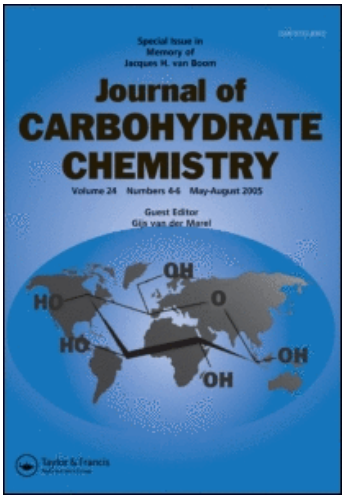

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Synthesis of Methyl 3-Acetamido-3,6-dideoxy-l-galactopyranosides and of Methyl 3-Acetamido-3,6-dideoxy-l-gulopyranosides by Reduction of 3-Ulose *O*-Methyloximes

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SYNTHESIS OF METHYL 3-ACETAMIDO-3,6-DIDEOXY-L-GALACTOPYRANOSIDES AND OF METHYL 3-ACETAMIDO-3,6-DIDEOXY-L-GULOPYRANOSIDES BY REDUCTION OF 3-ULOSE *O*-METHYLOXIMES

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ABSTRACT

Both anomers of methyl 3-acetamido-3,6-dideoxy-L-galactopyranoside and of methyl 3-acetamido-3,6-dideoxy-L-gulopyranoside have been prepared by conversion of easily accessible derivatives of methyl 6-deoxy-(α and β)-L-galactopyranosides into 3-uloses and reduction of the corresponding *O*-methyloximes. The ^{1}H and ^{13}C NMR data of the four 3-acetamido methyl glycosides have been given.

INTRODUCTION

Recently[1] we elucidated the structure of the O-chain of the cell wall lipopolysaccharide from olive and oleander strains of the phytopathogenic bacterium *Pseudomonas syringae* ssp. *savastanoi*. We found that the O-chain consists of the tetrasaccharide repeating unit →3)-α-L-Rha*p*-(1→2)-[α-L-Fuc*p*3NAc-(1→3)]-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→.

For comparison purposes, we needed to have available ^{1}H and ^{13}C NMR data for both anomers of methyl 3-acetamido-3,6-dideoxy-L-galactopyranoside, **1a** and **1b**. To the best of our knowledge, only the ^{13}C spectrum of the α-anomer **1a** has been described.[2] Therefore, we prepared compounds **1a** and **1b** by more simple procedures than those

reported.[3-6] Besides **1a** and **1b**, the α, **2a**, and β, **2b**, anomers of methyl 3-acetamido-3,6-dideoxy-L-gulopyranoside were also obtained. For this pair too, only the ^{13}C NMR data of α-anomer **2a** have been given.[2] This paper reports the conversion of easily accessible derivatives of methyl 6-deoxy-α-L-galactopyranoside (**3a**) into **1a** and **2a** and of methyl 6-deoxy-β-L-galactopyranoside (**3b**) into **1b** and **2b**, *via* the reduction of the *O*-methyloximes of the corresponding 3-uloses, and the NMR data of the four 3-acetamido methyl glycosides. In addition, the MS peaks, not yet listed, of authentic 1-*d* alditol penta-acetates derived from 3-acetamido-3,6-dideoxy-L-gulo- and galactopyranose are given.

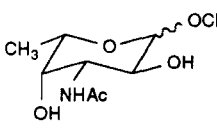
RESULTS AND DISCUSSION

Readily available methyl 2,4-di-*O*-benzyl-6-deoxy-α-L-galactopyranoside[7,8] (**4**) was submitted to reaction with pyridinium chlorochromate to give hexopyranosid-3-ulose **5** (86% yield; ^{13}C NMR: δ 203.6, C=O). Oximation of **5** with *O*-methylhydroxylamine hydrochloride[9] gave *O*-methyloxime **6** (88% yield; ^{13}C NMR: δ 151.7, C=NOMe) as the single *E* isomer. Both ^{1}H and ^{13}C NMR spectra displayed no pair of peaks and an NOE enhancement of the H-4 signal at δ 4.73 was observed upon irradiation of the $=NOCH_3$ signal at δ 3.97.

3-Oximes of underivatized methyl hexopyranosides have been described to give equatorial 3-amines by AlH_3 reduction.[9] In the case of **6**, treatment with AlH_3/THF afforded methyl 3-amino-2,4-di-*O*-benzyl-3,6-dideoxy-α-L-gulopyranoside (**7**), with an axial 3-amino group, as the sole isolated product, in poor yield (ca. 10%). The structure of the compound rests on its ^{1}H and ^{13}C NMR spectra. In particular, the configuration at C-3 was derived from the H-3 signal, which is displayed as a triplet at δ 3.25 with $J_{2,3} = J_{3,4} = 3.4$ Hz. On the other hand, treatment of **6** with BH_3/THF[10,11] even under forced conditions (2 h, 65 °C), followed by acetylation (Ac_2O/Py) of the reduction mixture, occurred with poor conversion yield (70% of **6** was recovered unchanged), although pure axial 3-acetamido derivative **8** was obtained (^{1}H NMR: H-3 multiplet at δ 4.64, changed to a dd with $J_{2,3} = 4.9$ Hz and $J_{3,4} = 3.4$ Hz by irradiation at δ 6.88 (-N*H*Ac)).

Convenient results were reached when **6** was submitted to reduction with lithium aluminium hydride in 1,4-dioxane. After reaction at 90 °C for 3 h, preparative-layer chromatography of a sample of the complex (TLC) product mixture allowed us to isolate the less polar components, namely **7** and a further compound. ^{1}H NMR data (H-3 signal at δ 3.13 dd, $J_{2,3} = 10.2$ Hz, $J_{3,4} = 3.4$ Hz) suggested structure **9** for the latter. A much more abundant, polar fraction was also recovered. The presence of signals at δ 5.0-5.5 due to C*H*OAc groups and the low intensity of the benzyl proton signals in the ^{1}H NMR spectrum of the acetylation mixture obtained from this band revealed that extensive

debenzylation had occurred. Thus, the unresolved reduction mixture was fully debenzylated by catalytic transfer hydrogenolysis using formic acid.[12] After acetylation (Ac_2O/Py), preparative-layer chromatography of the products afforded methyl 3-acetamido-2,4-di-*O*-acetyl-3,6-dideoxy-α-L-gulopyranoside (**10**, 36% yield from **6**) and methyl 3-acetamido-2,4-di-*O*-acetyl-3,6-dideoxy-α-L-galactopyranoside (**11a**, 29% yield from **6**). Clear evidence for the structure **11a** was provided by the ^{1}H NMR data, mainly by the H-3 ddd at δ 4.69 ($J_{2,3}$ = 11.5 Hz, $J_{3,4}$ = 3.2 Hz, and $J_{3,NH}$ = 8.6 Hz) and the N*H*Ac doublet at δ 5.56. By *O*-deacetylation with 0.1 M MeONa/MeOH of **10** and **11a**, methyl 3-acetamido-3,6-dideoxy-α-L-gulopyranoside (**2a**) and methyl 3-acetamido-3,6-dideoxy-α-L-galactopyranoside (**1a**), respectively, were obtained.



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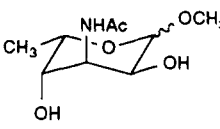

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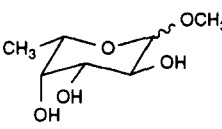

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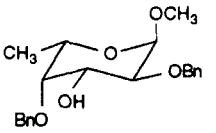

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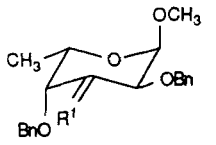
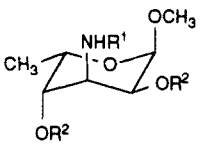
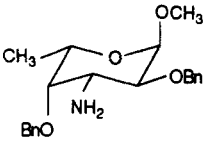


5 R^1 = O
6 R^1 = $NOCH_3$



7 R^1 = H R^2 = Bn
8 R^1 = Ac R^2 = Bn
10 R^1 = Ac R^2 = Ac



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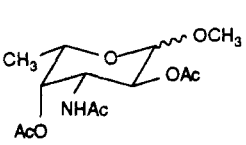

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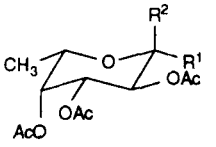
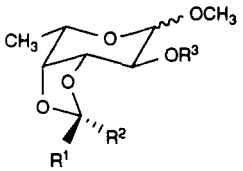
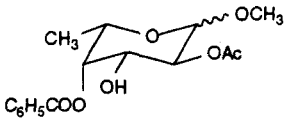


12 R^1 = H R^2 = Br
21 R^1 = OCH_3 R^2 = H



13 R^1 = H R^2 = C_6H_5 R^3 = H
14 R^1 = C_6H_5 R^2 = H R^3 = H
15 R^1 = H R^2 = C_6H_5 R^3 = Ac
16 R^1 = C_6H_5 R^2 = H R^3 = Ac



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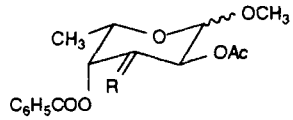
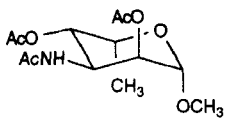


18 R = O
19 R = $NOCH_3$



20

CHART

1a-3a, **11a**, and **13a-19a**: 1_{ax}-OCH_3

1b-3b, **11b**, and **13b-19b**: 1_{eq}-OCH_3

The above stereochemical results confirm that, as a matter of fact, diastereoselectivity can be rarely anticipated for the reduction of hexose 3-oximes.[10,11] However, a stereochemical ratio in greater favour of the equatorial 3-amino compound could be expected in case of the 3-oxime from a methyl β-glycoside, with an equatorial 1-OCH_3 group, that could undergo axial delivery of hydride at the 3-position more easily. Thus, methyl 6-deoxy-β-L-galactopyranoside[13] (**3b**) (prepared from the bromide **12**[14] by reaction with MeOH/Ag_2O and subsequent deacetylation with 0.1 M MeONa/MeOH) was submitted to benzylidenation ($C_6H_5CH(OCH_3)_2$/*p*-TsOH/CH_3CN)[15] to give the diastereoisomeric mixture of **13b** and **14b** (72% yield; 1:1 ratio by ^1H NMR), that was chromatographically resolved into the components for characterization purposes. The two stereoisomers were distinguished on the basis of the different chemical shift of the benzyl proton (δ 5.96 for the *R*-isomer **13b** and δ 6.18 for the *S*-isomer **14b**)[15]. Acetylation (Ac_2O/Py) of **13b** and **14b** afforded the esters **15b** and **16b**, respectively. The *O*-benzylidene ring of **15b** and **16b** was opened by UV irradiation in the presence of *N*-bromosuccinimide and water to give the expected[16] single compound **17b** (74% yield), with an axial benzoyloxy group at C-4 and a free equatorial hydroxy group at C-3. Proof of the location of the substituents in **17b** came from inspection of the ^1H NMR spectrum, where the signal of the 4-proton appears further downfield (δ 5.40) than the H-3 signal (δ 3.90). For preparative purposes, the mixture of **13b** and **14b** was acetylated and irradiated without prior resolution to afford **17b** (51% yield from **3b**). Oxidation (pyridinium chlorochromate) of **17b** to ketone **18b** (^{13}C NMR: δ 195.7, C=O) and subsequent oximation (*O*-methylhydroxylamine hydrochloride) to **19b** (^{13}C NMR: δ 147.9, C=NOMe) occurred with an overall 81% yield. Configuration *E* for the oxime was indicated by the NOE enhancement of the H-4 signal at δ 6.45 upon irradiation of the $=NOCH_3$ signal at δ 3.90.

From the lithium aluminium hydride treatment of **19b**, followed by acetylation (Ac_2O/Py) of the reduction mixture, two 3-acetamido products were isolated by preparative-layer chromatography in the 1:1 ratio, with a 58% total yield. The more polar product was identified as to the desired methyl 3-acetamido-2,4-di-*O*-acetyl-3,6-dideoxy-β-L-galactopyranoside (**11b**), from which **1b** was obtained by *O*-deacetylation. The less polar compound was the C-3-epimer, methyl 3-acetamido-2,4-di-*O*-acetyl-3,6-dideoxy-β-L-gulopyranoside (**20**). In fact, mp and $[\alpha]_D$ values were in accord with those reported[17] for the D-enantiomer, although minor discrepancies were noted between the 400 MHz ^1H NMR spectrum in $CDCl_3$ of the compound and that recorded[17] at 100 MHz, apart from the H-6 signal, that was displayed at δ 1.37 (lit.: δ 1.23). It should also be noted that the $J_{1,2}$ (3.9 Hz), $J_{2,3}$ (3.9 Hz), and $J_{3,4}$ (8.3 Hz) values suggest a prevailing $^4C_1$(L) conformation for **20**. Accordingly, upon irradiation of the methyl proton signal at δ 1.37 the NOE

enhancement of the H-3 signal at δ 4.69 was observed, showing spatial proximity between the relevant protons. However, *O*-deacylation of **20** gave quantitatively **2b**. The $J_{1,2}$ (6.8 Hz in $CDCl_3$ and 7.8 Hz in D_2O), $J_{2,3}$ (4.9 Hz in both solvents), and $J_{3,4}$ (4.9 Hz in $CDCl_3$ and 3.4 Hz in D_2O) values indicated that the compound mainly assumes the $^1C_4$(L) conformation.

Since the procedure *via* *O*-benzylidene derivatives appeared to be simple and to give satisfactory yields, it was also checked to prepare 3-acetamido methyl α-glycosides **11a**, **1a**, **10** and **2a**. Thus, the mixture of the known[15] *O*-benzylidene derivatives **13a** and **14a**, prepared from methyl 6-deoxy-α-L-galactopyranoside[16] (**3a**), was converted to *O*-methyloxime **19a** (47% yield from **3a**; ^{13}C NMR: δ 146.7, C=NOMe; configuration *E* indicated by the NOE enhancement of the H-4 doublet at δ 6.50 upon irradiation of the $=NOCH_3$ signal at δ 3.94) by the above reaction sequence through the intermediate compounds **15a**-**18a**. Lithium aluminium hydride treatment of **19a**, followed by acetylation (Ac_2O/Py) gave **11a** and **10** with a 55% yield, in the 0.7:1 ratio in accord with the expected effect of the 1-axial methoxyl group on the preferred direction of the hydride attack.

Samples of both compounds **1b** and **2b** were separately hydrolyzed, reduced with sodium borodeuteride and then acetylated. The two 1-*d* alditol pentaacetates so obtained were analyzed by GLC-MS. Their MS peaks are listed in the Experimental.

EXPERIMENTAL

The ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded with a 400-AM FT spectrometer equipped with a dual probe (Bruker). DEPT experiments were performed using a polarization transfer pulse of 135° and a delay adjusted to an average C,H coupling of 160 Hz. ^1H chemical shifts were measured relative to Me_4Si (in $CDCl_3$) or to sodium 3-trimethylsilylpropionate-2,2,3,3-d_4 (in D_2O) and ^{13}C chemical shifts relative to $CDCl_3$ (δ 77.05) or to 1,4-dioxane (δ 67.4). GLC-MS was performed with a Hewlett Packard 5890 instrument equipped with a Supelco SP-2330 capillary column. Optical rotations were determined on a Perkin Elmer model 141 polarimeter at 18-22 °C. TLC and preparative-layer chromatography were performed using silica gel plates F_{254} (Merck), column chromatography on silica gel 60 (Merck).

Methyl 2,4-Di-*O*-benzyl-6-deoxy-α-L-*xylo*-hexopyranosid-3-ulose (5). Methyl 2,4-di-*O*-benzyl-6-deoxy-α-L-galactopyranoside[7,8] (**4**, 260 mg) and pyridinium chlorochromate (610 mg) were stirred in dry dichloromethane (7 mL) at room temperature. The reaction mixture was filtered through a short silica-gel column (dichloromethane) to give **5** as an oil (223 mg, 86%): $[\alpha]_D$ +19.3° (*c* 1.2, chloroform); ^1H

NMR ($CDCl_3$) δ 1.30 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6), 3.36 (s, 3H, OCH_3), 3.62 (d, 1H, $J_{4,5}$ = 1.5 Hz, H-4), 4.12 (dq, 1H, H-5), 4.40 (ABq, 2H, J_{gem} = 11.7 Hz, OCH_2Ph), 4.67 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-2), 4.68 (ABq, 2H, J_{gem} = 12.2 Hz, OCH_2Ph), 4.98 (d, 1H, H-1), 7.2-7.4 (10H, 2xPh); ^{13}C NMR ($CDCl_3$) δ 15.4 (C-6), 55.4 (OCH_3), 72.1, 72.6 (2xOCH_2Ph), 68.3, 78.5, 84.3 (C-2, C-4, C-5), 101.5 (C-1), 203.6 (C-3), 128.1-128.4, 136.5, 137.0 (aromatic C).

Anal. Calcd for $C_{21}H_{24}O_5$ (356.4): C, 70.8; H, 6.8. Found: C, 70.7; H, 6.8.

Methyl 2,4-Di-*O*-benzyl-6-deoxy-α-L-*xylo*-hexopyranosid-3-ulose (*E*)-*O*-Methyloxime (6). Compound **5** (200 mg), *O*-methylhydroxylamine hydrochloride (70 mg) and sodium hydrogencarbonate (70 mg) in dry methanol (10 mL) were heated under reflux for 3 h. The reaction mixture was filtered and concentrated to dryness. The residue was purified by column chromatography on silica gel (chloroform) to give oxime **6** (190 mg, 88%): mp 68-70 °C (from hexane); $[\alpha]_D$ +13.5° (*c* 1.4, chloroform); ^1H NMR ($CDCl_3$) δ 1.23 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6), 3.38 (s, 3H, OCH_3), 3.95 (dq, 1H, $J_{4,5}$ = 1.6 Hz, H-5), 3.97 (s, 3H, $=NOCH_3$), 4.42 (ABq, 2H, J_{gem} = 11.9 Hz, OCH_2Ph), 4.51 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-2), 4.73 (d, 1H, H-4), 4.75 (ABq, 2H, J_{gem} = 12.3 Hz, OCH_2Ph), 4.82 (d, 1H, H-1), 7.2-7.4 (10H, 2xPh); ^{13}C NMR ($CDCl_3$) δ 15.9 (C-6), 55.3 (OCH_3), 62.0 ($=NOCH_3$), 66.8, 70.3, 72.8 (C-2, C-4, C-5), 71.1, 72.4 (2xOCH_2Ph), 99.9 (C-1), 151.7 (C-3), 127.8-128.4, 137.75, 137.8 (aromatic C).

Anal. Calcd for $C_{22}H_{27}NO_5$ (385.5): C, 68.6; H, 7.1; N, 3.6. Found: C, 68.8; H, 7.2; N, 3.7.

Reduction of 6. - a) With Aluminium hydride. *O*-Methyloxime **6** (20 mg) was dissolved in tetrahydrofuran (0.5 mL) and treated with 0.5 M aluminium hydride-tetrahydrofuran (1 mL) at room temperature for 12 h, the excess of reagent was decomposed with water and sodium hydrogencarbonate was added. The reaction mixture was filtered and concentrated. By preparative-layer chromatography (silica gel 1 mm; chloroform/methanol, 98:2; 1 run) of the residue only one pure compound was isolated (2 mg, syrup): $[\alpha]_D$ -22° (*c* 0.4, chloroform). The NMR data suggested it was methyl 3-amino-2,4-di-*O*-benzyl-3,6-dideoxy-α-L-gulopyranoside (**7**): ^1H NMR ($CDCl_3$) δ 1.18 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6), 3.25 (bt, 1H, $J_{2,3}$ = $J_{3,4}$ = 3.4 Hz, H-3), 3.37 (bd, 1H, H-4), 3.40 (s, 3H, OCH_3), 3.78 (t, 1H, $J_{1,2}$ = 3.4 Hz, H-2), 4.09 (bq, 1H, H-5), 4.55 (ABq, 2H, J_{gem} = 11.9 Hz, OCH_2Ph), 4.62 (s, 2H, OCH_2Ph), 4.72 (bd, 1H, H-1), 7.2-7.45 (10H, 2xPh); ^{13}C NMR ($CDCl_3$) δ 16.1 (C-6), 49.4 (C-3), 55.7 (OCH_3), 61.3, 72.4, 81.2 (C-2, C-4, C-5), 71.3, 72.5 (2xOCH_2Ph), 99.6 (C-1), 127.8-128.3, 138.1, 138.15 (aromatic C). Acetylation of **7** (3:1 pyridine-acetic anhydride; 0.3 mL; 12 h at room temperature) gave (TLC) compound **8** (see below).

b) With Borane-tetrahydrofuran. Borane-tetrahydrofuran complex (1 M in THF, 0.2 mL) was added with a syringe to a solution of *O*-methyloxime **6** (20 mg) in tetrahydrofuran (0.5 mL) at -20 °C contained in a septum vial, under argon. The mixture was allowed to warm to room temperature and then kept at 65 °C for 2 h. After cooling, water (0.1 mL) and then 0.1 M KOH (0.1 mL) were added. After 2 h at 60 °C, the mixture was concentrated to dryness and acetylated (3:1 pyridine-acetic anhydride; 0.3 mL; 12 h at room temperature). Usual work up gave a crude product that was extracted with chloroform. Preparative-layer chromatography (silica gel 0.5 mm; 95:5 chloroform-diethyl ether; 2 runs) of the residue from the solvent yielded unchanged **6** (14 mg) and methyl 3-acetamido-2,4-di-*O*-benzyl-3,6-dideoxy-α-L-gulopyranoside (**8**, 2 mg, 10%) as a syrup: $[\alpha]_D$ +10.5° (*c* 0.7, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.12 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6), 2.02 (s, 3H, NHCOC*H*$_3$), 3.42 (dd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{4,5}$ = 1.5 Hz, H-4), 3.45 (s, 3H, OCH_3), 3.91 (dd, 1H, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 4.9 Hz, H-2), 3.98 (dq, 1H, H-5), 4.54 (ABq, 2H, J_{gem} = 12.2 Hz, OC*H*$_2$Ph), 4.64 (m, 1H, H-3), 4.67 (ABq, 2H, J_{gem} = 12.2 Hz, OC*H*$_2$Ph), 4.72 (d, 1H, H-1), 6.88 (bd, 1H, $J_{3,NH}$ = 6.8 Hz, NHAc), 7.3-7.4 (10H, 2xPh).

Anal. Calcd for $C_{23}H_{29}NO_5$ (399.5): C, 69.15; H, 7.3; N, 3.5. Found: C, 69.3; H, 7.5; N, 3.4.

c) With Lithium aluminium hydride. *O*-Methyloxime **6** (128 mg) and lithium aluminium hydride (120 mg) in dry 1,4-dioxane (10 mL) were heated at 90 °C for 3 h. The excess of reagent was decomposed with water and the mixture was filtered through a Celite pad. The residue was washed with hot methanol-chloroform and the combined filtrate and washings were concentrated to dryness. Preparative-layer chromatography (silica gel 0.5 mm; 9:1, chloroform-methanol; 1 run) of a sample (18 mg) of the residue yielded methyl 3-amino-2,4-di-*O*-benzyl-3,6-dideoxy-α-L-gulopyranoside (**7**, 2 mg) and methyl 3-amino-2,4-di-*O*-benzyl-3,6-dideoxy-α-L-galactopyranoside (**9**, 2 mg). Structure of the latter was suggested by its ^{1}H NMR ($CDCl_3$) δ 1.24 (d, 1H, $J_{5,6}$ = 6.5 Hz, H-6), 3.13 (dd, 1H, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 3.4 Hz, H-3), 3.37 (s, 3H, OCH_3), 3.51 (dd, 1H, $J_{1,2}$ = 3.4 Hz, H-2), 3.58 (bd, 1H, H-4), 3.95 (bq, 1H, H-5), 4.62 (ABq, 2H, J_{gem} = 12.0 Hz, OC*H*$_2$Ph), 4.70 (d, 1H, H-1), 4.73 (ABq, 2H, J_{gem} = 11.9 Hz, OC*H*$_2$Ph), 7.2-7.45 (10H, 2xPh). A much more polar band (6 mg) was also recovered, that was acetylated (3:1 pyridine-acetic anhydride; 0.3 mL; 12 h at room temperature). After usual work up, the ^{1}H NMR spectrum ($CDCl_3$) of the residue displayed signals in the 5.0-5.5 ppm region, indicative of the presence of CHOAc groupings, while the intensity of the benzyl signals (phenyl protons at δ 7.0-7.5 and methylene AB quartets) appeared relatively low.

The remaining unresolved reduction mixture (141 mg) was dissolved in a mixture of methanol (15 mL) and formic acid (1.5 mL).[12] Palladium on activated charcoal (10%,

300 mg, moistened with methanol) was added under argon atmosphere. The mixture was kept in a sonic bath for 2 h, the temperature of which rose to 50 °C, and then filtered and concentrated to dryness. The residue was acetylated (3:1 pyridine-acetic anhydride; 2 mL; 18 h at room temperature). After usual work up the reaction product was extracted with 1:1 chloroform-diethyl ether. Preparative-layer chromatography (silica gel 1 mm; 7:3 chloroform-diethyl ether; 2 runs) of the residue from evaporation of the solvent gave methyl 3-acetamido-2,4-di-*O*-acetyl-3,6-dideoxy-α-L-gulopyranoside (**10**, 32 mg, 36%) and methyl 3-acetamido-2,4-di-*O*-acetyl-3,6-dideoxy-α-L-galactopyranoside (**11a**, 26 mg, 29%).

Compound **10**: mp 127-8 °C (from ethyl acetate-hexane); $[\alpha]_D$ -100° (*c* 1.4, chloroform) (lit.[18]: 127-8 °C, $[\alpha]_D$ +101° (chloroform) for D-enantiomer); ^{1}H NMR ($CDCl_3$) δ 1.14 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 2.04 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 2.17 (s, 3H, $COCH_3$), 3.47 (s, 3H, OCH_3), 4.14 (q, 1H, H-5), 4.39 (ddd, 1H, $J_{2,3}$ = 4.6 Hz, $J_{3,4}$ = 3.2, $J_{3,NH}$ = 7.6 Hz, H-3), 4.88 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 4.99 (d, 1H, H-4), 5.17 (dd, 1H, H-2), 6.62 (d, 1H, NHAc); ^{13}C NMR ($CDCl_3$) δ 15.9 (C-6), 20.6, 20.65, 23.5 ($COCH_3$), 48.6 (C-3), 55.9 (OCH_3), 61.5, 65.2, 71.4 (C-2, C-4, C-5), 98.2 (C-1), 169.5, 169.7, 169.9 ($COCH_3$).

Anal. Calcd for $C_{13}H_{21}NO_7$ (303.3): C, 51.5; H, 7.0; N, 4.6. Found: C, 51.6; H, 6.9; N, 4.5.

Compound **11a**: mp 159-162 °C (from ethyl acetate-hexane); $[\alpha]_D$ -127° (*c* 1.1, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.12 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.91 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 2.20 (s, 3H, $COCH_3$), 3.44 (s, 3H, OCH_3), 4.15 (dq, 1H, $J_{4,5}$ = 0.9 Hz, H-5), 4.69 (ddd, 1H, $J_{2,3}$ = 11.5 Hz, $J_{3,4}$ = 3.2 Hz, $J_{3,NH}$ = 8.6 Hz, H-3), 4.79 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.11 (dd, 1H, H-2), 5.27 (dd, 1H, H-4), 5.56 (d, 1H, NHAc); ^{13}C NMR ($CDCl_3$) δ 16.2 (C-6), 20.6, 20.9, 23.2 ($COCH_3$), 48.1 (C-3), 55.4 (OCH_3), 65.1, 68.3, 72.7 (C-2, C-4, C-5), 97.9 (C-1), 169.9, 170.3, 172.0 ($COCH_3$).

Anal. Calcd for $C_{13}H_{21}NO_7$ (303.3): C, 51.5; H, 7.0; N, 4.6. Found: C, 51.4 H, 6.9; N, 4.6.

O-Deacetylation of samples of compounds **10** and **11a** (6 mg each) with 0.1 M MeONa/MeOH (15 min at room temperature) quantitatively gave methyl 3-acetamido-3,6-dideoxy-α-L-gulopyranoside (**2a**) and methyl 3-acetamido-3,6-dideoxy-α-L-galactopyranoside (**1a**), respectively.

Compound **2a**: mp 166-7 °C (from acetone-hexane); $[\alpha]_D$ -99° (*c* 0.8, water) (lit.[18]: mp 166.5-168.5 °C, $[\alpha]_D$ +101.5° (water) for D-enantiomer); ^{1}H NMR (D_2O) δ 1.22 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6), 2.06 (s, 3H, $COCH_3$), 3.47 (s, 3H, OCH_3), 3.66 (bd, 1H,

$J_{3,4}$ = 3.4 Hz, H-4), 4.11 (dd, 1H, $J_{1,2}$ = 3.9 Hz, $J_{2,3}$ = 4.9 Hz, H-2), 4.20 (bq, 1H, H-5), 4.27 (dd, 1H, H-3). ^{13}C NMR (D_2O) data matched those previously reported.[2]

Anal. Calcd for $C_9H_{17}NO_5$ (219.2): C, 49.3; H, 7.8; N, 6.4. Found: C, 49.5; H, 7.8; N, 6.3.

Compound **1a**: mp 200-2 °C (from ethyl acetate-hexane); $[\alpha]_D$ -235° (*c* 0.7, water) (lit.[5]: mp 200-2 °C, $[\alpha]_D$ -234.5° (water)). Differently from compound **2a**, compound **1a** was sufficiently soluble in $CDCl_3$, so that NMR data were collected in both $CDCl_3$ and D_2O: ^1H NMR (D_2O) δ 1.25 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6), 2.09 (s, 3H, $COCH_3$), 3.48 (s, 3H, OCH_3), 3.78 (bd, 1H, $J_{3,4}$ = 2.9 Hz, H-4), 3.88 (dd, 1H, $J_{1,2}$ = 3.9 Hz, $J_{2,3}$ = 11.2 Hz, H-2), 4.14 (bq, 1H, H-5), 4.18 (dd, 1H, H-3), 4.84 (d, 1H, H-1); ^1H NMR ($CDCl_3$) δ 1.25 (d, 3H, $J_{5,6}$ = 6.8 Hz, H-6), 2.06 (s, 3H, $COCH_3$), 3.45 (s, 3H, OCH_3), 3.69 (dd, 1H, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 11.2 Hz, H-2), 3.73 (bd, 1H, $J_{3,4}$ = 2.9 Hz, H-4), 4.05 (bq, 1H, H-5), 4.22 (ddd, 1H, $J_{3,NH}$ = 8.3 Hz, H-3), 4.74 (d, 1H, H-1), 6.08 (d, 1H, NHAc); ^{13}C NMR ($CDCl_3$) δ 16.0 (C-6), 23.3 ($COCH_3$), 52.4 (C-3), 55.6 (OCH_3), 65.7, 68.6, 71.8 (C-2, C-4, C-5), 173.3 ($COCH_3$). ^{13}C NMR data in D_2O matched those previously reported.[2]

Anal. Calcd for $C_9H_{17}NO_5$ (219.2): C, 49.3; H, 7.8; N, 6.4. Found: C, 49.4; H, 7.7; N, 6.6.

Methyl 6-Deoxy-β-L-galactopyranoside (3b). To a solution of 2,3,4-tri-*O*-acetyl-6-deoxy-α-L-galactopyranosyl bromide[14] (**12**, 980 mg) in dry benzene (2 mL) were added dry methanol (2 mL) and silver oxide (490 mg). The mixture was stirred at room temperature for 1 h and then at 50 °C for 1 h. After cooling, filtration, and concentration, the residue was purified by column chromatography (silica gel, 20 g, toluene) to give methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-L-galactopyranoside (**21**, 642 mg, 76%): mp 97-8 °C (from ethanol) (lit.[10]: 96.5-98.0 °C). ^1H NMR ($CDCl_3$) data matched those previously reported.[10]

Deacetylation of compound **21** (600 mg) with 0.1 M MeONa/MeOH (10 mL; 1 h at room temperature) gave methyl 6-deoxy-β-L-galactopyranoside (**3b**, 344 mg, 98%): mp 124-5 °C (from ethanol) (lit.[13]: 123 °C). ^1H NMR (D_2O) data matched those previously reported.[13]

Methyl 3,4-*O*-(*R* and *S*)-Benzylidene-6-deoxy-β-L-galactopyranoside (13b and 14b), Methyl 2-*O*-Acetyl-3,4-*O*-(*R* and *S*)-benzylidene-6-deoxy-β-L-galactopyranoside (15b and 16b). Methyl 6-deoxy-β-L-galactopyranoside (**3b**, 267 mg), α,α-dimethoxytoluene (0.4 mL), and *p*-toluenesulphonic acid (5 mg) in dry acetonitrile (3 mL) were stirred overnight at room temperature and then warmed (ca. 50 °C) under reduced pressure (water pump) for 20 min. After addition of triethylamine (0.1 mL) and concentration, the residue was dissolved in ethyl acetate and washed with 5% sodium

hydrogencarbonate and water. The residue (475 mg, containing α,α-dimethoxytoluene) from evaporation of the organic phase was purified by column chromatography (silica gel, 15 g; chloroform), that gave a ca. 1:1 (^{1}H NMR) mixture of **13b** and **14 b** (288 mg, 72%). Preparative-layer chromatography (silica gel 1 mm; 3:2 hexane-ethyl acetate; 2 runs) of a sample (101 mg) of the diastereoisomeric mixture gave pure **13b** (46 mg) and **14b** (49 mg).

Compound **13b** (*R*-isomer): mp 94-6 °C (from benzene-hexane); $[\alpha]_D$ +5° (*c* 2.8, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.51 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 3.57 (dd, 1H, $J_{1,2}$ = 8.3 Hz, $J_{2,3}$ = 7.2 Hz, H-2), 3.57 (s, 3H, OCH_3), 3.97 (dq, 1H, $J_{4,5}$ = 2.3 Hz, H-5), 4.09 (dd, 1H, $J_{3,4}$ = 5.9 Hz, H-4), 4.15 (d, 1H, H-1), 4.20 (dd, 1H, H-3), 5.96 (s, 1H, C*H*Ph), 7.3-7.6 (5H, Ph).

Anal. Calcd for $C_{14}H_{18}O_5$ (266.3): C, 63.15; H, 6.8. Found: C, 63.3; H, 6.6.

Compound **14b** (*S*-isomer): mp 96-7 °C (from benzene-hexane); $[\alpha]_D$ -18° (*c* 1.6, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.47 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 3.71 (dd, 1H, $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 7.4 Hz, H-2), 3.55 (s, 3H, OCH_3), 3.84 (dq, 1H, $J_{4,5}$ = 2.0 Hz, H-5), 4.00 (dd, 1H, $J_{3,4}$ = 5.4 Hz, H-4), 4.14 (d, 1H, H-1), 4.39 (dd, 1H, H-3), 6.18 (s, 1H, C*H*Ph), 7.3-7.6 (5H, Ph).

Anal. Calcd for $C_{14}H_{18}O_5$ (266.3): C, 63.15; H, 6.8. Found: C, 63.3; H, 6.7.

Samples of **13b** and **14b** (30 mg each) were acetylated (3:1 pyridine-acetic anhydride; 0.5 mL; 12 h at room temperature) to give compounds **15b** (34 mg) and **16b** (33 mg), respectively.

Compound **15b**: mp 142-4 °C (from benzene-hexane); $[\alpha]_D$ -56.5° (*c* 1.0, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.49 (d, 3H, $J_{5,6}$ = 6.8 Hz, H-6), 2.11 (s, 3H, $COCH_3$), 3.49 (s, 3H, OCH_3), 3.98 (dq, 1H, $J_{4,5}$ = 2.4 Hz, H-5), 4.12 (dd, 1H, $J_{3,4}$ = 5.8 Hz, H-4), 4.33 (dd, 1H, $J_{2,3}$ = 7.8 Hz, H-3), 4.35 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 5.02 (t, 1H, H-2), 5.91 (s, 1H, C*H*Ph), 7.35-7.6 (5H, Ph).

Anal. Calcd for $C_{16}H_{20}O_6$ (308.3): C, 62.3; H, 6.5. Found: C, 62.3; H, 6.4.

Compound **16b**: syrup; $[\alpha]_D$ -27° (*c* 0.8, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.47 (d, 3H, $J_{5,6}$ = 6.8 Hz, H-6), 2.13 (s, 3H, $COCH_3$), 3.49 (s, 3H, OCH_3), 3.85 (dq, 1H, $J_{4,5}$ = 2.0 Hz, H-5), 4.07 (dd, 1H, $J_{3,4}$ = 5.4 Hz, H-4), 4.32 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.47 (dd, 1H, $J_{2,3}$ = 7.8 Hz, H-3), 5.10 (t, 1H, H-2), 6.21 (s, 1H, C*H*Ph), 7.35-7.5 (5H, Ph).

Anal. Calcd for $C_{16}H_{20}O_6$ (308.3): C, 62.3; H, 6.5. Found: C, 62.2; H, 6.5.

Methyl 2-*O*-Acetyl-4-*O*-benzoyl-6-deoxy-β-L-galactopyranoside (17b). Compound **15b** (23 mg) was dissolved in carbon tetrachloride (1.5 mL). *N*-Bromosuccinimide (15 mg), barium carbonate (30 mg), and water (0.1 mL) were added. The mixture was purged with argon for 30 min and then stirred while being irradiated with

a 500-W high-pressure mercury-vapour lamp (Helios Italquarz) in a Pyrex vessel for 30 min. The reaction mixture was filtered and the residue was washed with ethyl acetate. The solution was washed with water and concentrated to dryness. Preparative-layer chromatography (silica gel 1 mm; 3:2 hexane-ethyl acetate; 2 runs) gave **17b** (18 mg, 74%). By the same procedure a sample of compound **16b** was converted into **17b**, with an identical yield.

The above mixture of **13b** and **14b** (187 mg) that had not been submitted to chromatographic resolution was acetylated (3:1 pyridine-acetic anhydride; 3 mL; 12 h at room temperature) and the mixture of **15b** and **16b** so obtained was irradiated in the presence of *N*-bromosuccinimide (138 mg), barium carbonate (270 mg) and water (1 mL) in carbon tetrachloride (15 mL) as above to give compound **17b** (164 mg, 72%; purified by column chromatography on silica gel with hexane-diethyl ether): mp 151-2 °C (from ethyl acetate-hexane); $[\alpha]_D$ -54° (*c* 2.1, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.23 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6), 2.04 (s, 3H, $COCH_3$), 3.52 (s, 3H, OCH_3), 3.78 (dq, 1H, $J_{4,5}$ = 0.7 Hz, H-5), 3.90 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 3.7 Hz, H-3), 4.35 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 5.05 (dd, 1H, H-2), 5.40 (dd, 1H, H-4), 7.4-7.6, 8.1-8.2 (5H, Ph); ^{13}C NMR ($CDCl_3$) δ 16.3 (C-6), 20.9 ($COCH_3$), 56.7 (OCH_3), 69.6, 71.6, 72.6, 73.5 (C-2, C-3, C-4, C-5), 101.7 (C-1), 166.6 ($COCH_3$), 171.2 (*C*OPh), 128.4, 129.2, 130.0, 133.4 (aromatic C).

Anal. Calcd for $C_{16}H_{20}O_7$ (324.3): C, 59.2; H, 6.2. Found: C, 59.4; H, 6.3.

Methyl 2-*O*-Acetyl-4-*O*-benzoyl-6-deoxy-β-L-*xylo*-hexopyranosid-3-ulose (18b). Compound **17b** (120 mg) and pyridinium chlorochromate (320 mg) in dry benzene (8 mL) were heated under reflux for 45 min. The reaction mixture was filtered through a short silica-gel column (benzene) to give compound **18b** (115 mg, 96%): mp 82-3 °C (from hexane-ethyl acetate); $[\alpha]_D$ -7° (*c* 2.8, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.43 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6), 2.20 (s, 3H, $COCH_3$), 3.61 (s, 3H, OCH_3), 3.94 (dq, 1H, $J_{4,5}$ = 1.2 Hz, H-5), 4.59 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 5.34 (d, 1H, H-4), 5.46 (d, 1H, H-2), 7.4-7.55, 8.1-8.2 (5H, Ph); ^{13}C NMR ($CDCl_3$) δ 15.8 (C-6), 20.3 ($CO*C*H_3$), 57.0 (OCH_3), 70.1, 76.6, 77.3 (C-2, C-4, C-5), 102.7 (C-1), 165.1 ($O*C*OCH_3$), 169.1 (*C*OPh), 128.2, 128.5, 129.9, 133.7 (aromatic C), 195.7 (C-3).

Anal. Calcd for $C_{16}H_{18}O_7$ (322.3): C, 59.6; H, 5.6. Found: C, 59.6; H, 5.8.

Methyl 2-*O*-Acetyl-4-*O*-benzoyl-6-deoxy-β-L-*xylo*-hexopyranosid-3-ulose (*E*)-*O*-Methyloxime (19b). Compound **18b** (102 mg), *O*-methylhydroxylamine hydrochloride (35 mg) and sodium hydrogencarbonate (35 mg) in dry methanol (5 mL) were heated under reflux for 6 h. The reaction mixture was filtered and concentrated to dryness. Column chromatography of the residue (silica gel, chloroform) afforded oxime **19b** (95 mg, 85%) as an oil: $[\alpha]_D$ -75.5° (*c* 1.1, chloroform);

^{1}H NMR ($CDCl_3$) δ 1.31 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6), 2.16 (s, 3H, $COCH_3$), 3.58 (s, 3H, OCH_3), 3.84 (dq, 1H, $J_{4,5}$ = 1.7 Hz, H-5), 3.90 (s, 3H, =$NOCH_3$), 4.55 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 5.52 (d, 1H, H-2), 6.45 (d, 1H, H-4), 7.4-7.55, 8.0-8.1 (5H, Ph); ^{13}C NMR ($CDCl_3$) δ 16.0 (C-6), 20.6 ($COCH_3$), 56.6 (OCH_3), 62.6 (=$NOCH_3$), 64.8, 69.5, 71.5 (C-2, C-4, C-5), 102.6 (C-1), 147.9 (C-3), 165.1 ($COCH_3$), 169.2 (*C*OPh), 128.4, 129.0, 130.0, 133.4 (aromatic C).

Anal. Calcd for $C_{17}H_{21}NO_7$ (351.4): C, 58.1; H, 6.0; N, 4.0. Found: C, 58.3; H, 6.1; N, 3.8.

Methyl 3-Acetamido-2,4-di-*O*-acetyl-3,6-dideoxy-β-L-galactopyranoside (11b), Methyl 3-Acetamido-2,4-di-*O*-acetyl-3,6-dideoxy-β-L-gulopyranoside (20), Methyl 3-Acetamido-3,6-dideoxy-β-L-galactopyranoside (1b), Methyl 3-Acetamido-3,6-dideoxy-β-L-gulopyranoside (2b). Lithium aluminium hydride reduction of *O*-methyloxime **19b** (64 mg) was performed as described above for **5**. The reaction time was 2 h. After acetylation (3:1 pyridine-acetic anhydride; 1 mL; 12 h at room temperature) of the crude reaction product, preparative-layer chromatography (silica gel 0.5 mm; 7:3 chloroform-diethyl ether; 2 runs) afforded compounds **11b** (16 mg, 29%) and **20** (16 mg, 29%).

Compound **11b**: mp 187.5-189 °C (from ethyl acetate-hexane); $[\alpha]_D$ -21° (*c* 0.8, chloroform) (lit.[6]: mp 188-189.5 °C, $[\alpha]_D$ +22° for D-enantiomer); ^{1}H NMR ($CDCl_3$) δ 1.21 (d, 3H, $J_{5,6}$ = 6.8 Hz, H-6), 1.93 (s, 3H, $COCH_3$), 2.11 (s, 3H, $COCH_3$), 2.21 (s, 3H, $COCH_3$), 3.54 (s, 3H, OCH_3), 3.84 (q, 1H, H-5), 4.33 (ddd, 1H, $J_{2,3}$ = 11.2 Hz, $J_{3,4}$ = 2.9 Hz, $J_{3,NH}$ = 8.3 Hz, H-3), 4.44 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.90 (dd, 1H, H-2), 5.23 (dd, 1H, H-4), 5.70 (d, 1H, NHAc); ^{13}C NMR ($CDCl_3$) δ 16.4 (C-6), 20.7, 20.75, 23.0 ($COCH_3$), 52.2 (C-3), 57.0 (OCH_3), 70.1, 70.4, 71.8 (C-2, C-4, C-5), 102.0 (C-1), 170.2, 170.4, 171.6 ($COCH_3$).

Anal. Calcd for $C_{13}H_{21}NO_7$ (303.3): C, 51.5; H, 7.0; N, 4.6. Found: C, 51.7; H, 7.1; N, 4.5.

Compound **20**: mp 194-6 °C (from ethyl acetate-hexane); $[\alpha]_D$ +5.5° (*c* 0.9, chloroform) (lit.[17]: mp 194-6 °C, $[\alpha]_D$ -6.0° for D-enantiomer); ^{1}H NMR ($CDCl_3$) δ 1.37 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6), 2.01 (s, 3H, $COCH_3$), 2.14 (s, 3H, $COCH_3$), 2.16 (s, 3H, $COCH_3$), 3.49 (s, 3H, OCH_3), 4.15 (dq, 1H, $J_{4,5}$ = 4.8 Hz, H-5), 4.63 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 4.69 (dt, 1H, $J_{2,3}$ = 3.9 Hz, $J_{3,4}$ = $J_{3,NH}$ = 8.3 Hz, H-3), 5.04 (t,1H, H-2), 5.24 (dd, 1H, H-4), 5.56 (d, 1H, NHAc); ^{13}C NMR ($CDCl_3$) δ 16.2 (C-6), 20.9, 23.3, 23.4 ($COCH_3$), 46.4 (C-3), 56.1 (OCH_3), 69.3, 69.5, 70.9 (C-2, C-4, C-5), 99.2 (C-1), 169.7, 169.9, 170.8 ($COCH_3$).

Anal. Calcd for $C_{13}H_{21}NO_7$ (303.3): C, 51.5; H, 7.0; N, 4.6. Found: C, 51.4; H, 7.3; N; 4.5.

O-deacetylation of samples of **11b** and **20** (9 mg each) with 0.1 M MeONa/MeOH (15 min at room temperature) quantitatively gave methyl 3-acetamido-3,6-dideoxy-β-L-galactopyranoside **1b** and methyl 3-acetamido-3,6-dideoxy-β-L-gulopyranoside **2b**, respectively.

Compound **1b**: mp 245-8 °C (from ethanol); $[\alpha]_D$ -46.5° (*c* 0.5, water) (lit.[6]: mp 246-8 °C, $[\alpha]_D$ +48° for D-enantiomer); ^{1}H NMR (D_2O) δ 1.26 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6), 2.07 (s, 3H, $COCH_3$), 3.51 (dd, 1H, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.7 Hz, H-2), 3.58 (s, 3H, OCH_3), 3.71 (dd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{4,5}$ = 1.0 Hz, H-4), 3.90 (dq, 1H, H-5), 3.95 (dd, 1H, H-3), 4.40 (d, 1H, H-1); ^{1}H NMR ($CDCl_3$) δ 1.33 (d, 3H, $J_{5,6}$ = 6.3 Hz, H-6), 2.09 (s, 3H, $COCH_3$), 3.59 (s, 3H, OCH_3), 3.46 (dd, 1H, $J_{1,2}$ = 7.3 Hz, $J_{2,3}$ = 10.7 Hz, H-2), 3.66 (bd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{4,5}$ = 1.0 Hz, H-4), 3.75 (dq, 1H, H-5), 3.99 (ddd, 1H, $J_{3,NH}$ = 7.8 Hz, H-3), 4.25 (d, 1H, H-1), 6.26 (d, 1H, NHAc); ^{13}C NMR (D_2O) δ 15.9 (C-6), 22.5 ($COCH_3$), 52.7 (C-3), 55.4 (OCH_3), 68.9, 70.5, 72.5 (C-2, C-4, C-5), 104.8 (C-1), 174.9 ($COCH_3$).

Anal. Calcd for $C_9H_{17}NO_5$ (219.2): C, 49.3; H, 7.8; N, 6.4. Found: C, 49.4; H, 7.7; N, 6.4.

Compound **2b** was crystallized from wet ethyl acetate[17] as a monohydrate: mp 76-8 °C; $[\alpha]_D$ +45° (*c* 0.6, methanol) (lit.[17]: mp 78-80 °C, $[\alpha]_D$ -48° (methanol) for D-enantiomer); ^{1}H NMR (D_2O) δ 1.18 (d, 3H, $J_{5,6}$ = 6.8 Hz, H-6), 2.00 (s, 3H, $COCH_3$), 3.50 (s, 3H, OCH_3), 3.61 (dd, 1H, $J_{3,4}$ = 3.4 Hz, $J_{4,5}$ = 1.5 Hz, H-4), 3.76 (dd, 1H, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 4.9 Hz, H-2), 3.96 (dq, 1H, H-5), 4.29 (dd, 1H, H-3), 4.55 (d, 1H, H-1); ^{1}H NMR ($CDCl_3$) δ 1.32 (d, 3H, $J_{5,6}$ = 6.8 Hz, H-6), 2.05 (s, 3H, $COCH_3$), 2.32 (bd, 1H, 2-OH), 2.39 (1H, bs, 4-OH), 3.57 (s, 3H, OCH_3), 3.92 (ddd, 1H, $J_{1,2}$ = 6.8 Hz, $J_{2,3}$ = 4.9 Hz, $J_{2,2\text{-OH}}$ = 7.3 Hz, H-2), 3.95 (dq, 1H, $J_{4,5}$ = 1.9 Hz, H-5), 4.05 (1H, m, H-4), 4.26 (ddd, 1H, $J_{3,NH}$ = 4.5 Hz, $J_{3,4}$ = 4.9 Hz, H-3), 4.40 (d, 1H, H-1), 5.84 (1H, bd, NHAc); ^{13}C NMR (D_2O) δ 15.6 (C-6), 22.4 ($COCH_3$), 53.6 (C-3), 57.3 (OCH_3), 66.4, 70.3, 70.5 (C-2, C-4, C-5), 102.0 (C-1), 175.2 ($COCH_3$).

Anal. Calcd for $C_9H_{17}NO_5 \cdot H_2O$ (237.25): C, 45.6; H, 8.1; N, 5.9. Found: C, 45.8; H, 8.2; N, 5.8.

Methyl 2-*O*-Acetyl-4-*O*-benzoyl-3,6-dideoxy-α-L-galactopyranoside (17a). A diastereoisomeric 1:1 mixture of **13a** and **14a** (250 mg; prepared from methyl 6-deoxy-α-L-galactopyranoside[16] (**3a**) by the procedure of Bundle and Josephson;[15] 75% yield) was acetylated (3:1 pyridine-acetic anhydride; 3 mL; 12 h at room temperature) to give the 1:1 mixture of 2-*O*-acetyl derivatives **15a** and **16a** (276 mg, 95%). Both crystallization and column chromatography failed to give either pure isomer. Preparative-layer chromatography (silica gel; 3:2 hexane-ethyl acetate) of a sample of the mixture afforded only enriched bands for the two compounds. From their ^{1}H NMR spectra

separate sets of data for *R*-isomer **15a** (more polar band) and *S*-isomer **16a** (less polar band) could be collected. Compound **15a:** ^{1}H NMR ($CDCl_3$) δ 1.44 (d, 3H, $J_{5,6}$ = 6.8 Hz, H-6), 2.13 (s, 3H, $COCH_3$), 3.41 (s, 3H, OCH_3), 4.18-4.25 (2H, H-4, H-5), 4.48 (dd, 1H, $J_{2,3}$ = 7.9 Hz, $J_{3,4}$ = 5.9 Hz, H-3), 4.88 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.97 (dd, 1H, H-2), 5.90 (s, 1H, C*H*Ph), 7.35-7.55 (5H, Ph). Compound **16a:** ^{1}H NMR ($CDCl_3$) δ 1.41 (d, 3H, $J_{5,6}$ = 6.8 Hz, H-6), 2.18 (s, 3H, $COCH_3$), 3.42 (s, 3H, OCH_3), 4.08-4.15 (2H, H-4, H-5), 4.62 (dd, 1H, $J_{2,3}$ = 8.4 Hz, $J_{3,4}$ = 5.9 Hz, H-3), 4.91 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.08 (dd, 1H, H-2), 6.18 (s, 1H, C*H*Ph), 7.35-7.5 (5H, Ph).

The mixture of **15a** and **16a** (154 mg) was irradiated in the presence of *N*-bromosuccinimide, barium carbonate and water in carbon tetrachloride following the procedure used for **15b+16b**. The crude product was purified by column chromatography (silica gel; hexane-diethyl ether) to give compound **17a** (147 mg; 90%) as a syrup: $[\alpha]_D$ -153° (*c* 1.4, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.17 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 2.09 (s, 3H, $COCH_3$), 3.39 (s, 3H, OCH_3), 4.12 (1H, dq, $J_{4,5}$ = 1.4 Hz, H-5), 4.28 (dd, 1H, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.7 Hz, H-3), 4.95 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.10 (dd, 1H, H-2), 5.46 (dd, 1H, H-4), 7.3-7.6, 8.0-8.1 (5H, Ph)

Anal. Calcd for $C_{16}H_{20}O_7$ (324.3): C, 59.2; H, 6.2. Found: C, 59.4; H, 6.1.

Methyl 2-*O*-Acetyl-4-*O*-benzoyl-6-deoxy-α-L-*xylo*-hexopyranosid-3-ulose (18a). Treatment of compound **17a** (118 mg) with pyridinium chlorochromate in dry benzene as described above for **17b** gave compound **18a** (107 mg; 91%) as a syrup: $[\alpha]_D$ -115.5° (*c* 0.9, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.36 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 2.18 (s, 3H, $COCH_3$), 3.45 (s, 3H, OCH_3), 4.39 (dq, 1H, $J_{4,5}$ = 1.3 Hz, H-5), 5.20 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 5.36 (d, 1H, H-4), 5.77 (d, 1H, H-2), 7.45-7.55, 8.0-8.1 (5H, Ph).

Anal. Calcd for $C_{16}H_{18}O_7$ (322.3): C, 59.6; H, 5.6. Found: C, 59.4; H, 5.7.

Methyl 2-*O*-Acetyl-4-*O*-benzoyl-6-deoxy-α-L-*xylo*-hexopyranosid-3-ulose (*E*)-*O*-Methyloxime (19a). Oximation of compound **18a** (88 mg) was performed as described above for **18b** and gave *O*-methyloxime **19a** (79 mg; 82%), mp 132-3 °C (from ethyl acetate-hexane), $[\alpha]_D$ -231° (*c* 0.8, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.25 (d, 3H, $J_{5,6}$ = 6.6 Hz, 1), 2.13 (s, 3H, $COCH_3$), 3.47 (s, 3H, OCH_3), 3.94 (s, 3H, $=NOCH_3$), 4.20 (dq, 1H, $J_{4,5}$ = 1.8 Hz, H-5), 5.01 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.82 (d, 1H, H-2), 6.50 (d, 1H, H-4), 7.45-7.6, 8.0-8.1 (5H, Ph); ^{13}C NMR ($CDCl_3$) δ 16.3 (C-6), 21.2 ($COCH_3$), 56.0 (OCH_3), 63.1 ($=NOCH_3$), 66.1, 66.9, 68.4 (C-2, C-4, C-5), 99.0 (C-1), 146.7 (C-3), 165.7 ($COCH_3$), 167.7 (COPh), 129.0, 129.7, 130.4, 133.9 (aromatic C).

Anal. Calcd for $C_{17}H_{21}NO_7$ (351.4): C, 58.1; H, 6.0; N, 4.0. Found: C, 58.1; H, 6.1; N, 3.9.

Reduction of *O*-Methyloxime 19a with Lithium aluminium hydride. Reduction of *O*-methyloxime **19a** (71 mg) was performed as described above for compound **5**. The reaction time was 2 h. The crude product was acetylated (3:1 pyridine-acetic anhydride; 1 mL; 12 h at room temperature). Preparative-layer chromatography (silica gel; chloroform-diethyl ether, 7:3) of acetylation product afforded compounds **11a** (14 mg; 23%) and **10** (20 mg; 32%), identical with the compounds obtained by lithium aluminium hydride reduction of **5**.

MS of 3-Acetamido-1,2,4,5-tetra-*O*-acetyl-1-*C*-deuterio-3,6-dideoxy-L-galactitol and 3-Acetamido-1,2,4,5-tetra-*O*-acetyl-1-*C*-deuterio-3,6-dideoxy-L-gulitol. Samples of **1b** and **2b** (1 mg each) were treated with 2 M H_2SO_4 (200 µL) and glacial acetic acid (1.8 mL) at 100 °C for 9 h (sealed tube). After removal of acetic acid by repeated codistillations with water *in vacuo*, H_2SO_4 was neutralized by the addition of water (1 mL) and barium carbonate (120 mg). The slurry was centrifuged and the supernatant solution was filtered through a C_{18} Sep-Pak. Sodium borodeuteride (5 mg) was added to the filtrate and the mixture was left for 1 h at room temperature. After evaporation of water, the sample was acetylated with pyridine-acetic anhydride (2:1, 0.2 mL; 20 min, 120 °C). Methanol and then toluene were added. After solvent evaporation *in vacuo*, alditol acetates were extracted with dichloromethane from the residue and analyzed by GLC-MS. The mass spectrum of 3-acetamido-1,2,4,5-tetra-*O*-acetyl-1-*C*-deuterio-3,6-dideoxy-L-galactitol (from **1b**) displayed the following main peaks: *m/z* 217 (32%), 157 (32%, 217-AcOH), 115 (52%, 217-AcOH-CH_2CO), and 97 (100%, 217-2AcOH) derived from the C-1/C-3 fragment, and *m/z* 230 (6%), 170 (19%, 230-AcOH), 128 (35%, 230-Ac_2O), and 110 (44%, 230-2AcOH) derived from the C-3/C-6 fragment. The peaks in the spectrum of 3-acetamido-1,2,4,5-tetra-*O*-acetyl-1-*C*-deuterio-3,6-dideoxy-L-gulitol (from **2b**) were as follows: 230 (37%), 217 (9%), 170 (52%), 157 (15%), 128 (82%), 115 (37%), 110 (100%), 97 (54%).

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