared from **3** and methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[16] (**28**). In a first experiment 1.1 equiv. of **28** was used to give **17** in 55% yield after column chromatography (8:1 ethyl acetate–acetone), in a second experiment only 0.55 equiv. and the yield decreased to 35%. Compound **17** showed m.p. 202° (ethanol), $[\alpha]_D^{20}$ +10.5° (*c* 1.0, chloroform); R_F (8:1 ethyl acetate–acetone) 0.66; ^1H-n.m.r. (300 MHz, $CDCl_3$): δ 7.34–7.23 (m, 10 H, 2 C_6H_5), 6.28 (d, 1 H, $J_{NH,2'}$ 8.5 Hz, NH), 5.16 (dd, 1 H, $J_{3',2'}$ 9.6, $J_{3',4'}$ 9.6 Hz, H-3'), 5.06 (dd, 1 H, $J_{4,3}$ 9.3, $J_{4,5}$ 9.3 Hz, H-4), 5.02 (dd, 1 H, $J_{4',5'}$ 9.5 Hz, H-4'), 4.91–4.80 (m, 4 H, 2 $CH_2C_6H_5$), 4.61 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.38 (d, 1 H, $J_{1',2'}$ 8.5 Hz, H-1'), 4.21 (dd, 1 H, $J_{6'a,5'}$ 4.6, $J_{6'a,6'b}$ 12.5 Hz, H-6'a), 4.11 (dd, 1 H, $J_{6'b,5'}$ 2.1 Hz, H-6'b), 4.10–4.01 (m, 2 H, H-5,6a), 3.91 (dd, 1 H, $J_{3,2}$ 9.2, $J_{3,4}$ 9.2 Hz, H-3), 3.72–3.64 (m, 2 H, H-2',5'), 3.54 (dd, 1 H, H-2), 3.35 (s, 3 H, CH_3O), 3.26 (dd, 1 H, $J_{6b,5}$ 2.6, $J_{6a,6b}$ 11.2 Hz, H-6b), 2.06, 2.03, 2.00, 1.91 (4s, 4 OAc), and 1.91 (s, NAc); ^{13}C-n.m.r. (75.5 MHz, $CDCl_3$): δ 170.8, 170.7, 170.6, 170.0, 169.3 (5 C=O), 138.7, 137.8, 128.5–127.4 (12 C, 2 C_6H_5), 101.8 (C-1'), 98.0, (C-1), 79.6, 78.9 (C-2,3), 75.1, 73.5 (2 $CH_2C_6H_5$), 73.2, 71.9 (C-3',5'), 70.0 (C-5), 68.5, 68.1 (C-4,4'), 68.0 (C-6), 62.0 (C-6'), 55.4 (CH_3O), 54.1 (C-2'), 23.2 (NAc), 20.9, 20.7, 20.7, and 20.6 (4 OAc).

Anal. Calc. for $C_{37}H_{47}NO_{15}$: C, 59.59; H, 6.35; N, 1.88. Found: C, 59.36; H, 6.31; N, 1.84.

Methyl 3-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-2-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (**18**). — This compound was prepared from **3** and methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside[17] (**29**) in a 42% yield after column chromatography (7:1 ethyl acetate–acetone), m.p. 235° (ethanol), $[\alpha]_D^{20}$ −11.6° (*c* 1.0, chloroform); R_F (7:1 ethyl acetate–acetone) 0.68; ^1H-n.m.r. (300 MHz, $CDCl_3$): δ 7.48–7.28 (m, 10 H, 2 C_6H_5), 5.51 (s, 1 H, CHC_6H_5), 5.37 (d, 1 H, $J_{NH,2'}$ 9.2 Hz, NH), 5.09 (dd, 1 H, $J_{3',2'}$ 10.2, $J_{3',4'}$ 9.3 Hz,

H-3′), 5.06 (dd, 1 H, $J_{4',5'}$ 9.3 Hz, H-4′), 4.80 (d, 1 H, $J_{1',2'}$ 8.5 Hz, H-1′), 4.70 (d, 1 H, *J* 12.3 Hz, $CH_2C_6H_5$), 4.63 (d, 1 H, *J* 12.3 Hz, $CH_2C_6H_5$), 4.55 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.21 (dd, 1 H, $J_{6a,5}$ 3.8 Hz, $J_{6a,6b}$ 9.3 Hz, H-6a), 4.14 (dd, 1 H, $J_{6b.5}$ 9.3 Hz, H-6b), 4.09 (dd, 1 H, $J_{6'a,6'b}$ 12.4 Hz, $J_{6'a,5'}$ 4.1 Hz, H-6′ a), 4.03 (m, 1 H, H-2′), 3.88 (dd, 1 H, $J_{6'b,5'}$ 2.2 Hz, H-6′b), 3.78 (ddd, 1 H, $J_{5,4}$ 9.1 Hz, H-5), 3.70 (dd, 1 H, $J_{3,2}$ 9.2, $J_{3,4}$ 9.1 Hz, H-3), 3.59 (dd, 1 H, H-4), 3.56 (dd, 1 H, H-2), 3.47 (m, 1 H, H-5′), 3.34 (s, 3 H, CH_3O), 1.97 (3s, 3 OAc), and 1.72 (s, NAc); ^{13}C-n.m.r. (75.5 MHz, $CDCl_3$): δ 170.9, 170.7, 170.1, 169.3 (4 C=O), 138.1, 137.2, 129.1–126.1 (12 C, 2 C_6H_5), 101.5, 101.3 (2 C, C-1′, CHC_6H_5), 98.5 (C-1), 80.0, 79.5, 78.3 (3 C, C-2,3,4), 73.3 ($CH_2C_6H_5$), 73.1 (C-5′), 71.7 (C-3′), 68.9 (C-6), 68.3 (C-4′), 62.3 (C-5), 62.0 (C-6′), 55.3 (CH_3O), 54.6 (C-2′), 23.2 (NAc), 20.7, 20.6, and 20.6 (3 OAc).

Anal. Calc. for $C_{35}H_{43}NO_{14}$: C, 59.90; H, 6.18; N, 2.00. Found: C, 59.65; H, 6.26; N, 2.00.

*2-Propyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-mannopyranoside* (**22**). — This compound was prepared from **19** and 2-propanol. The phosphonium salt intermediate **21** was isolated in an 80% yield as an amorphous solid after column chromatography (5:1 ethyl acetate–methanol). The normal process gave **22**, also purified by column chromatography (7:1 ethyl acetate–acetone) in a 70% yield from **19**. Compound **21** showed $[\alpha]_D^{20}$ +25.2° (*c* 1.0, chloroform); R_F (5:1 ethyl acetate–methanol) 0.60; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 8.03–7.25 (m, 15 H, 3 C_6H_5), 5.44 (d, 1 H, $J_{1,2}$ 4.4 Hz, H-1), 5.18 (dd, 1 H, $J_{3,4}$ 5.7, $J_{4,5}$ 7.8 Hz, H-4), 4.93 (dd, 1 H, $J_{3,2}$ 3.4 Hz, H-3), 4.40 (dd, 1 H, $J_{6a,5}$ 7.0, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.20 (dd, 1 H, $J_{6a,5}$ 3.5 Hz, H-6′b), 3.92 (ddd, 1 H, H-5), 3.63 [m, 1 H, $CH(CH_3)_2$], 3.28 (ddd, 1 H, $J_{2,P}$ 12.3 Hz, H-2), 2.04, 2.00, 1.93 (3s, 3 OAc), 1.15 [d, 3 H, *J* 7.8 Hz, $(CH_3)C$], and 1.08 [d, 1 H, *J* 7.8 Hz, $(CH_3)C$]; ^{13}C-n.m.r. (75.5 MHz, $CDCl_3$): δ 170.7, 170.2, 169.2 (3 C=O), 135.3 (3 C, $J_{C,P}$ 2.5 Hz, C-*p*), 134.4 (6 C, $J_{C,P}$ 11.2 Hz, C-*o*), 130.0 (6 C, $J_{C,P}$ 13.4 Hz, C-*m*), 120.5 (3 C, $J_{C,P}$ 103.8 Hz, C-*ipso*), 96.8 ($J_{C,P}$ 5.5, C-1), 71.2 [$C(CH_3)_2$], 71.0, 69.0, 68.6 (C-3,4,5), 63.1 (C-8), 55.3 (C-2), 23.2, 22.1 [2 C, $C(CH_3)_2$], 21.7, 20.8, and 20.7 (3 OAc); ^{31}P-n.m.r. (32.4 MHz, $CDCl_3$): δ 40.9.

Compound **22** showed m.p. 137–138° (ethanol), $[\alpha]_D^{20}$ +66° (*c* 1.0, chloroform); R_F (7:1 ethyl acetate–acetone) 0.71; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 5.84 (d, 1 H, $J_{NH,2}$ 9.1 Hz, NH), 5.38 (dd, 1 H, $J_{3,2}$ 4.2, $J_{3,4}$ 10.0 Hz, H-3), 5.06 (dd, 1 H, $J_{4,5}$ 8.8 Hz, H-4), 4.62 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1), 4.48 (ddd, 1 H, H-2), 4.21 (dd, 1 H, $J_{6a,5}$ 6.2, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.15–4.00 (m, 2 H, H-5,6b), 3.98 [m, 1 H, *J* 6.1 Hz, $CH(CH_3)_2$]. 2.09, 2.05, 2.05 (3s, 3 OAc), 1.98 (s, NAc), 1.24 (d, 3 H, CH_3CH), and 1.17 (d, 3 H, CH_3CH); ^{13}C-n.m.r. (75.5 MHz, $CDCl_3$): δ 170.6, 170.2, 170.0, 170.0 (4 C=O), 97.5 (C-1), 71.0 [$C(CH_3)_2$], 69.3, 68.0, 66.5 (C-3,4,5), 62.7 (C-6), 51.0 (C-2), 23.3 (NAc), 23.0, 21.6 [2 C, $C(CH_3)_2$]. 20.8, 20.7, and 20.7 (3 OAc).

Anal. Calc. for $C_{17}H_{27}NO_9$: C, 52.43; H, 6.99; N, 3.60. Found: C, 52.60; H, 6.98; N, 3.76.

*Allyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-mannopyranoside* (**23**). —

This compound was prepared from **19** and allylic alcohol in a 49% yield after column chromatography (7:1 ethyl acetate–acetone), oil, $[\alpha]_D^{20}$ +56° (*c* 1.0, chloroform); R_F (7:1 ethyl acetate–acetone) 0.60; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 5.95 (d, 1 H, $J_{NH,2}$ 9.2 Hz, NH), 5.91 (m, 1 H, =CH–), 5.37 (dd, 1 H, $J_{3,4}$ 10.2, $J_{3,2}$ 4.2 Hz, H-3), 5.40–5.18 (m, 2 H, CH_2=), 5.10 (dd, 1 H, $J_{4,5}$ 9 Hz, H-4), 4.81 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1), 4.62 (ddd, 1 H, H-2), 4.30 (dd, 1 H, $J_{6a,5}$ 5.8, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.20–3.90 (m, 4 H, H-5,6b, –CH_2–O), 2.11, 2.05, 2.05 (3s, 3 OAc), and 1.99 (s, NAc); ^{13}C-n.m.r. (75.5 MHz, $CDCl_3$): δ 170.6, 170.3, 170.0, 169.9 (4 C=O), 133.0 (=C–), 118.4 (CH_2=), 98.1 (C-1), 68.7 (–CH_2–), 69.2, 68.1, 66.2 (C-3,4,5), 62.6 (C-6), 50.4 (C-2), 23.3 (NAc), 20.8, 20.8, and 20.7 (3 OAc).

Anal. Calc. for $C_{17}H_{25}NO_9$: C, 52.70; H, 6.51; N, 3.62. Found: C, 52.70; H, 6.54; N, 3.59.

*Benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-mannopyranoside* (**24**). — This compound was prepared from **19** and benzyl alcohol in a 48% yield after column chromatography, m.p. 63° (ether–hexane), $[\alpha]_D^{20}$ +67° (*c* 1.2, chloroform); R_F (7:1 ethyl acetate–acetone) 0.65; ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 7.45–7.30 (m, 5 H, C_6H_5), 5.71 (d, 1 H, $J_{NH,2}$ 8.6 Hz, NH), 5.38 (dd, 1 H, $J_{3,2}$ 4.2, $J_{3,4}$ 10.1 Hz, H-3), 5.10 (dd, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 4.83 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 4.72, 4.52 (d, 1 H, *J* 12 Hz, $CH_2C_6H_5$), 4.65 (ddd, 1 H, H-2), 4.26 (dd, 1 H, $J_{6a,5}$ 5.7, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.05–3.90 (m, 2 H, H-5,6b), 2.11, 2.03, 2.03 (3s, 3 OAc), and 1.98 (s, NAc); ^{13}C-n.m.r. (75.5 MHz, $CDCl_3$): δ 170.6, 170.2, 170.0, 169.9 (4 C=O), 136.2, 128.6–128.1 (6 C, C_6H_5), 98.1 (C-1), 69.7 ($CH_2C_6H_5$), 69.3, 68.2, 66.2 (C-3,4,5), 62.6 (C-6), 50.3 (C-2), 23.2 (NAc), 20.8, 20.8, and 20.7 (3 OAc).

Anal. Calc. for $C_{21}H_{27}NO_9$: C, 57.66; H, 6.26; N, 3.20. Found: C,. 57.92; H, 6.32; N, 3.18.

*6-*O*-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-mannopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**25**). — This compound was prepared from **19** and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[15] (**27**) in a 50% yield after column chromatography (7:1 ethyl acetate–acetone), m.p. 78° (ether–hexane), $[\alpha]_D^{20}$ +3.7° (*c* 5.0, chloroform); R_F 0.58 (7:1 ethyl acetate–acetone); ^{1}H-n.m.r. (80 MHz, $CDCl_3$): δ 5.65 (d, 1 H, $J_{NH,2'}$ 8.8 Hz, NH), 5.49 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 5.33 (dd, 1 H, $J_{3',2'}$ 4.1 Hz, $J_{3',4'}$ 10.1 Hz, H-3'), 5.09 (dd, 1 H, $J_{4',5'}$ 9.0 Hz, H-4'), 4.78 (d, 1 H, $J_{1',2'}$ 1.5 Hz, H-1'), 4.68 (ddd, 1 H, H-2'), 4.63 (dd,. 1 H, $J_{3,2}$ 7.9 Hz, $J_{3,4}$ 2.4 Hz, H-3), 4.35–3.68 (m, 8 H, H-2,4,5,6a,6b,5',6'a,6'b), 2.10, 2.05, 2.05 (3s, 3 OAc), 1.97 (s, NAc), 1.56, 1.42, 1.34, and 1.34 (4s, 4 CH_3C); ^{13}C-n.m.r. (75.5 MHz, $CDCl_3$): δ 170.7, 170.2, 170.0, 170.0 (4 C=O), 109.4, 108.8 [2 $C(CH_3)_2$], 99.4 (C-1'), 96.3 (C-1), 70.9, 70.6, 70.6, 69.4 (C-2,3,5,5'), 68.2 (C-4), 67.3 (C-6), 66.6, 66.1 (C-3',4'), 62.5 (C-6'), 50.3 (C-2'), 26.2, 26.0, 25.0, 24.4 [4 C, 2(CH_3)$_2$C], 23.3 (NAc), 20.8, 20.8, and 20.8 (3 OAc).

Anal. Calc. for $C_{26}H_{39}NO_{14}$: C, 52.96; H, 6.67; N, 2.38. Found: C, 52.84; H, 6.67; N, 2.35.

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