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Note

2-*C*-Carbamoyl-, 2-*C*-cyano-, and 2-*C*-acetamidomethyl-substituted glycosides

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Methyl 2-carbamoyl-2-deoxyglycopyranosides[1] (**1**) represent a new class of branched monosaccharides[2] that provide a ready access to various 2-deoxy-2-*C*-substituted glycosides. The protected anomeric centre and the carbamoyl group in **1** form a masked malonyl unit suitable for the synthesis of sugar derivatives that have a fused heterocyclic system.

We have reported[1] the synthesis of the title compounds by cycloaddition of trichloroacetyl isocyanate to trimethylsilylated or benzylated glycals, followed by methanolysis of the intermediate [2 + 2] and [4 + 2] cycloadducts, **2** and **3**, respectively.

We now report an alternative synthesis of 2-carbamoyl-2-deoxyglycosides, using tosyl isocyanate and the benzylated glycals **4–6**. Only the [2 + 2] cycloadduct was formed in the first step of these reactions.

The glycals **4–6** were each treated with 2 molar equiv. of tosyl isocyanate, to give the respective unstable cycloadducts **7–9**, which were not isolated but methanolysed to afford the glycosides **10–12**. The benzyl and tosyl groups were removed simultaneously from **10–12** by reduction with sodium in liquid ammonia to give **13–15**.

The tosyl substituent could be removed selectively from **10–12** by reduction with sodium naphthalene in 1,2-dimethoxyethane, to give the respective glycosides **16–18**.

The carbamoyl-branched carbohydrates **16–18** are useful intermediates for the synthesis of 2-*C*-cyano and 2-*C*-acetamidomethyl derivatives. The usual methods for the introduction of cyano groups involve addition or substitution reactions and a variety of cyanide nucleophiles[2]. However, there are examples that involve a photocarbamoylation–dehydration process[3,4]. 2-*C*-Aminomethyl derivatives have been obtained by hydrogenolysis of the 2-*C*-cyano precursor[5].

Compounds **16–18** were each reduced with lithium aluminium hydride in tetrahydrofuran to give, in good or moderate yields, the respective 2-*C*-aminomethyl-2-deoxyglycosides, characterised as the *N*-acetyl derivatives **22–24**. Reduction of **16–18** with the borane–methyl sulfide complex afforded amines in a lower yield. Dehydration

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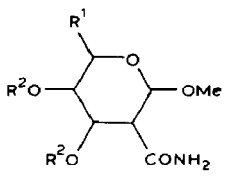
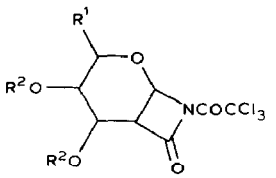


1

$R^1 = H, CH_3, CH_2OR^2$
$R^2 = H, Bn$



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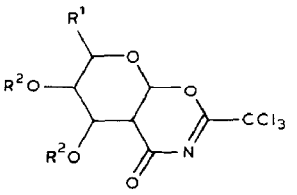
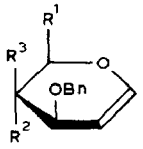
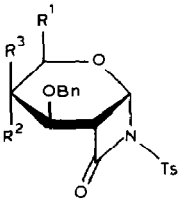


3

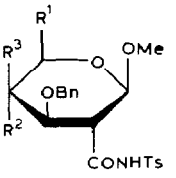
$R^1 = H\ CH_3, CH_2OR^2$
$R^2 = Me_3Si, Bn$



4 – 6

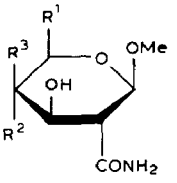


7 – 9



10 – 11

4,7,10 $R^1 = CH_2OBn, R^2 = OBn, R^3 = H$
5,8,11 $R^1 = CH_2OBn, R^2 = H, R^3 = OBn$
6,9,12 $R^1 = R^2 = H, R^3 = OBn$



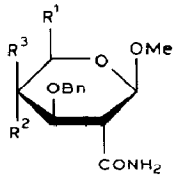
13 $R^1 = CH_2OH, R^2 = OH, R^3 = H$
14 $R^1 = CH_2OH, R^2 = H, R^3 = OH$
15 $R^1 = R^2 = H, R^3 = OH$

of **16–18** with thionyl chloride produced the respective nitriles **19–21** in good yield. Reduction of **22–24** with lithium aluminum hydride followed by acetylation yielded the amides **19–21**. Derivatives of 2-cyano-2-deoxyglycosides with the *β*-D-*galacto*[5] (**25**) and *α*-D-*gluco*[6] (**26**) configuration, as well as the 2-*C*-acetamidomethyl-2-deoxyglycoside with the *β*-D-*galacto*[5] configuration (**27**), are known.

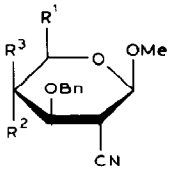
The cycloaddition of isocyanates to glycals enables regio- and stereo-specific functionalisation of the double bond. The chemistry of the carbamoyl group is normal for such structures and allows the introduction of a desired function at C-2 of the pyranoside ring.

EXPERIMENTAL

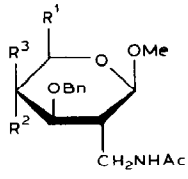
All melting points are uncorrected. Optical rotations were measured using a Perkin–Elmer 141 spectropolarimeter. ^{1}H-N.m.r. spectra (500 MHz) were recorded



16–18

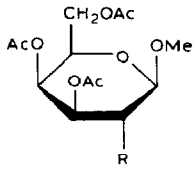


19–21

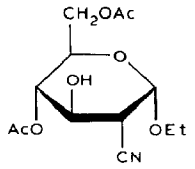


22–24

16, 19, 22 $R^1 = CH_2OBn, R^2 = OBn, R^3 = H$
17, 20, 23 $R^1 = CH_2OBn, R^2 = H, R^3 = OBn$
18, 21, 24 $R^1 = R^2 = H, R^3 = OBn$



25 R = CN
27 R = CH_2NHAc



26

with a Bruker AM 500 spectrometer, and i.r. spectra with a Beckman 4240 spectrophotometer.

Column chromatography was carried out using Merck Kieselgel 70–230 or 230–400 mesh.

Glycals **4–6** were prepared by the benzylation method[7]. Glycosides **16** and **17** were prepared previously, using the trichloroacetyl isocyanate method.

2-Deoxy-2-(tosylcarbamoyl)glycosides. — To a solution of the glycal (**4–6**, 10 mmol) in dry acetonitrile (30 mL) was added *p*-toluenesulphonyl isocyanate (20 mmol) with stirring. After disappearance of the substrate (^{1}H-n.m.r. spectroscopy), the reaction was stopped by the addition of methanol (30 mL). The solvents were evaporated, a solution of the residue in methanol was left overnight and then concentrated, and the glycosides were purified by column chromatography. The following compounds were prepared in this manner.

*Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-(tosylcarbamoyl)-β-*D*-glucopyranoside* (**10**). — Prepared from 1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol[7] (tri-*O*-benzyl-D-glucal, **4**; 22-h reaction), **10** (47%) had m.p. 170–171°, $[\alpha]_D$ +30° (*c* 1, dichloromethane); ν_{max}^{KBr} 3140 (NH) and 1710 cm^{-1} (C=O). ^{1}H-N.m.r. data ($CDCl_3$): δ 2.39 (s, 3 H, TsMe), 2.46 (dd, 1 H, $J_{1,2}$ 8.4, $J_{2,3}$ 10.6 Hz, H-2), 3.38 (s, 3 H, OMe), 3.41 (dt, 1 H, $J_{4,5}$ 9.7 Hz, H-5), 3.58 (t, 1 H, H-4), 3.69 (m, 2 H, H-6,6'), 3.95 (dd, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 4.32 (d, 1 H, H-1).

Anal. Calc. for $C_{36}H_{39}NO_8S$: C, 66.95; H, 6.1; N, 2.2. Found: C, 66.9; H, 6.1; N, 2.2.

*Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-(tosylcarbamoyl)-β-*D*-galactopyranoside* (**11**). — Prepared from 1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-D-*lyxo*-hex-1-entiol[7] (tri-*O*-benzyl-D-galactal, **5**; 5-h reaction), **11** (50%) had m.p. 175–176°, $[\alpha]_D$ +32° (*c* 1, dichloromethane); ν_{max}^{KBr} 3200 (NH) and 1720 cm^{-1} (C=O). ^{1}H-N.m.r. data ($CDCl_3$): δ

2.37 (s, 3 H, TsMe), 2.84 (dd, 1 H, $J_{1,2}$ 8.4, $J_{2,3}$ 10.9 Hz, H-2), 3.31 (s, 3 H, OMe), 3.47 (m, 1 H, H-5), 3.57 (dd, 1 H, $J_{5,6}$ 5.6, $J_{6,6'}$ 9.3 Hz, H-6), 3.59 (dd, 1 H, $J_{5,6'}$ 7.5 Hz, H-6'), 3.75 (dd, 1 H, $J_{3,4}$ 2.7 Hz, H-3), 3.81 (dd, 1 H, H-4), 4.30 (d, 1 H, H-1).

Anal. Calc. for $C_{36}H_{39}NO_8S$: C, 66.95; H, 6.1; N, 2.2. Found: C, 67.3; H, 5.8; N, 2.3.

*Methyl 3,4-di-*O*-benzyl-2-deoxy-2-(tosylcarbamoyl)-α-*L*-arabinopyranoside* (**12**). — Prepared from 1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-L-*threo*-pent-1-enitol[7] (**6**, 4-h reaction), **12** (76%) had m.p. 69–70°, $[\alpha]_D$ +68° (*c* 1, dichloromethane); $\nu_{max}^{CHCl_3}$ 3200 (NH) and 1735 cm^{-1} (C=O). ^{1}H-N.m.r. data ($CDCl_3$): δ 2.39 (s, 3 H, Ts*Me*), 2.82 (dd, $J_{1,2}$ 8.3, $J_{2,3}$ 11.0 Hz, H-2), 3.19 (dd, 1 H, $J_{4,5}$ 0.7, $J_{5,5'}$ 13.0 Hz, H-5), 3.37 (s, 3 H, OMe), 3.56 (m, 1 H, H-4), 3.69 (dd, $J_{3,4}$ 3.1 Hz, H-3), 4.10 (dd, 1 H, $J_{4,5'}$ 2.1 Hz, H-5'), 4.24 (d, 1 H, H-1).

Anal. Calc. for $C_{28}H_{30}NO_7S$: C, 64.0; H, 5.9; N, 2.7. Found: C, 63.7; H, 5.6; N, 2.9.

Removal in the N-*tosyl and* O-*benzyl groups.* — To a solution of the *N*-tosylglycoside (**10–12**, 0.3 mmol) in refluxing ammonia (10 mL) was added sodium in pieces until the blue colour persisted for 20 min. Ammonium chloride was then added until the blue colour disappeared, the ammonia was allowed to evaporate, and the residue was purified by column chromatography (ethyl acetate–2-propanol, 2:1). The following compounds were prepared in this way.

*Methyl 2-carbamoyl-2-deoxy-β-*D*-glucopyranoside* (**13**). — Prepared from **10**, **13** (71%) had m.p. 199–200°, $[\alpha]_D$ −28° (*c* 1, water; ν_{max}^{Nujol} 3400 (OH), 1680 and 1630 cm^{-1} (amide). ^{1}H-N.m.r. data (D_2O): δ 2.49 (dd, 1 H, $J_{1,2}$ 8.6, $J_{2,3}$ 10.8 Hz, H-2), 3.41 (t, 1 H, H-4), 3.50 (ddd, 1 H, $J_{4,5}$ 9.9, $J_{5,6}$ 5.9, $J_{5,6'}$ 2.2 Hz, H-5), 3.54 (s, 3 H, OMe), 3.78 (dd, 1 H, $J_{6,6'}$ 12.3 Hz, H-6), 3.84 (dd, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 3.97 (dd, 1 H, H-6'), 4.65 (d, 1 H, H-1).

Anal. Calc. for $C_8H_{15}NO_6$: C, 43.4; H, 6.8; N, 6.3. Found: C, 43.4; H, 7.0; N, 6.1.

*Methyl 2-carbamoyl-2-deoxy-β-*D*-galactopyranoside* (**14**). — Prepared from **11**, **14** (70%) had m.p. 201–203°, $[\alpha]_D$ +3.0° (*c* 1, water); ν_{max}^{KBr} 3420 (OH), 1670 and 1625 cm^{-1} (amide). ^{1}H-N.m.r. data (D_2O): δ 2.64 (dd, 1 H, $J_{1,2}$ 8.7, $J_{2,3}$ 11.1 Hz, H-2), 3.54 (s, 3 H, OMe), 3.69 (dd, 1 H, $J_{5,6}$ 4.5, $J_{6,6'}$ 7.7 Hz, H-6), 3.75–3.94 (m, 3 H, H-4,5,6'), 3.99 (dd, $J_{3,4}$ 3.2 Hz, H-3), 4.56 (d, 1 H, H-1).

Anal. Calc. for $C_8H_{15}NO_6$: C, 43.4; H, 6.8; N, 6.3. Found: C, 43.5; H, 7.1; N, 6.4.

*Methyl 2-carbamoyl-2-deoxy-α-*L*-arabinopyranoside* (**15**). — Prepared from **12**, **15** (50%) had m.p. 194–196°, $[\alpha]_D$ +21° (*c* 1, water); ν_{max}^{KBr} 3400 (OH), 1680, 1665 and 1620 cm^{-1} (amide). ^{1}H-N.m.r. data (D_2O): δ 2.67 (dd, 1 H, $J_{1,2}$ 8.6, $J_{2,3}$ 11.0 Hz, H-2), 3.52 (s, 3 H, OMe), 3.69 (dd, 1 H, $J_{4,5}$ 1.2, $J_{5,5'}$ 13.1 Hz, H-5), 3.90 (m, 1 H, H-4), 4.01 (dd, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 4.02 (dd, 1 H, $J_{4,5'}$ 2.1 Hz, H-5'), 4.99 (d, 1 H, H-1).

Anal. Calc. for $C_7H_{13}NO_5$: C, 43.9; H, 6.8; N, 7.3. Found: C, 43.9; H, 7.2; N, 7.1.

Removal of the N-*tosyl group.* — A solution of naphthalene (0.48 mmol) in dry 1,2-dimethoxyethane (2 mL) was stirred with sodium (0.01 g) under nitrogen for 30 min, then cooled to −30°, and a solution of the glycoside (**10–12**, 0.08 mmol) in 1,2-dimethoxyethane (1 mL) was added slowly. Stirring and cooling were continued for 10 min, water was added dropwise until the blue colour disappeared, and the mixture was diluted with water and extracted with dichloromethane (3 × 10 mL). The combined extracts were dried and concentrated, and the residue was purified by chromatography,

to give the product (**16–18**, 45–70%). Methyl 3,4,6-tri-*O*-benzyl-2-carbamoyl-2-deoxy-β-D-glucopyranoside (**16**) and methyl 3,4,6-tri-*O*-benzyl-2-carbamoyl-2-deoxy-β-D-galactopyranoside (**17**) were identical with those obtained previously[1].

Methyl 3,4-di-O-benzyl-2-carbamoyl-2-deoxy-α-L-arabinopyranoside (**18**). — Prepared from **12**, **18** had m.p. 195–197°, $[\alpha]_D$ +43.5° (*c* 1, dichloromethane), $\nu_{max}^{CHCl_3}$ 3410 (NH_2), 1690 and 1600 cm^{-1} (amide). ^{1}H-N.m.r. data ($CDCl_3$): δ 2.84 (dd, 1 H, $J_{1,2}$ 8.4, $J_{2,3}$ 11.0 Hz, H-2), 3.30 (dd, 1 H, $J_{4,5}$ 0.9, $J_{5,5'}$ 13.0 Hz, H-5), 3.49 (s, 3 H, OMe), 3.61 (m, 1 H, H-4), 3.85 (dd, 1 H, $J_{3,4}$ 3.1 Hz, H-3), 4.14 (dd, 1 H, $J_{4,5'}$ 2.2 Hz, H-5'), 4.43 (d, 1 H, H-1).

Anal. Calc. for $C_{21}H_{25}NO_5$: C, 67.9; H, 6.8; N, 3.8. Found: C, 67.8; H, 6.6; N, 4.0.

Preparation of 2-cyano-2-deoxyglycosides. — A suspension of substrate (**16–18**, 15 mmol) in benzene (25 mL) was treated with pyridine (0.5 mL) and thionyl chloride (0.5 mL). The mixture was stirred overnight at room temperature, then washed with water, aqueous sodium hydrogen carbonate, and brine, dried, and concentrated. The product was purified by column chromatography (hexane–ether, 7:3), The following compounds were prepared in this way.

Methyl 3,4,6-tri-O-benzyl-2-cyano-2-deoxy-β-D-glucopyranoside (**19**). — Prepared from **16**, **19** (85%) was a syrup, $[\alpha]_D$ +17.5° (*c* 1, chloroform); ν_{max}^{KBr} 2240 cm^{-1} (C≡N). ^{1}H-N.m.r. data ($CDCl_3$): δ 2.81 (dd, 1 H, $J_{1,2}$ 8.5, $J_{2,3}$ 11.0 Hz, H-2), 3.45 (dt, 1 H, $J_{4,5}$ 9.8, $J_{5,6}$ + $J_{5,6'}$ 6.2 Hz, H-5), 3.57 (t, 3 H, OMe), 3.58 (dd, 1 H, $J_{3,4}$ 8.7 Hz, H-4), 3.72 (m, 2 H, H-6,6'), 3.82 (dd, 1 H, H-3) , 4.48 (d, 1 H, H-1).

Anal. Calc. for $C_{29}H_{31}NO_5$: C, 73.55; H, 6.6; N, 2.95. Found: C, 73.2; H, 6.6; N, 2.9.

Methyl 3,4,6-tri-O-benzyl-2-cyano-2-deoxy-β-D-galactopyranoside (**20**). — Prepared from **17**, **20** (79%) had m.p. 128–130°, $[\alpha]_D$ +8° (*c* 1, chloroform); ν_{max}^{KBr} 2240 cm^{-1} (C≡N). ^{1}H-N.m.r. data ($CDCl_3$): δ 3.22 (dd, 1 H, $J_{1,2}$ 8.5, $J_{2,3}$ 11.4 Hz, H-2), 3.52 (ddd, 1 H, $J_{4,5}$ 1.0, $J_{5,6}$ 4.5, $J_{5,6'}$ 2.5 Hz, H-5), 3.53 (s, 3 H, OMe), 3.58 (dd, 1 H, $J_{6,6'}$ 8.2 Hz, H-6), 3.61 (dd, 1 H, H-6'), 3.66 (dd, 1 H, $J_{3,4}$ 2.5 Hz, H-3), 3.89 (d, 1 H, H-4), 4.42 (d, 1 H, H-1).

Anal. Calc. for $C_{29}H_{31}NO_5$: C, 73.55; H, 6.6; N, 2.95. Found: C, 73.4; H, 6.4; N, 2.9.

Methyl 3,4-di-O-benzyl-2-cyano-2-deoxy-α-L-arabinopyranoside (**21**). — Prepared from **18**, **21** (76%) had m.p. 102–104°, $[\alpha]_D$ +55° (*c* 1, chloroform); ν_{max}^{KBr} 2280 cm^{-1} (C≡N). ^{1}H-N.m.r. data ($CDCl_3$): δ 3.23 (dd, 1 H, $J_{1,2}$ 8.3, $J_{2,3}$ 10.5 Hz, H-2), 3.28 (dd, 1 H, $J_{4,5}$ 1.0, $J_{5,5'}$ 13.0 Hz, H-5), 3.55 (s, 3 H, OMe), 3.65 (m, 2 H, H-3,4), 4.13 (dd, 1 H, $J_{4,5'}$ 2.3 Hz, H-5'), 4.37 (d, 1 H, H-1).

Anal. Calc. for $C_{21}H_{23}NO_4$: C, 71.4; H, 6.5; N, 4.0. Found: C, 71.2; H, 6.6; N, 3.9.

Formation of methyl 2-C-acetamidomethyl-2-deoxyglycosides. — (*a*). A solution of carbamoylglycoside (**16–18**, 1 mmol) in dry tetrahydrofuran (20 mL) was treated with lithium aluminum hydride (4 mmol). The mixture was heated to reflux until the substrate has disappeared (t.l.c.), then cooled. Saturated aqueous sodium sulphate was added dropwise, followed by solid sodium sulphate. The mixture was diluted with ether, and organic layer was dried (Na_2SO_4) and concentrated. The residue was treated with 2:1 pyridine–acetic anhydride (3 mL) and left overnight. The solution was poured into cold water and extracted with chloroform, and the extract was washed with brine and

dried. The product was purified by column chromatography (hexane–ether–methanol, 1:1: 0.01). Yields, 42–52%.

(*b*) To a solution of 2-cyano-2-deoxyglycoside (**19–21**, 1 mmol) in dry tetrahydrofuran (15 mL) was added lithium aluminum hydride (4 mmol). The mixture was stirred at room temperature for 2 days, and saturated aqueous sodium sulphate was added dropwise, followed by solid sodium sulphate. The mixture was diluted with ether (20 mL), and the organic phase was dried and concentrated. The residue was acetylated and the product was isolated as in (*a*). Yields, 38–54%.

The following compounds were prepared is this way.

*Methyl 2-acetamidomethyl-3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-glucopyranoside* (**22**). — Prepared from **16**, **22** had m.p. 98–100°, $[\alpha]_D$ +30° (*c* 1, chloroform); ν_{max}^{KBr} 3460, 3320 (NH), 1660, and 1640 cm^{-1} (C=O). ^{1}H-N.m.r. data (toluene-d_8; 90°): δ 1.53 (s, 3 H, Ac), 1.78 (m, 1 H, H-2), 3.20 (bm, 1 H, CH_AH$_B$NHAc), 3.27 (dd, 1 H, $J_{2,3}$ 10.6, $J_{3,4}$ 8.5, Hz, H-3), 3.30 (ddd, 1 H, $J_{4,5}$ 9.2, $J_{5,6}$ 2.7, $J_{5,6'}$ 4.4 Hz, H-5), 3.32 (s, 3 H, OMe), 3.60 (t, 1 H, H-4), 3.63 (bm, 1 H, CH$_A$$H_B$NHAc), 3.66 (dd, 1 H, $J_{6,6'}$ 10.9 Hz, H-6), 3.68 (dd, 1 H, H-6'), 3.98 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1).

Anal. Calc. for $C_{31}H_{37}NO_6$: C, 71.65; H, 7.2; N, 2.7. Found: C, 71.7; H, 7.4; N, 2.7.

*Methyl 2-acetamidomethyl-3,4,6-tri-*O*-benzyl-2-deoxy-β-*D*-galactopyranoside* (**23**). — Prepared from **17**, **23** had m.p. 84–85°, $[\alpha]_D$ +32° (*c* 1, chloroform), ν_{max}^{KBr} 3500, 3280 (NH), 1650, and 1570 cm^{-1} (C=O). ^{1}H-N.m.r. data (C_6D_6; 50°): δ 2.42 (m, 1 H, H-2), 3.05 (dd, 1 H, $J_{2,3}$ 11.2, $J_{3,4}$ 2.6 Hz, H-3), 3.35 (s, 3 H, OMe), 3.36 (m, 2 H, H-5 and CH_AH$_B$NHAc), 3.65 (dd, 1 H, $J_{5,6}$ 5.5, $J_{6,6'}$ 9.0 Hz, H-6), 3.72 (dd, 1 H, $J_{2,B}$ 4.6, $J_{A,B}$ 13.7 Hz, CH$_A$$H_B$NHAc), 3.82 (dd, 1 H, $J_{5,6'}$ 7.6 Hz, H-6'), 3.83 (bs, 1 H, H-4), 3.94 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1).

Anal. Calc. for $C_{31}H_{37}NO_6$; C, 71.65; H, 7.2; N, 2.7. Found: C, 71.2; H, 7.4; N, 2.7.

*Methyl 2-acetamidomethyl-3,4-di-*O*-benzyl-2-deoxy-α-*L*-arabinopyranoside* (**24**). — Prepared from **18**, **24** had m.p. 99–100°, $[\alpha]_D$ +70° (*c* 1, chloroform); ν_{max}^{KBr} 3340 (NH_2), 1650 and 1570 cm^{-1} (C=O). ^{1}H-N.m.r. data (C_6D_6, 50°): δ 2.43 (m, 1 H, H-2), 2.88 (bd, 1 H, $J_{5,5'}$ 12.6 Hz, H-5), 3.05 (bd, 1 H, $J_{2,3}$ 9.0 Hz, H-3), 3.34 (s, 4 H, OMe and H-4), 3.43 (dd, 1 H, $J_{2,A}$ 6.0, $J_{A,B}$ 13.5 Hz, CH_AH$_B$NHAc), 3.64 (dd, 1 H, $J_{2,B}$ 5.0 Hz, CH$_A$$H_B$HAc), 3.88 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 3.97 (bd, 1 H, H-5').

Anal. Calc. for $C_{23}H_{29}NO_5$: C, 69.15; H, 7.3; N, 3.5. Found: C, 68.8; H, 7.3; N, 3.5.

REFERENCES

1 D. Mostowicz, C. Bełżecki, and M. Chmielewski, *J. Carbohydr. Chem.*, 7 (1988) 805–810.
2 J. Yoshimura, *Adv. Carbohydr. Chem. Biochem.*, 42 (1984) 69–134.
3 A. Rosenthal and M. Ratcliffe, *Can. J. Chem.*, 54 (1976) 91–96; M. Chmielewski, J. N. BeMiller, and D. P. Cerretti, *J. Org. Chem.*, 46 (1981) 3903–3908.
4 G. Grynkiewicz and J. N. BeMiller, *Carbohydr. Res.*, 112 (1983) 324–327.
5 R. H. Hall, K. Bischofberger, A. J. Brink, O. G. de Villiers, and A. Jordaan, *J. Chem. Soc., Perkin Trans. 1*, (1979) 781–796.
6 F. G. De las Heras, A. San Felix, A. Calvo-Mateo, and P. Fernandez-Resa, *Tetrahedron*, 41 (1985) 3867–3879.
7 M. Chmielewski, I. Fokt, J. Grodner, G. Grynkiewicz, and W. Szeja, *J. Carbohydr. Chem.*, 8 (1989) 735–741.