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Note

Some protected *O*-amino sugars and their derivatives*

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Hydroxylamines are powerful nucleophiles toward low-lying LUMO electrophiles (π systems) owing to their α-effect[1]. Hydroxylamines *O*-substituted by sugar moieties should constitute strongly nucleophilic compounds — structurally close to their natural counterparts — whose biological activity is potentially interesting.

Using Mitsunobu's general procedure[2] of increasing the nucleofugal properties of a hydroxyl group by reaction with the betaine formed from triphenylphosphine and diethyl azodicarboxylate, Grochowski *et al.*[3] prepared the first examples of *O*-phthalimido sugar derivatives, namely **1** and some novel "C-O-N" nucleoside analogs.[4] They also described[5] the hydrazinolysis of simple *O*-phthalimido alcohols to the corresponding *O*-alkylhydroxylamines, but did not report until recently[6] the synthesis of sugar derivatives bearing a free *O*-amino group. The first example of this type of compound, **2**, was described in a preliminary communication[7] from this laboratory. The biological potential of these compounds as analogs of natural products has been confirmed by the synthesis of *O*-amino nucleosides[8].

Hydrazinolysis of **1** gave the *O*-amino sugar derivative **2**, the difficulty in the synthesis coming from the extreme reactivity of the *O*-amino sugars toward traces of aldehydes and ketones.

This reactivity was exploited to prepare oximes **3–9**. The formyl group of **9**, which constitutes a starting point for further extension of the molecule[9], could be reduced to give **10**, a further reduction leading to **11**. Reduction of **3** gave **12**. Reaction of **2** with different types of acid derivatives led to compounds **13–16**.

We expected the *O*-amino sugars to be good substrates for $E_{C=O}$ reactions. In fact, under the conditions used (sodium nitrite, trifluoroacetic acid, dimethyl sulfoxide), diazotization of **2** led to 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose in 64% yield. The most probable explanation is a preferred attack on the terminal nitrogen atom of the intermediate diazonium cation by a nucleophile from the medium.

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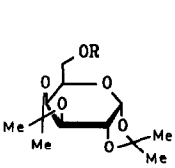
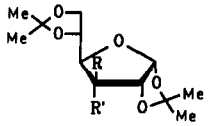
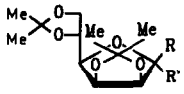


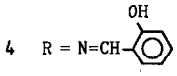
1 R = NPhth
2 R = NH_2
3 R = N=CMe_2



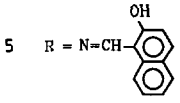
17 R = H, R' = OH
18 R = ONPhth, R' = H
19 R = ONH_2, R' =H
20 R = ON=CMe_2, R' = H



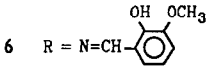
21 R = H, R' = OH
22 R = ONPhth, R' = H
23 R = ONH_2, R' = H
24 R = ON=CMe_2, R' = H



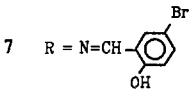
4 R = N=CH-



5 R = N=CH-

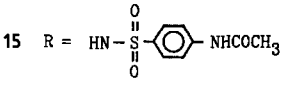


6 R = N=CH-



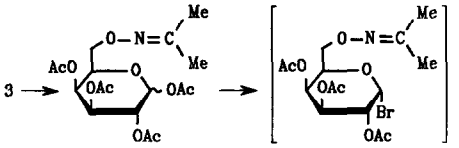
7 R = N=CH-

8 R = N=CPr_2
9 R = N=CH CHO
10 R = N=CH CH_2OH
11 R = $NHCH_2CH_2OH$
12 R = $NHCHMe_2$
13 R = $NHCOCH_3$
14 R = $NHCOCF_3$

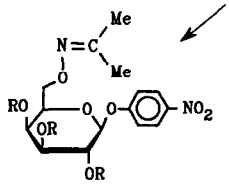


15 R =

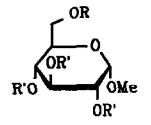
16 R = NHP(0)(OMe)$_2$



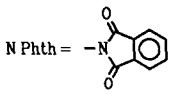
25 26



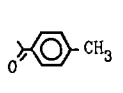
27 R = $COCH_3$
28 R = H



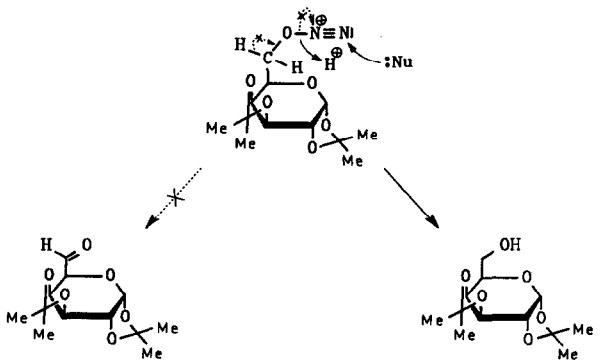
29 R = H, R' = Tol
30 R = NPhth, R' = Tol
31 R = NH_2, R' = Tol
32 R = N=CPr_2, R' = Tol
33 R = N=CPr_2, R' = H



N Phth =



Tol =



The reaction was extended to a secondary position of a sugar derivative by reacting the allofuranose **17** with triphenylphosphine, diethyl azodicarboxylate, and *N*-hydroxyphthalimide in tetrahydrofuran to get the *gluco* *O*-phthalimido sugar **18**. The hydrazinolysis of **18** gave **19**, which was *N*-alkylidenated to **20**.

The same reaction was applied to the anomeric position of the mannofuranose **21**, leading mainly to the β anomer **23** (63%), together with a little of the α anomer (5%), which was not isolated in pure form, but whose structure was established by spectroscopy (^{1}H-n.m.r.: δ 5.62, s, 1 H, $J_{1,2}$ <0.5 Hz, H-1).

To obtain more hydrophilic compounds and to test the ability of the *O*-(alkylidenamino) group to resist both acidic and alkaline deblocking conditions, **3** was selectively *O*-de-isopropylidenated then acetylated to **25** which was converted *via* the (mostly α) glycosyl bromide **26** to the tri-*O*-acetylated-*p*-nitrophenyl β-D-galactopyranoside **27**. The latter was successfully *O*-deacetylated to **28**. In a similar way, the methyl 2,3,4-tri-*O*-toluoyl-α-D-glucopyranoside[10] **29** was converted to its 6-*O*-phthalimido derivative **30**, and this was hydrazinolyzed to **31**, which was not isolated but converted to the oxime **32**, then *O*-deacylated to **33**.

Some of the compounds prepared were submitted to preliminary biological testing. None was active against a panel of Gram + and Gram − bacteria, but marginal antiviral activities were found at maximum noncytotoxic concentrations. Thus, there was partial inhibition of the herpes virus at 327μM for **33** and of the polyoma virus at 182μM for **23** and at 159μM for **3**. Under the same conditions **2** was neither antiviral nor cytotoxic. The most cytotoxic of the compounds tested was **22** (123μM on 3T6 cells, 74μM on ovine embryonic cells).

EXPERIMENTAL

General methods. — These were given in ref. 11. Optical rotations were obtained for solutions in chloroform. Column chromatography was conducted on silica gel (Merck) 70–230 mesh. Biological testing was performed according to ref. 12.

Preparation of the O*-phthalimido sugars.* — To a solution of the partially blocked sugar (20 mmol) in dry tetrahydrofuran (200 mL), 5.3 g (20 mmol) of triphenylphosphine, 3.3 g (20 mmol) of *N*-hydroxyphthalimide, and 3.1 mL (20 mmol) of diethyl azodicarboxylate were added. After 36 h of vigorous stirring, 25 g of silica gel was suspended in the medium and the solvent was evaporated to dryness. The reddish residue was extracted with heptane in a Soxhlet apparatus for 12 h. The solvent was then evaporated, leaving a yellow syrup which gave the pure phthalimido sugar by crystallization from ethanol.

Hydrazinolysis of the O*-phthalimido sugars.* — To a solution of *O*-phthalimido sugar (25 mmol) in ethanol (200 mL) hydrazine hydrate (1.25 g, 25 mmol) was added. The mixture was heated for 1 h under reflux, diluted with water (250 mL), then extracted with ether (3 × 100 mL). The organic fractions were collected, dried (sodium sulfate), and evaporated. The analytically pure *O*-amino sugar was obtained by distillation and crystallization (ethanol).

Preparation of the O-*glycosyl oximes*. — To a solution of the crude *O*-amino sugar (2 mmol) in ethanol (50 mL), 4 mmol of the carbonyl compound (aldehyde or ketone) was added. The mixture was heated for 1 h under reflux, then evaporated to dryness. The *O*-glycosyl oximes were purified by column chromatography on silica gel. Compound **9** was prepared following a slightly different procedure (see below).

*6-*O*-Amino-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**2**). — Hydrazinolysis of **1** gave **2** (72%), m.p. 69.2–70.2°, $[\alpha]_D^{28}$ −51.8° (*c* 1.0); λ_{max}^{EtOH} 217 nm (ε 77); ν_{max}^{KBr} 1595 (NH), 1387, and 1377 (CMe_2) cm^{-1}; ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 5.55 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 5.46 (br. s, 1 H, NH_2), 4.61 (dd, 1 H, $J_{2,3}$ 2.4, $J_{3,4}$ 7.5 Hz, H-3), 4.32 (dd, 1 H, H-2), 4.29–4.09 (m, 2 H, H-4,5), 3.84 (d, 2 H 2 H-6), 1.56, 1.46, and 1.34 [3 s, 4 × 3 H, 2 C(CH_3)$_2$]; e.i.m.s: *m/z* 275 (27,$M^{\cdot+}$ − Me$^{\cdot}$), 202 (21), 142 (26), 127 (31), 113 (23), 97 (22), 85 (36), 81 (26), and 59 (29).

Anal. Calc. for $C_{12}H_{21}NO_6$ (275.30): C, 52.35; H, 7.69; N 5.09. Found: C, 52.28; H, 7.72; N, 4.98.

*1,2:3,4-Di-*O*-isopropylidene-6-*O*-isopropylideneamino-α-*D*-galactopyranose* (**3**). — *N*-Alkylidenation of **2** with acetone gave **3** (91%), m.p. 66.8–68.1°, $[\alpha]_D^{29}$ −83° (*c* 0.2); λ_{max}^{EtOH} 216 nm (ε 2090); ν_{max}^{KBr} 1390, 1375, 1270, 1250, 1225, 1175, 1080, and 1005 cm^{-1}; ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 5.52 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.62 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7.5 Hz, H-3), 4.30–4.10 (m, 5 H, H-2,4,5, and 2 H-6), and 1.59–1.35 [m, 18 H, CH_3 C=N and 2 (CH_3)$_2$C]; e.i.m.s.: *m/z* 315 (8,$M^{\cdot+}$), 3.00 (100), 243 (93), 242 (70), 134 (18), 125 (26), 85 (40), 81 (47), 74 (30), 71 (53), and 56 (51).

Anal. Calc. for $C_{15}H_{25}NO_6$ (315.37): C, 57.13; H, 7.99; N, 4.44. Found: C, 57.13; H, 8.03; N, 4.51.

*6-*O*-(2-Hydroxybenzylideneamino)-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**4**). — *N*-Alkylidenation of **2** with salicylaldehyde gave **4** (70%), syrup, $[\alpha]_D^{28}$ −33° (*c* 1.0); R_F 0.3 (1:2 ether–hexane); λ_{max}^{EtOH} 224 (ε 9630), 260 (8330), 264 (10 100), 272 (7220), and 309 nm (4260); ν_{max}^{NaCl} 1615 and 1575 (Ph), 1490, 1385, and 1375 (CMe_2) cm^{-1}; ^{1}H-n.m.r. (90 MHz, $CDCl_3$): δ 9.50 (s, 1 H, O*H*), 8.14 (s, 1 H, ArC*H*=N), 7.27–6.70 (m, 4 H, Ar-H), 5.42 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 4.54 (dd, 1 H, $J_{2,3}$ 2.2, $J_{3,4}$ 8 Hz, H-3), 4.42–3.94 (m, 5 H, H-2,4,5, and 2 H-6), 1.45, 1.33, and 1.28 [3 s, 4 × 3 H, 2 (CH_3)$_2$C]; e.i.m.s.: *m/z* 380 (28, $M^{\cdot+}$ + 1), 379 (100, $M^{\cdot+}$), 364 (58, $M^{\cdot+}$ − Me$^{\cdot}$), 306 (15), 185 (11), 137 (33), 121 (14), 120 (33), 119 (15), and 81 (15).

Anal. Calc. for $C_{19}H_{25}NO_7$ (379.41): C, 60.15; H, 6.64; N, 3.69. Found: C, 60.32; H, 6.77; N, 3.58.

*6-*O*-(2-Hydroxy-1-naphthylmethyleneamino)-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose* (**5**). — *N*-Alkylidenation of **2** with 2-hydroxynaphthalene-1-carbaldehyde gave **5** (65%), m.p. 53.7–54.5°, $[\alpha]_D^{22}$ −60° (*c* 1.04); R_F 0.40 and 0.51 (1:1 ether–hexane); λ_{max}^{EtOH} 203 (ε 18 046), 233 (34 316), 300 (6731), 313 (8342), and 341 nm (4955); $\nu_{max}^{CCl_4}$ 1630 and 1610 (Ar), 1390, 1265, 1220, 1080, and 1015 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): *E* isomer: δ 10.70 (s, 1 H, O*H*), 9.25 (s, 1 H, C*H*=N), 8.00–7.15 (m, 6 H, Ar-H), 5.63 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.70 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 8 Hz, H-3), 4.51–4.25 (m, 5 H, H-2,4,5, and 2 H-6), 1.55, 1.50, 1.38, and 1.31 [4 s, 4 × 3 H, 2 (CH_3)$_2$C]; e.i.m.s.: *m/z* 429 (41, $M^{\cdot+}$), 414 (16, $M^{\cdot+}$ − Me$^{\cdot}$), 371 (17), 313 (11), 187 (21), 169 (100), 115 (32), 71 (27), and 59 (33).

Anal. Calc. for $C_{23}H_{27}NO_7$ (429.47): C, 64.32; H, 6.34; N, 3.26. Found: C, 64.08; H, 6.44, N, 3.36.

6-O-(2-Hydroxy-3-methoxybenzylideneamino)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**6**). — *N*-Alkylidenation of **2** with 2-hydroxy-3-methoxybenzaldehyde gave **6** as a 4:1 mixture of *E* and *Z* isomers (81%), $[\alpha]_D^{23}$ −35° (*c* 1.68); R_F 0.43 (*E*), 0.32 (*Z*) (1:2 ethyl acetate–hexane); λ_{max}^{EtOH} 222 (ε 17 454), 270 (11 023), and 367 nm (3123); $\nu_{max}^{CCl_4}$ 1575 and 1610 (Ph), 1460, 1380, 1210, 1070, and 1005 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): *E* isomer, δ 9.60 (s, 1 H, O*H*), 8.25 (s, 1 H, C*H*=N), 6.95–6.79 (m, 3 H, Ph-H), 5.55 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.62 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 8 Hz, H-3), 4.30 (dd, 1 H, H-2), 4.36 (dd, 1 H, $J_{5,6b}$ 6, $J_{6a,6b}$ 11 Hz, H-6b), 4.28 (dd, 1 H, $J_{5,6a}$ 6 Hz, H-6a), 4.25 (dd, 1 H, $J_{4,5}$ 2.5 Hz, H-4), 4.18 (dt, 1 H, H-5), 3.85 (s, 3 H, CH_3O), 1.50, 1.35, and 1.30 [3 s, 4 × 3 H, 2 C(CH_3)$_2$]; *Z* isomer, δ 7.72 (s, 1 H, C*H*=N), 7.55–6.80 (m, 3 H, Ph-H), 6.66 (s, 1 H, O*H*), 5.60 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.68 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7 Hz, H-3), 4.43–4.25 (m, 5 H, H-2,4,5, and 2 H-6), 3.90 (s, 3 H, CH_3O), 1.55, 1.49, 1.39, and 1.35 [4 s, 4 × 3 H, 2 (CH_3)$_2$C]; e.i.m.s.: *m/z* 409 (28, $M^{\cdot+}$), 394 (10, $M^{\cdot+}$ − Me$^{\cdot}$), 167 (37), 149 (88), 135 (46), 108 (24), 81 (55), 71 (43), and 59 (100).

Anal. Calc. for $C_{20}H_{27}NO_8$ (409.44); C, 58.67; H, 6.65; N, 3.42. Found: C, 58.40; H, 6.72; N, 3.32.

6-O-(5-Bromo-2-hydroxybenzylideneamino)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**7**). — *N*-Alkylidenation of **2** with 5-bromo-2-hydroxybenzaldehyde gave **7** as a 5:1 mixture of *E* and *Z* isomers (85%), syrup, $[\alpha]_D^{24}$ −53° (*c* 1.0); λ_{max}^{EtOH} 218 (ε 19 850), 265 (10 890), and 322 nm (5040); $\nu_{max}^{CCl_4}$ 1480, 1385, 1270, 1210, 1075, and 1010 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): *E* isomer, δ 9.76 (s, 1 H, O*H*), 8.18 (s, 1 H, C*H*–N), 7.30, 7.25, 6.88 (3 m, 3 H, Ph-H), 5.55 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.68 (dd, 1 H, $J_{2,3}$ 2, $J_{3,4}$ 9 Hz, H-3), 4.35–4.21 (m, H-2,4, and 2 H-6), 4.11 (m, 1 H, H-5), 1.60, 1.48, 1.35, and 1.30 [4 s, 4 × 3 H, 2 (CH_3)$_2$C]; e.i.m.s.: *m/z* 459 (22), 444 (12), 199 (24), 171 (12), 113 (21), 100 (22), 81 (83), 71 (48), and 59 (100).

Anal. Calc. for $C_{19}H_{24}NO_7Br$ (458.31): C, 49.79; H, 5.28; N, 3.06; Br, 17.44. Found: C, 49.94; H, 5.44; N, 3.16; Br, 17.37.

1,2:3,4-Di-O-isopropylidene-6-O-propylbutylideneamino)-α-D-galactopyranose (**8**). — *N*-Alkylidenation of **2** with 4-heptanone gave **8** (89%), b.p. 170°/0.7 mm Hg, $[\alpha]_D^{21}$ −53° (*c* 1.82); λ_{max}^{EtOH} 204 nm (ε 6130); ν_{max}^{KBr} 1385, 1260, 1215, 1075, and 1010 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 5.60 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.65 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 8 Hz, H-3), 4.35 (dd, 1 H, H-2), 4.30 (dd, 1 H, $J_{4,5}$ 2 Hz, H-4), 4.28 (m, 3 H, H-5 and 2 H-6), 2.25–2.10 (m, 4 H, 2 CH_2-C=N), 1.50–1.30 [m, 16 H, 2 $CH_2CH_2CH_3$ and 2 (CH_3)$_2$C], and 0.95 (m, 6 H, 2 $CH_2CH_2CH_3$); e.i.m.s.: *m/z* 371 (4, $M^{\cdot+}$), 356 (4), 185 (18), 130 (19), 112 (20), 100 (19), 85 (18), 70 (100), and 59 (19).

Anal. Calc. for $C_{19}H_{33}NO_6$ (371.48): C, 61.44; H, 8.95; N, 3.77. Found: C, 61.53; H, 8.79; N, 3.99.

6-O-(Formylmethyleneamino)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**9**). — To a large excess of glyoxal (1.16 g, 20 mmol) in solution in chloroform (20 mL), a solution of **2** (556 mg, 2 mmol) in chloroform was slowly added. After 30 min stirring at room temperature, the reaction mixture was dried and concentrated, then submitted to

shortpath distillation to give analytically pure **9** (410 mg, 65%), b.p. 110°/5μm Hg, $[\alpha]_D^{25}$ −65° (*c* 0.8); λ_{max}^{EtOH} 209 (ε 3910) and 230 nm (2960); ν_{max}^{KBr} 1690, 1570, 1380, 1250, 1210, 1060, and 1015 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 9.50 (d, 1 H, *J* 8 Hz, N=CHC*H*O), 7.52 (d, 1 H, N=C*H*CHO), 5.49 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.58 (dd, 1 H, $J_{2,3}$ 2.7, $J_{3,4}$ 8 Hz, H-3), 4.40 (d, 2 H, $J_{5,6a}$ 6, $J_{5,6b}$ 6 H, 2 H-6), 4.28 (dd, 1 H, H-2), 4.19 (dd, 1 H, $J_{4,5}$ 1.5 Hz, H-4), 4.12 (dt, 1 H, H-5), 1.44, 1.40, 1.29, and 1.27 [4 s, 4 × 3 H, 2 (CH_3)$_2$C]; e.i.m.s.: *m/z* 300 (39), 113 (32), 100 (55), 81 (100), 71 (44), and 59 (96).

Anal. Calc. for $C_{14}H_{21}NO_7$ (315.33): C, 53.33; H, 6.71; N, 4.44. Found: C, 53.30; H, 6.72; N, 4.45.

6-O-(2-Hydroxyethylideneamino)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**10**). — To a solution of **9** (630 mg, 2 mmol) in ethanol (50 mL), sodium borohydride (150 mg, 42 mmol) was added and the reaction mixture was stirred for 2 h at room temperature, then concentrated, and submitted to column chromatography (1:1 ethyl acetate–hexane) to give **10** (440 mg, 69%) as a 2:1 mixture of *E* and *Z* isomers, syrup, $[\alpha]_D^{30}$ −79° (*c* 0.6), λ_{max}^{EtOH} 210 nm (ε 3600), $\nu_{max}^{CCl_4}$ 1380, 1260, 1210, 1075, and 1010 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): *E* isomer, δ 7.60 (t, 1 H, *J* 4.5 Hz, N=C*H*), 5.66 (d, 1 H, $J_{1,2}$ 2.3 Hz, H-1), 4.62 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 8 Hz, H-3), 4.33 (dd, 1 H, H-2), 4.20–4.04 (m, 6 H, H-4,5, 2 H-6, and CH_2OH), 2.26 (br. s, 1 H, O*H*), 1.53, 1.47, 1.35, and 1.32 [4 s, 4 × 3 H, 2 (CH_3)$_2$C]; *Z* isomer, δ 6.98 (t, 1 H, *J* 4.25 Hz, N=C*H*), 5.56 (d, 1 H, $J_{1,2}$ 2.3 Hz, H-1), 4.62 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 8 Hz, H-3), 4.33 (dd, 1 H, H-2), 4.20–4.04 (m, 6 H, H-4,5, 2 H-6, and CH_2OH), 1.53, 1.47, 1.35, and 1.32 [4 s, 4 × 3 H, 2 (CH_3)$_2$C]; e.i.m.s.: *m/z* 302 (32), 185 (41), 169 (38), 127 (53), 113 (65), 100 (86), 81 (100), 71 (80), and 59 (90).

Anal. Calc. for $C_{14}H_{23}NO_7$ (317.34): C, 52.99; H, 7.31; N, 4.44. Found: C, 52.87; H, 7.29; N, 4.58.

6-O-(2-Hydroxyethylamino)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**11**). — To a solution of **10** (317 mg, 1 mmol) and sodium cyanoborohydride (75 mg, 1.1 mmol) in methanol (50 mL) at room temperature, M hydrochloric acid was slowly and carefully added in order to maintain the pH at 2–3. After 2 h, the reaction was complete (t.l.c.). The reaction mixture was neutralized (saturated aqueous sodium hydrogencarbonate), diluted with water (50 mL), and extracted (chloroform, 2 × 50 mL). The dried (sodium sulfate) collected organic phases, gave, after column chromatography (1:1 ethyl acetate–hexane) 190 mg (60%) of **11**. The analytical sample was obtained by distillation (170°/0.7 mm Hg), syrup, $[\alpha]_D^{26}$ −42.5° (*c* 1.0); λ_{max}^{EtOH} 203 nm (ε 530); $\nu_{max}^{CCl_4}$ 1385, 1255, 1215, 1180, and 1075 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 5.58 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.70 (dd, 1 H, $J_{2,3}$ 3, $J_{3,4}$ 8 Hz, H-3), 4.62 (dd, 1 H, H-2), 4.45–4.12 (m, 2 H, H-4,5), 3.88 (m, 2 H, 2 H-6), 3.77 (t, 2 H, OCH_2CH$_2$N), 3.06 (t, 2 H, OCH$_2$CH_2N), 1.60, 1.48, 1.29, and 1.27 [4 s, 4 × 3 H, 2 (CH_3)$_2$C]; e.i.m.s.: *m/z* 319 (17, $M^{\cdot+}$), 288 (15), 230 (21), 172 (23), 149 (17), 127 (51), 113 (31), 97 (36), 81 (100), and 59 (98).

Anal. Calc. for $C_{14}H_{25}NO_7$ (319.36): C, 52.65; H, 7.89; N, 4.39. Found: C, 52.57; H, 7.91; N, 4.33.

6-O-Isopropylamino-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**12**). — Prepared from **3** (315 mg, 1 mmol), as described for **11**, **12** (285 mg, 90%) was obtained as a syrup, $[\alpha]_D^{22}$ −43° (*c* 1.63); λ_{max}^{EtOH} 201 nm (ε 500); $\nu_{max}^{CCl_4}$ 1380, 1250, 1210, 1175, 1070,

and 1000 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 5.58 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.62 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 8 Hz, H-3), 4.33 (dd, 1 H, H-2), 4.22 (dd, 1 H, $J_{4,5}$ 2 Hz, H-4), 4.17 (ddd, 1 H, $J_{5,6a}$ 6, $J_{5,6b}$ 7 Hz, H-5), 3.89 (dd, 1 H, $J_{6a,6b}$ 12 Hz, H-6b), 3.83 (dd, 1 H, H-6a), 3.19 [sept, 1 H, J 6 Hz, $CH(CH_3)_2$], 1.57, 1.46, 1.33, and 1.31 [4 s, 4 × 3 H, 2 $(CH_3)_2C$], 1.07, and 1.02 [2 d, 2 × 3 H, $CH(CH_3)_2$]; e.i.m.s.: *m/z* 317 (29, $M^{\cdot+}$), 302 (69), 244 (37), 185 (24), 127 (55), 101 (36), 85 (76), and 59 (100).

Anal. Calc. for $C_{15}H_{27}NO_6$ (317.39): C, 56.77; H, 8.57; N, 4.41. Found: C, 56.73; H, 8.61; N, 4.45.

6-O-Acetamido-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**13**). — To a solution of **2** (275 mg, 1 mmol) in dichloromethane (50 mL), 2-acetoxypropenenitrile (122 mg, 1.1 mmol) was added. After 5 h at room temperature, evaporation of the solvent and crystallization (ethanol) gave **13** (290 mg, 81%), m.p. 172–173.5°, $[\alpha]_D^{29}$ −67° (*c* 0.5); λ_{max}^{EtOH} 213 nm (ε 670); ν_{max}^{NaCl} 1690, 1385, 1265, 1220, 1070, and 1015 cm^{-1}; ^{1}H-n.m.r. (360 MHz, CD_3SOCD_3): δ 5.44 (d, 1 H, $J_{1,2}$ Hz, H-1), 4.59 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 8 Hz, H-3), 4.31 (dd, 1 H, H-2), 4.23 (dd, 1 H, $J_{4,5}$ 1, H-4), 3.99 (m, 2 H, 2 H-6), 3.71 (m, 1 H, H-5), 1.70, 1.44, 1.32, and 1.27 [4 s, 4 × 3 H, 2 $(CH_3)_2C$]; e.i.m.s.: *m/z* 317 (4, $M^{\cdot+}$), 302 (69), 243 (42), 202 (37), 185 (100), 127 (29), and 59 (29).

Anal. Calc. for $C_{14}H_{23}NO_7$ (317.34): C, 52.99; H, 7.31; N, 4.41. Found: C, 52.89; H, 7.34; N, 4.42.

1,2:3,4-Di-O-isopropylidene-6-O-trifluoroacetamido-α-D-galactopyranose (**14**). — To a solution of **2** (275 mg, 1 mmol) in dry pyridine (50 mL), trifluoroacetyl chloride (160 mg, 1.2 mmol) was added. After 2 h at room temperature, the reaction mixture was concentrated, and residual volatile components were removed by coevaporation with toluene (2 × 10 mL). The residue was then submitted to a column chromatography (2:1 ethyl acetate–hexane) to give **14** (270 mg, 73%), m.p. 115.3–115.8°, $[\alpha]_D^{29}$ −53° (*c* 1.3); λ_{max}^{EtOH} 218 nm (ε 1000); $\nu_{max}^{CLl_3}$ 1745, 1390, 1170, 1075, and 905 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 5.56 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.62 (dd, 1 H, $J_{2,3}$ 2, $J_{3,4}$ 8 Hz, H-3), 4.50–4.10 (m, 5 H, H-2,4,5, and 2 H-6), 1.52, 1.48, 1.35, and 1.33 [4 s, 4 × 3 H, 2 $(CH_3)_2C$]; e.i.m.s.: *m/z* 356 (100), 297 (11), 127 (11), 113 (15), 100 (20), 85 (13), 81 (37), and 59 (22).

Anal. Calc. for $C_{14}H_{20}NO_7F_3$ (371.31): C, 45.29; H, 5.43; N, 3.77; F. 15.35. Found: C, 45.21; H, 5.64; N, 3.86; F, 15.08.

6-O-(p-Acetamidobenzenesulfonamido)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**15**). — To a solution of **2** (500 mg, 1.8 mmol) in dry pyridine (50 mL) *p*-acetamidobenzenesulfonyl chloride (420 mg, 1.8 mmol) was added. The reaction mixture was kept at room temperature for 12 h under stirring, then concentrated, and submitted to dry column chromatography (2:1 ethyl acetate–hexane) to give **15** (63%), which was recrystallized (ethyl acetate–hexane), m.p. 111.5–118.8°, $[\alpha]_D^{22}$ 0° (*c* 1.0); R_F 0.53 (1:2 ethyl acetate–hexane); λ_{max}^{EtOH} 204 (ε 16 042) and 262 nm (17 247); ν_{max}^{KBr} 1685, 1590, 1530, 1165, 1070,m and 1005 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 7.00 (br. s, 1 H, N*H*), 5.55 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.65 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7 Hz, H-3), 4.35 (dd, 1 H, H-2), 4.30–4.10 (m, 4 H, H-4,5, 2 H-6), 2.22 (s, 3 H, CH_3CO), 1.71, 1.45, and 1.35 [3 s, 4 × 3 H, 2 $(CH_3)_2C$]; e.i.m.s.: *m/z* 457 (52, $M^{\cdot+}$ − Me), 414 (94), 214 (20), 198 (100), 172 (64), 156 (31), 134 (28), 113 (28), 100 (41), 92 (32), 81 (63), 71 (45), and 59 (70).

Anal. Calc. for $C_{20}H_{28}N_2O_9S$ (472.52): C, 50.84; H, 5.97; N, 5.93; S, 6.79. Found: C, 51.05; H, 6.23; N, 5.65; S, 7.02.

6-O-(Dimethoxyphosphinylamino)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**16**). — To a solution of **2** (500 mg, 1.8 mmol) in carbon tetrachloride (50 mL) a catalytic amount of benzyltriethylammonium chloride and dimethyl phosphite (220 mg, 2 mmol) were added. A 50% aqueous solution of sodium hydroxide (50 mL) was added during 1 h, with vigorous stirring. The reaction mixture was kept 30 min at room temperature, then the organic layer was dried (sodium sulfate), concentrated, and submitted to dry column chromatography (1:2 ethyl acetate–hexane) to give **16** (450 mg, 59%) as a syrup, $[\alpha]_D^{23}$ −600° (*c* 1.0); R_F 0.53 (1:2 ethyl acetate–hexane); $\lambda_{max}^{CH_2Cl_2}$ 226 (ε 1064) and 267 nm (213); ν_{max}^{NaCl} 1700, 1370, 1240, 1200, and 1060 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 7.00 (br. s, 1 H, N*H*), 5.55 (d, 1 H, $J_{1,2}$ 5 Hz, H-1), 4.65 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7 Hz, H-3), 4.35 (dd, 1 H, H-2), 4.30–4.10 (m, 2 H, H-4,5), 4.00–3.90 (m, 2 H, 2 H-6), 3.90–3.70 (m, 6 H, 2 CH_3O), 1.55, 1.40, and 1.35 [3 s, 4 × 3 H, 2 $(CH_3)_2C$]; e.i.m.s.: *m/z* 383 (1, $M^{\cdot+}$), 368 (1, $M^{\cdot+}$ − Me·), 245 (34), 234 (50), 204 (70), 199 (44), 173 (50), 156 (67), 139 (46), 92 (70), and 91 (100).

Anal. Calc. for $C_{14}H_{26}NO_9P$ (383.34): C, 43.87; H, 6.84; N, 3.65; P, 8.08. Found: C, 44.19; H, 7.21; N, 3.40; P, 7.89.

1,2:5,6-Di-O-isopropylidene-3-O-phthalimido-α-D-glucofuranose (**18**). — Obtained from[13] **17** in 56% yield, m.p. 119.4–121.7°, $[\alpha]_D^{22}$ +8.5° (*c* 1.22); λ_{max}^{EtOH} 220 nm (ε 38 740); ν_{max}^{KBr} 1740, 1380, 1225, and 1085 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 7.90–7.77 (m, 4 H, Ar-H), 6.12 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.90 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 4.76 (d, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 4.70 (q, 1 H, $J_{4,5}$ 6, $J_{5,6a}$ 6, $J_{5,6b}$ 6 Hz, H-5), 4.40 (dd, 1 H, H-4), 4.12 (dd, 1 H, $J_{6a,6b}$ 8 Hz, H-6b), 4.09 (dd, 1 H, H-6a), 1.53, 1.51, 1.41, and 1.34 [4 s, 4 × 3 H, 2 $(CH_3)_2C$]; e.i.m.s.: *m/z* 390 (82), 332 (15), 263 (16), 148 (4), 129 (6), 104 (6), and 101 (100).

Anal. Calc. for $C_{20}H_{23}NO_8$ (405.41): C, 59.25; H, 5.72; N, 3.45. Found: C, 59.38; H, 5.92; N, 3.53.

3-O-Amino-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (**19**). — Hydrazinolysis of **18** gave **19** (41%), m.p. 84.3–84.6°, $[\alpha]_D^{21}$ −55° (*c* 0.96); λ_{max}^{EtOH} 203 nm (ε 360); ν_{max}^{KBr} 1600, 1390, 1375, and 1075 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 5.86 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 5.57 (br. s, 2 H, NH_2), 4.84 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 4.29 (ddd, 1 H, $J_{4,5}$ 8, $J_{5,6a}$ 5, $J_{5,6b}$ 5.8 Hz, H-5), 4.19 (d, 1 H, $J_{3,4}$ 3.3 Hz, H-3), 4.12 (dd, 1 H, H-4), 4.10 (dd, 1 H, $J_{6a,6b}$ 8.5 Hz, H-6b), 4.03 (dd, 1 H, H-6a), 1.52, 1.47, 1.37, and 1.35 [4 s, 4 × 3 H, 2 $(CH_3)_2C$]; e.i.m.s.: *m/z* 260 (100), 217 (23), 131 (24), 116 (23), 114 (23), 101 (97), and 59 (24).

Anal. Calc. for $C_{12}H_{21}NO_6$ (275.30): C, 52.35; H, 7.69; N, 5.09. Found: C, 52.61; H, 7.92; N, 5.19.

1,2:5,6-Di-O-isopropylidene-3-O-isopropylideneamino-α-D-glucofuranose (**20**). — *N*-Alkylidenation of **19** with acetone gave **20** (95%), m.p. 97.1–97.9°, $[\alpha]_D^{25}$ −49.5° (*c* 0.96); λ_{max}^{EtOH} 202 nm (ε 6680); $\nu_{max}^{CCl_4}$ 1560, 1405, 1365, 1150, 1080, and 1020 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 5.89 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.75 (d, 1 H, $J_{2,3}$ 0 Hz, H-2), 4.60 (d, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 4.35 (dt, 1 H, $J_{4,5}$ 7.2, $J_{5,6a}$ 6, $J_{5,6b}$ 6 Hz, H-5), 4.30 (dd, 1 H, H-4), 4.08 (dd, 1 H, $J_{6a,6b}$ 8.5 Hz, H-6b), 4.03 (dd, 1 H, H-6a), 1.98, 1.93 [2 s, 2 × 3 H, $(CH_3)_2C{=}N$), 1.53, 1.46, 1.40, and 1.36 [4 s, 4 × 3 H, 2 $(CH_3)_2C$].

Anal. Calc. for $C_{15}H_{25}NO_6$ (315.37): C, 57.13; H, 7.99; N, 4.44. Found: C, 57.00; H, 8.17; N, 4.57.

2,3:5,6-Di-O-isopropylidene-1-O-phthalimido-β-D-mannofuranose (**22**). — Obtained from[14] **21** in 63% yield after elimination of small amounts of its *α* anomer by crystallization, m.p. 143.5–148.5°, $[\alpha]_D^{25}$ −145° (*c* 0.96); λ_{max}^{EtOH} 220 nm (ε 41 640); ν_{max}^{KBr} 1380, 1220, 1135, and 980 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 5.45 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.80–5.00 (m, 2 H, H-2,3), 4.25 (dd, 1 H, $J_{4,5}$ 8, $J_{5,6a}$ 6, $J_{5,6b}$ 4 Hz, H-5), 4.05 (m, 2 H, 2 H-6), 1.69, 1.42, and 1.40 [4 s, 4 × 3 H, 2 $(CH_3)_2C$]; e.i.m.s.: *m/z* 390 (10), 204 (5), 185 (13), 143 (6), 127 (2), 101 (100), 85 (54), 69 (46), and 59 (77).

Anal. Calc. for $C_{20}H_{23}NO_8$ (405.41): C, 59.25; H, 5.72; N, 3.45. Found: C, 59.09; H, 5.67; N, 3.47.

1-O-Amino-2,3:5,6-di-O-isopropylidene-β-D-mannofuranose (**23**). — Hydrazinolysis of **22** gave **23** (70%) as a syrup, $[\alpha]_D^{26}$ −33° (*c* 1.78); λ_{max}^{EtOH} 204 nm (ε 220); ν_{max}^{KBr} 1380, 1215, 1170, 1140, and 1070 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$); δ 5.90 (br. s, 2 H, NH_2), 4.99 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.75 (dd, 1 H, $J_{2,3}$ 6, $J_{3,4}$ 4 Hz, H-3), 4.70 (dd, 1 H, H-2), 4.44 (ddd, 1 H, H-4), 1.50, 1.45, 1.37, and 1.35 [4 s, 4 × 3 H, 2 $(CH_3)_2C$]; e.i.m.s.: *m/z* 260 (20), 243 (13), 185 (62), 127 (21), 101 (100), 85 (45), 69 (29), and 59 (62).

Anal. Calc. for $C_{12}H_{21}NO_6$ (275.30): C, 52.35; H, 7.69; N, 5.09. Found: C, 52.13; H, 7.72; N, 5.11.

2,3:5,6-Di-O-isopropylidene-1-O-isopropylideneamino-β-D-mannofuranose (**24**). — Obtained by the general procedure described above, from **23** and propanone in 90% yield; syrup, $[\alpha]_D^{26}$ +6.5° (*c*, 1.08); λ_{max}^{EtOH} 209 nm (ε 2020); ν_{max}^{KBr} 1370, 1205, 1065, and 915 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 5.42 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.80 (dd, 1 H, $J_{2,3}$ 6, $J_{3,4}$ 4 Hz, H-3), 4.75 (dd, 1 H, H-2), 4.47 (ddd, 1 H, $J_{4,5}$ 8, $J_{5,6a}$ 6, $J_{5,6b}$ 4 Hz, H-5), 4.10 (dd, 1 H, $J_{6a,6b}$ 9 Hz, H-6b), 4.08 (dd, 1 H, H-6a), 3.61 (dd, 1 H, H-4), 1.91, 1.99 [2 s, 2 × 3 H, $(CH_3)_2C{=}N$], 1.60, 1.58, 1.42 and 1.39 [4 s, 4 × 3 H, $(CH_3)_2C$]; e.i.m.s.: *m/z* 300 (7), 243 (4), 185 (23), 156 (5), 126 (6), 114 (6), 101 (4), 68 (6), 59 (13), and 56 (100).

Anal. Calc. for $C_{16}H_{29}NO_6$ (315.37): C, 57.13; H, 7.99; N, 4.44. Found: C, 57.07; H, 8.04; N, 4.43.

1,2,3,4-Tetra-O-acetyl-6-O-isopropylideneamino-α-and-β-D-galactopyranose (**25**). — A solution of **3** (390 mg, 1.4 mmol) in 60% aqueous acetic acid (10 mL) was heated for 3 h under reflux, then the solvent was evaporated and the residue treated for 12 h at room temperature with a mixture of dry pyridine (30 mL) and acetic anhydride (10 mL). The reaction mixture was extracted with ether (200 mL) and the organic layer was washed (saturated aqueous sodium hydrogenocarbonate, 30 mL), dried (magnesium sulfate), concentrated, and submitted to a dry-column chromatography (2:1 ether–hexane) to give a 7:3 mixture of *α* and *β* **25**. The *α* anomer was crystallized (hexane), and the *β* anomer was obtained by evaporation of the mother liquors. The *α* anomer had m.p. 124.0–125.3°, $[\alpha]_D^{25}$ +78° (*c* 0.31), R_F 0.37 (2:1 ether–hexane); λ_{max}^{EtOH} 202 nm (ε 4681); ν_{max}^{KBr} 1750 (C=O), 1370, 1250, 1220, and 1070 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 6.37 (d, 1 H, $J_{1,2}$ 2.6 Hz, H-1), 5.50 (m, 1 H, $J_{3,4}$ 11.6, $J_{4,5}$ 2 Hz, H-4), 5.39 (dd, 1 H, $J_{2,3}$ 2.2 Hz, H-3), 5.33 (dd, 1 H, H-2), 4.42 (dt, 1 H, $J_{5,6a}$ 8.4, $J_{5,6b}$ 6 Hz, H-5), 4.12 (dd, 1 H, $J_{6a,6b}$ 12 Hz, H-6b), 3.97 (dd, 1 H, H-6a), 2.16, 2.02, and 2.00 (3 s, 4 × 3 H, 4 CH_3CO), 1.85, and

1.80 [2 s, 2 × 3 H, $(CH_3)_2C=N$]; e.i.m.s.: *m/z* 403 (14), 345 (72), 301 (22), 271 (29), 197 (43), 169 (87), 141 (86), and 56 (100). The *β* anomer had m.p. 80.5–82.5°, R_F 0.33 (2:1 ether–hexane); λ_{max}^{EtOH} 202 nm (*ε* 6938); ν_{max}^{KBr} 1750 (C=O), 1370, 1250, 1220, and 1070 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): *δ* 5.70 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 5.41 (dd, 1 H, $J_{2,3}$ 3, $J_{3,4}$ 3.6 Hz, H-3), 5.32 (dd, 1 H, H-2), 5.09 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.22–3.95 (m, 3 H, H-5 and 2 H-6), 2.17, 2.12, 2.04, 2.00 (4 s, 4 × 3 H, 4 CH_3CO), 1.85, and 1.81 [2 s, 2 × 3 H, $(CH_3)_2C=N$].

Anal. (*α* anomer). Calc. for $C_{17}H_{24}NO_{10}$ (402.38): C, 50.62; H, 6.25; N, 3.47. Found: C, 50.72; H, 6.15; N, 3.55.

p-*Nitrophenyl 2,3,4-tri-O-acetyl-6-*O*-isopropylideneamino-β-*D*-galactopyranoside* (**27**). — Dry hydrogen bromide gas was passed during 30 min through a solution of **25** (650 mg, 1.45 mmol) in dry benzene (50 mL) kept at 4°. The solution was then brought to room temperature and the excess hydrogen bromide eliminated by bubbling nitrogen for 30 min. Evaporation of the benzene, dissolution in chloroform, and washing first with saturated aqueous sodium hydrogencarbonate (10 mL) then water (2 × 10 mL) gave, after drying (magnesium sulfate) and concentration, 508 mg (82%) of syrupy 2,3,4-tri-*O*-acetyl-6-*O*-isopropylideneamino-*α*-D-galactopyranosyl bromide (**26**), ν_{max}^{KBr} 1750, 1370, 1240, 1105, and 1080 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$); *δ* 6.65 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.42 (dd, 1 H, $J_{3,4}$ 3.5, $J_{4,5}$ 3 Hz, H-4), 5.35 (dd, 1 H, $J_{2,3}$ 10 Hz, H-3), 4.98 (dd, 1 H, H-2), 4.48 (ddd, 1 H, $J_{5,6a}$ 7, $J_{5,6b}$ 6 Hz, H-5), 4.05 (dd, 1 H, $J_{6a,6b}$ 12 Hz, H-6b), 3.95 (dd, 1 H, H-6a), 2.07, 2.02, 1.94 (3 s, 3 × 3 H, 3 CH_3CO), 1.77, and 1.75 [2 s, 2 × 3 H, $(CH_3)_2C=N$].

To a solution of *p*-nitrophenol (302 mg, 2.18 mmol) in M sodium hydroxide (3 mL), a solution of **26** (680 mg, 1.6 mmol) in acetone (5 mL) was added, and the reaction mixture was stirred for 3.5 h, then evaporated to dryness. Crystallization of the residue gave **27** (108 mg, 14%), m.p. 173.3–173.6°, $[\alpha]_D^{26}$ +18.6° (*c* 0.89); λ_{max}^{EtOH} 290 nm (*ε* 9390); $\nu_{max}^{CCl_4}$ 1750, 1575, 1410, 1345, 1230, 1150, and 1040 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$: *δ* 8.17, 7.07 (AA'BB' system, 4 H, Ph-H), 5.51 (dd, 1 H, $J_{1,2}$ 8, $J_{2,3}$ 11 Hz, H-2), 5.46 (d, 1 H, $J_{3,4}$ 3, $J_{4,5}$ 0 Hz, H-4), 5.14 (d, 1 H, H-1), 5.13 (dd, 1 H, H-3), 4.25 (m, 1 H, $J_{5,6a}$ 5, $J_{5,6b}$ 6.5 Hz, H-5), 4.13 (dd, 1 H, $J_{6a,6b}$ 10.5 Hz, H-6a), 4.06 (dd, 1 H, H-6b), 2.17, 2.07, 2.02 (3 s, 3 × 3 H, 3 CH_3CO), 1.89, and 1.85 [2 s, 2 × 3 H, $(CH_3)_2C=N$]; e.i.m.s.: *m/z* 344 (27), 182 (71), 127 (11), 118 (15), 115 (11), 81 (17), 74 (69), 73 (25), and 56 (100).

Anal. Calc. for $C_{21}H_{26}N_2O_{11}$ (482.45): C, 52.28; H, 5.43; N, 5.81. Found: C, 52.18; H, 5.29; N, 5.71.

p-*Nitrophenyl 6-*O*-isopropylideneamino-β-*D*-galactopyranoside* (**28**). — To a suspension of **27** (150 mg, 0.28 mmol) in dry methanol (3 mL) a catalytic amount of sodium methoxide was added, and the mixture was heated for 5 min under reflux, then neutralized with Dowex 50 (H^+) and evaporated to dryness. Crystallization of the residue gave **28** (100 mg, 95%), m.p. 217.4–218.0°, $[\alpha]_D^{23}$ −1.0° (*c* 0.46); λ_{max}^{EtOH} 202 (*ε* 21 265), and 296 nm (13 505); $\nu_{max}^{CCl_4}$ 1580, 1410, 1150, 1080, and 1030 cm^{-1}; ^{1}H-n.m.r. (200 MHz, CD_3OD): *δ* 8.19, 7.20 (AA'BB' system, 4 H, Ph-H), 5.00 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 4.20 (d, 2 H, $J_{5,6}$ 6 Hz, 2 H-6), 4.02 (t, 1 H, $J_{4,5}$ 1 Hz, H-5), 3.89 (d, 1 H, $J_{3,4}$ 4 Hz, H-4), 3.85 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 3.62 (dd, 1 H, H-3), 1.89, and 1.88 [2 s, 2 × 3 H,

$(CH_3)_2C=N$]; e.i.m.s.: *m/z* 218 (18), 139 (5), 109 (9), 81 (7), 74 (53), 73 (35), 71 (13), and 56 (100).

Anal. Calc. for $C_{15}H_{20}N_2O_8$ (356.34): C, 50.56; H, 5.66; N, 7.86. Found: C, 50.79; H, 5.88; N, 7.73.

*Methyl 6-*O*-phthalimido-2,3,4-tri-*O*-*p*-toluoyl-α-*D*-glucopyranoside* (**30**). — This was prepared from[10] **29** in 65% yield, m.p. 182.4–182.6°, $[\alpha]_D^{22}$ +62° (*c* 1.01); λ_{max}^{EtOH} 203 (ε 69 580), 222 (44 490), and 239 nm (49 550); ν_{max}^{KBr} 1735, 1720, 1280, 1255, and 1010 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 7.00–7.90 (m, 16 H, Ar-H), 6.18 (t, 1 H, $J_{2,3}$ 10 Hz, $J_{3,4}$ 10 Hz, H-3), 5.61 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.25 (m, 2 H, H-1,2), 4.30–4.60 (m, 3 H, H-5 and 2 H-6), 3.51 (s, 3 H, OCH_3), 2.39, 2.38, and 2.29 (3 s, 3 × 3 H, 3 $PhCH_3$); e.i.m.s.: *m/z* 531 (4), 335 (8), 309 (5), 245 (10), 216 (7), 215 (9), 119 (100), and 91 (8).

Anal. Calc. for $C_{39}H_{35}NO_{11}$ (693.71): C, 67.53; H, 5.09; N, 2.02. Found: C, 67.54; H, 5.15; N, 2.07.

*Methyl 6-*O*-(1-propylbutylideneamino)-2,3,4-tri-*O*-*p*-toluoyl-α-*D*-glucopyranose* (**32**). — Hydrazinolysis of **30** gave crude **31**, ^{1}H-n.m.r.: δ 6.20 (t, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 10 Hz, H-3), 5.70 (br. s, 2 H, NH_2), 5.65 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.23 (m, 1 H, H-5), 3.88, and 3.90 (m, 2 H, 2 H-6). This was directly reacted with 4-heptanone to give **32** (overall yield from **30**, 81%), syrup, $[\alpha]_D^{29}$ +72° (*c* 0.2); λ_{max}^{EtOH} 207 (ε 25 000) and 240 nm (37 770); $\nu_{max}^{CCl_4}$ 1730, 1610, 1280, 1270, and 1105 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 7.85, 7.50 (2 m, 2 × 6 H, Ph-H), 6.12 (m, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 10 Hz, H-3), 5.48 (t, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.22 (m, 2 H, H-1,2), 4.37 (dt, 1 H, $J_{5,6}$ 4.5 Hz, H-5), 4.22 (d, 2 H, 2 H-6), 4.46 (s, 3 H, OCH_3), 2.37, 2.35, 2.29 (3 s, 3 × 3 H, 3 $PhCH_3$), 2.27, and 2.10 (2 t, 2 × 2H, *J* 7.5 Hz, $2 N=CCH_2$), 1.50 (m, 4 H, $2 N=CCHCH_2$), 0.95, and 0.92 (2t, 2 × 3 H, *J* 7 Hz, $2 CH_2CH_3$); e.i.m.s.: *m/z* 659 (3), 523 (6), 181 (8), 119 (100), 91 (18), 70 (21), and 57 (10).

Anal. Calc. for $C_{38}H_{45}NO_9$ (659.78): C, 69.18; H, 6.87; N, 2.12. Found: C, 69.19; H, 6.96; N, 2.19.

*Methyl 6-*O*-(1-propylbutylideneamino)-α-*D*-glucopyranose* (**33**). — One g (2.1 mmol) of **32** was dissolved in methanol (50 mL) and heated for 2 h under reflux with saturated methanolic sodium methoxide (50 mL). The mixture was then neutralized (M hydrochloric acid, pH 7), washed with ether (2 × 30 mL), and evaporated to dryness. The viscous syrup obtained was distilled to give **33** (295 mg, 46%), b.p. 140°/10 μm Hg, $[\alpha]_D^{23}$ +71° (*c* 0.8); λ_{max}^{EtOH} 206 nm (ε 4400); ν_{max}^{KBr} 3250, 2940, 2900, 1450, and 1040 cm^{-1}; ^{1}H-n.m.r. (200 MHz, $CDCl_3$): δ 4.75 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 3.35–4.30 (m, 9 H, H-2,3,4,5, 2 H-6, and 3 O*H*), 3.30 (s, 3 H, OCH_3), 2.10–2.40 (m, 4 H, $2 N=CCH_2$), 1.10–1.70 (m, 4H, $2 N=CCH_2CH_2$), and 0.70–1.00 (m, 6 H, $2 CH_2CH_3$); e.i.m.s.: *m/z* 177 (20), 159 (51), 145 (26), 130 (85), 129 (39), 114 (35), 101 (76), 99 (45), 85 (36), 75 (53), 74 (64), 73 (72), 71 (92), and 70 (100).

Anal. Calc. for $C_{14}H_{27}NO_6$ (305.37): C, 55.07; H, 8.91; N, 4.59. Found: C, 55.26; H, 9.14; N, 4.40.

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