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Note

The preparation of nucleosides from 3-deoxy-3-*C*-(*R*)-ethoxycarbonyl(formylamino)methyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose

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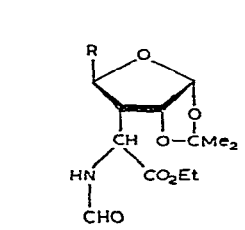
In a previous paper[1], we described the synthesis of 3-deoxy-3-*C*-(*R*)-ethoxycarbonyl(formylamino)methyl-1,2 5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**), which is a sugar derivative containing a protected glycine moiety as a branched chain at C-3 At present, there is much interest in the synthesis of nucleoside peptide antibiotics[2] and analogues of the polyoxin group of antifungal agents[3] This, together with the discovery that profound changes in the biological activity of naturally occuring nucleosides can be achieved by the introduction of branching at C-3 of the sugar moiety[4], has prompted us to synthesize nucleosides from **1** This paper describes the synthesis of 1-[3-*C*-(*R*)-(1-acetamido-2-hydroxyethyl)-3-deoxy-β-D-ribofuranosyl]-uracil (**16**) and its α anomer (**17**) by the modified Hilbert–Johnson reaction[5]

Acid hydrolysis of **1** followed by acetylation gave the diacetate **2** Preliminary experiments indicated that acetolysis of **2** gave a mixture of the *N*-formyl and *N*-acetyl compounds **3** and **4**, which could not be separated chromatographically The ratio of **3** **4** showed very little change on varying the reaction time and the concentration of acid Hydrolysis of **2** with trifluoroacetic acid[6] followed by acetylation gave a complex reaction mixture from which the lactone **5** was isolated in fairly high yield. To circumvent these difficulties, **1** was reduced with lithium aluminium hydride and then deformylated to the α-amino-alcohol[1] **6**

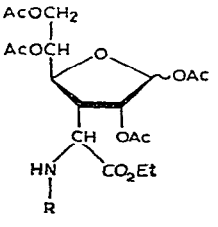
Acetylation of **6** with acetic anhydride in pyridine gave a mixture of the *N*,*N*-diacetyl compound **8** (main product) and the partially acetylated compound **7** Hydrolysis of the 5,6-*O*-isopropylidene groups in **7** and **8**, periodate cleavage of the resulting diols **9** and **10**, and reduction of the products with borohydride gave compounds **11** and **12**, respectively Acetylation of **11** with pyridine–acetic anhydride gave **13**. During acetylation of **12** with pyridine–acetic anhydride and work-up in the usual manner, one of the *N*-acetyl groups was lost, and the same product (**13**) was obtained as in the acetylation of **11**.

Acetolysis of **13** for at least three days[7] gave crystalline 3-*C*-(*R*)-(1-acetamido-2-acetoxyethyl)-1,2,5-tri-*O*-acetyl-3-deoxy-β-D-ribofuranose (**14**) as the only product



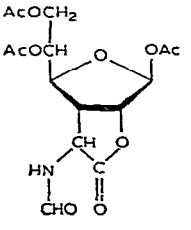
1 R = 

2 R = 

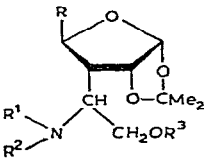


3 R = CHO

4 R = $COCH_3$



5



6 R =  $R^1 = R^2 = R^3 = H$

7 R =  , $R^1 = H$ $R^2 = R^3 = Ac$

8 R =  , $R^1 = R^2 = R^3 = Ac$

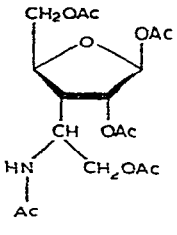
9 R =  , $R^1 = H$, $R^2 = R^3 = Ac$

10 R =  , $R^1 = R^2 = R^3 = Ac$

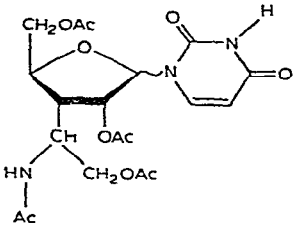
11 R = CH_2OH, $R^1 = H$, $R^2 = R^3 = Ac$

12 R = CH_2OH $R^1 = R^2 = R^3 = Ac$

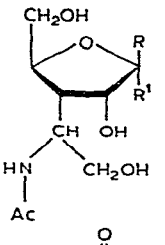
13 R = CH_2OAc, $R^1 = H$ $R^2 = R^3 = Ac$

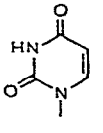


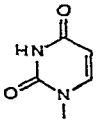
14



15



16 R =  , $R^1 = H$

17 R = H , R^1 = 

The anomeric configuration of **14** was deduced from its n m r. spectrum, where the resonance for H-1 appears at τ 3 65 as a singlet, indicating the β configuration[7,8]

Reaction of **14** with bis(trimethylsilyl)uracil[9], using the procedure described by Niedballa *et al* [5], gave an anomeric mixture (**15**) of nucleosides which could not be fractionated. The mixture was therefore deacetylated by refluxing with 0 1M methanolic sodium methoxide to give a mixture of the deprotected nucleosides **16** and **17** in a

1 2 ratio Fractionation of this mixture by chromatography on silica gel gave crystalline **16** (16%) and **17** (30% yield from **14**) The empirical rule[10] that the resonance for H-1′ in the n m r. spectrum occurs at lower field when the substituents are *cis* than when they are *trans* indicated the β configuration for **16** and the α configuration for **17** These anomeric assignments for **16** and **17** were unequivocally established by o r d. data The o r d spectrum of **16** exhibited a positive Cotton effect characteristic of the β-D configuration of furanosyl pyrimidine nucleosides[11], whereas the spectrum of **15** exhibited a negative Cotton effect which is consistent with an α-D configuration (Fig 1)

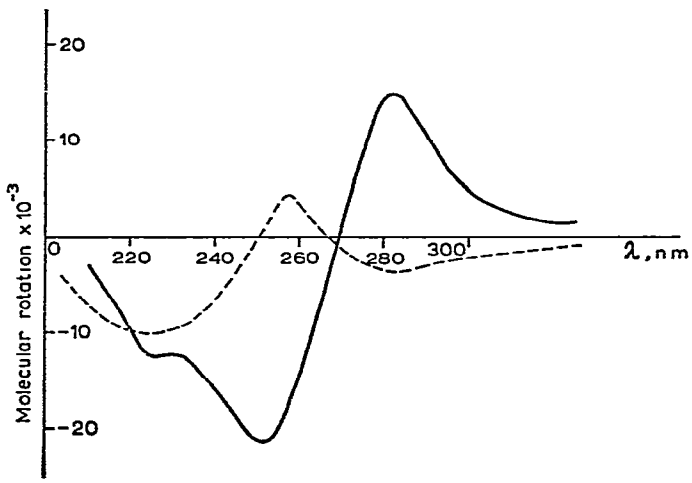


Fig 1 Rotatory dispersion curves of the β-nucleoside **16** (———) and the α-nucleoside **17** (— — —)

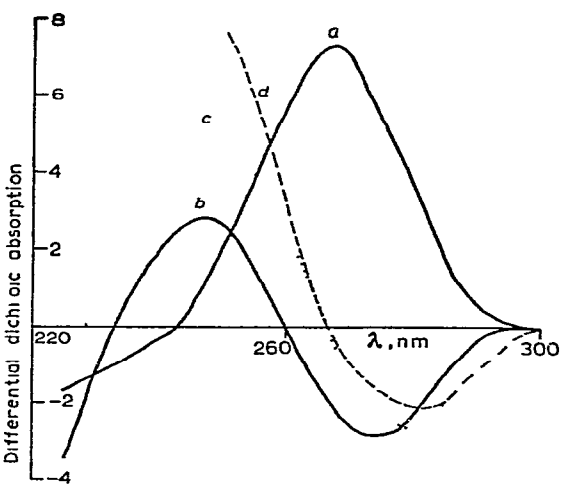


Fig 2 Circular dichroism curves of β-nucleoside **16** in methanol (*a*) and of α-nucleoside **17** in methanol (*b*), acetonitrile (*c*), and *p*-dioxane (*d*)

In methanol, the β-nucleoside **16** shows the expected c d maximum at 267 nm ($\Delta\varepsilon$ 7 23) due to the optically active uracil chromophore, in addition to the negative Cotton effect of the *N*-acetyl chromophore below 215 nm In contrast, the α-nucleoside **17** gave a c d spectrum in methanol with maxima at 272 ($\Delta\varepsilon$ −1 46) and 247 nm ($\Delta\varepsilon$ 1 40) (Fig 2) The presence of two relatively widely separated c d -maxima of opposite sign is usually indicative of solvation and/or conformational equilibrium[12] Further evidence for such equilibrium is furnished by the c d spectra of **17** in acetonitrile and *p*-dioxane, in which the intensity ratios of the two maxima were markedly different (Fig 2) These observations are compatible with an α-nucleoside conformation, in which the juxtaposition of the uracil and *N*-acetyl optically active chromophores clearly allows interaction of the two chromophores, as well as solvent-dependent conformational changes

EXPERIMENTAL

General methods — M p 's were determined with a Kofler hot-stage apparatus I r spectra were measured with a Perkin–Elmer 257 spectrophotometer, and electronic spectra were recorded on a Unicam S P 800 instrument N m r spectra were recorded on a Varian HA-100 instrument for solutions in $CDCl_3$ with tetramethylsilane as internal standard, unless otherwise stated Optical rotations were measured with a Bendix-NPL Automatic Polarimeter Type 143 on solutions in chloroform (*c* 1 0 ±0 5) unless otherwise stated O r d and c d spectra were recorded on a Jasco J-20 automatic recording spectropolarimeter on concentrations given as gmol/l Mass spectra were determined with an A E I MS-9 spectrometer, using the direct-insertion technique and an ionizing voltage of 70 eV. All solvent extracts were dried (Na_2SO_4), and solvent was then removed below 50° *in vacuo* T l c was performed on 0 1-mm plates of silica gel GF_{254} (Merck), spots were detected by u v light at 254 nm, or with cerium(IV) sulphate Column chromatography was conducted with Silica gel 60 (Merck) and chloroform–methanol (20 1), unless otherwise stated

*5,6-Di-*O*-acetyl-3-deoxy-3-*C*-(*R*)-ethoxycarbonyl(formylamino)methyl-1,2-*O*-isopropylidene-α-*D*-allofuranose* (**2**) — A solution of **1** (500 mg) in 75% acetic acid (5 ml) was heated in a water bath at 75° for 1 h The solvent was removed *in vacuo* and the product acetylated with pyridine–acetic anhydride to give **2** as an oil (446 mg, 75%), $[\alpha]_D^{20}$ +90°, $\nu_{max}^{CHCl_3}$ 1735 (ester), 1688 cm^{-1} (amide) Mass spectrum *m/e* 402 (M^+ −15) N m r data τ 1 72 (*s*, C*H*O), 3 12 (*d*, $J_{NH\ 1}$ 10 Hz, disappears on addition of D_2O–Et_3N, NH), 4 22 (*d*, $J_{1,2}$ 4 Hz, H-1), 4 91 (*q*, $J_{1',3}$ 5, $J_{1',NH}$ 10 Hz, H-1'), 5 31 (*t*, $J_{2\ 1}$ 4, $J_{2\ 3}$ 4 Hz, H-2), 5 76 (*q*, *J* 7 Hz, CH_2CH_3), 7 38 (*o*, $J_{3,1}$ 5, $J_{3,2}$ 4, $J_{3,4}$ 10 Hz, H-3), 7 87, 7 95 (2*s*, 2AcO), 8 42, 8 68(2*s*,$2CH_3$), 8 70 (*t*, *J* 7 Hz, CH_2CH_3)

Anal Calc for $C_{18}H_{27}NO_{10}$ C, 51 8. H, 6 5, N, 3 4. Found C, 51 8, H, 6 5, N, 3 3

Acetolysis of **2** — A solution of compound **2** (3 6 g, 8 8 mmoles) in acetic acid (50 ml) and acetic anhydride (5 ml) was cooled in an ice bath, and conc sulphuric acid (2 5 ml) was added dropwise. The ice bath was removed, and the mixture was

left at 20° for 3 days, and then poured into ice–water (500 ml) and extracted with chloroform (3 × 200 ml) The combined extracts were washed with aqueous sodium hydrogen carbonate (3 × 100 ml) and water (3 × 100 ml), and the solvent was removed to give an oil (2 1 g) Repeated chromatography of this oil gave a product (1 6 g) which was a mixture of **3** and **4** as evidenced by n m r [τ 1 76 (*s*, C*H*O) and 8 06 (*s*, NAc)] and mass spectrometry [*m/e* 401 ($M^+ - CH_3CO_2H$), **3**, and *m/e* 415 ($M^+ - CH_3CO_2H$), **4**]

*1,5,6-Tri-*O*-acetyl-2,3-dideoxy-3-*C*-(*R*)-formylaminomethyl-β-*D*-allofuranose-3*[1]*,2-carbolactone* (**5**) — A solution of **2** (310 mg) in 90% trifluoroacetic acid (10 ml) was kept[6] at 25° for 8 min and the solvent then removed *in vacuo* below 50° Acetylation of the residue gave a complex mixture of products, which was dissolved in a minimum of acetone and triturated with hexane to give a crystalline solid Recrystallisation from hexane–acetone gave **5** (152 mg, 55%) as colourless needles, m p 152–153°, $[\alpha]_D^{22}$ −145°, $\nu_{max}^{CHCl_3}$ 1793 (lactone), 1740 (ester), and 1690 cm^{-1} (amide) Mass spectrum· *m/e* 331 ($M^+ - CH_3CO_2$) N m r data τ 1 66 (*s*, C*H*O), 3 43 (*d*, $J_{NH,3'}$ 10 Hz, NH), 3 62 (*s*, H-1), 5 01 (*d*, $J_{2,3}$ 5 Hz, H-2), 4 80–6 60 (*m*, H-3,3[1],4,5,6,6', 7 85, 7 91, 7 96 (3*s*, 3AcO)

Anal Calc for $C_{15}H_{19}NO_{10}$ C, 48 3, H, 5 1, N, 3 8 Found C, 48 3, H, 5 1, N, 3 7

*3-*C*-(*R*)-(1-Acetamido-2-acetoxyethyl)-3-deoxy-1,2 5,6-di-*O*-isopropylidene-α-*D*-allofuranose* (**7**) *and 3-*C*-(*R*)-[2-acetoxy-1-(diacetylamino)ethyl]-1 2 5,6-di-*O*-isopropylidene-α-*D*-allofuranose* (**8**). — Compound **6** (5.1 g) was dissolved in dry pyridine (25 ml) and treated with acetic anhydride (5 ml) The mixture was left at 20° for 18 h and then poured into ice–water (250 ml) The mixture was extracted with chloroform (3 × 100 ml), and the combined extracts were successively washed with cold 3M hydrochloric acid (3 × 100 ml), saturated aqueous sodium hydrogen carbonate (3 × 100 ml), and water (3 × 100 ml) Removal of the solvent gave a mixture of two products, which was fractionated by column chromatography

Compound **7** was obtained as an oil (2 65 g, 41%), $[\alpha]_D^{20}$ +34°, $\nu_{max}^{CHC_3}$ 3415 (NH), 1730 (ester), and 1667 cm^{-1} (amide) Mass spectrum *m/e* 372 ($M^+ - 15$) N m r data τ 3 21 (*d*, $J_{NH,1}$ 9 5 Hz, disappears on addition of D_2O–Et_3N, NH), 4 25 (*d*, $J_{1,2}$ 4 Hz, H-1), 5 10–5 36 (*m*, H-1'), 5 19 (*t*, $J_{2,1}$ 4, $J_{2,3}$ 4 5 Hz, H-2), 7 76–7 90 (*m*, H-3), 7 95 (*s*, OAc), 8 08 (*s*, NAc), 8 43, 8 59, 8 66, 8 66 (4*s*, $4CH_3$)

Anal Calc. for $C_{18}H_{29}NO_8$ C, 55 8, H, 7 5, N, 3 6 Found C, 56 2; H, 7 6, N, 3 6

Compound **8** was recrystallized from hexane to give colourless needles (3 85 g, 53%), m p 94–95°, $\nu_{max}^{CHCl_3}$ 1627 cm^{-1} (ester and amide), $[\alpha]_D^{21}$ +63° Mass spectrum *m/e* 370 ($M^+ - CH_3CO_2^-$) N m r. data τ 4 28 (*d*, $J_{1,2}$ 4 Hz, H-1), 5 21–5 59 (*m*, H-1'), 5 37 (*t*, $J_{2,1}$ 4, $J_{2,3}$ 4 5 Hz, H-2), 7 53–7 88 (*m*, H-3), 7 81 (*s*, OAc), 8 33, 8 45 (2*s*, NAc_2), 8 47, 8 59, 8 67, 8 69 (4*s*, 4 CH_3)

Anal Calc for $C_{20}H_{31}NO_9$ C, 55 9, H, 7.3, N, 3 3. Found C, 56 2, H, 7 1, N, 3 2.

*3-*C*-(*R*)-(1-Acetamido-2-acetoxyethyl)-3-deoxy-1,2-*O*-isopropylidene-α-*D*-ribo-*

furanose (**11**) — A solution of **7** (2 6 g) in 75% acetic acid (50 ml) was heated at 75° for 30 min Removal of the solvent gave a quantitative yield of the 5,6-deprotected sugar **9** Mass spectrum *m/e* 332 ($M^+ - 15$) To a solution of **9** (2 4 g, 6 9 mmoles) in methanol (60 ml), a solution of sodium metaperiodate (1 48 g, 6 9 mmoles) in water (30 ml) was added. The reaction was monitored by t l c and was complete within 1 h The precipitated sodium iodate was filtered off, the solvent was removed, and the residue was taken up in acetone (500 ml) After filtration the solvent was again removed, and ethanol (50 ml) and sodium borohydride (66 mg, 1 75 mmoles) were added, and the mixture was stirred at 20° for 3 h The solvent was removed, the residue was extracted with chloroform (250 ml), and after filtration the solvent was removed to give **11** as an oil (2 01 g, 95%), $[\alpha]_D^{21}$ +32°, $\nu_{max}^{CHCl_3}$ 3410 (OH and NH), 1730 (acetate), and 1657 cm^{-1} (amide) Mass spectrum *m/e* 302 ($M^+ - 15$)

3-C-(R)-[2-Acetoxy-1-(diacetylamino)ethyl]-3-deoxy-1,2-O-isopropylidene-α-D-ribofuranose (**12**) — Hydrolysis of **8** (3 4 g) with 75% acetic acid (60 ml), as in the preparation of **9**, gave **10** as an oil in quantitative yield, mass spectrum *m/e* 330 ($M^+ - CH_3CO_2^{\cdot}$), $\nu_{max}^{CHCl_3}$ 3410 (OH and NH), 1730 (acetate), and 1655 cm^{-1} (amide) A solution of **10** (3 05 g, 7 75 mmoles) in methanol (60 ml) was treated with sodium metaperiodate (1 65 g, 7 75 mmoles) and sodium borohydride (76 mg, 2 mmoles), as in the preparation of **11**, to give **12** (2 16 g, 76%) as an oil, $[\alpha]_D^{21}$ +30°; $\nu_{max}^{CHCl_3}$ 3410 (OH and NH), 1735 (acetate), and 1657 cm^{-1} (amide) Mass spectrum *m/e* 344 ($M^+ - 15$)

5-O-Acetyl-3-C-(R)-(1-acetamido-2-acetoxyethyl)-3-deoxy-1,2-O-isopropylidene-α-D-ribofuranose (**13**) — Acetylation of **11** (2 15 g) with acetic anhydride–pyridine gave **13** (2 20 g) as an oil, $[\alpha]_D^{20}$ +43°, $\nu_{max}^{CHCl_3}$ 3425 (NH), 1735 (acetate), and 1669 cm^{-1} (amide) Mass spectrum *m/e* 344 ($M^+ - 15$) N m r data τ 3 43 (*d*, $J_{NH,1'}$ 10 Hz, NH), 4 19 (*d*, $J_{1,2}$ 4 Hz, H-1), 5 18 (*t*, $J_{2,1}$ 4, $J_{2\,3}$ 4 Hz, H-2), 5 29–5 54 (*m*, H-1'), 7 75–7 95 (*m*, H-3), 7 93 (*s*, OAc), 8 04 (*s*, NAc), 8 43, 8 65 (2*s*, $2CH_3$)

Anal Calc for $C_{16}H_{25}NO_8$ C, 53 5, H, 7 0, N, 3 9 Found C, 52 9, H, 6 9, N. 3 7 Calc for $C_{15}H_{22}NO_8$ ($M^+ - CH_3$) 344 135 Found 344 137

Acetylation of **12** (2 0 g) gave a product (2 16 g) identical (m s , i r , n m r , $[\alpha]_D$) to **13**

3-C-(R)-(1-Acetamido-2-acetoxyethyl)-1,2,5-tri-O-acetyl-3-deoxy-β-D-ribofuranose (**14**) — A solution of **13** (2 1 g) in a mixture of glacial acetic acid (20 ml) and acetic anhydride (2 ml) was stirred in an ice bath, and conc sulphuric acid (1 ml) was added dropwise The ice bath was removed, and the mixture was kept at 20° for 3 days, and then poured into ice–water (200 ml) and extracted with ethyl acetate (6 × 50 ml) The combined extracts were washed with saturated, aqueous sodium hydrogen carbonate (3 × 50 ml) and water (3 × 50 ml), and the solvent was removed to give impure **14** (1 7 g) Chromatographic purification gave **14** (1 25 g) as an oil which slowly crystallized Recrystallization from hexane gave **14** as colourless plates, m p 112–113°, $[\alpha]_D^{20}$ −10 5°, $\nu_{max}^{CHCl_3}$ 3440 (NH), 1730 (acetate), and 1670 cm^{-1} (amide) Mass spectrum· *m/e* 344 ($M^+ - CH_3CO_2^{\cdot}$) N m r data τ 3 65 (*d*, $J_{NH\,1'}$

9 5 Hz, NH), 3 99 (*s*, H-1), 4 68 (*d*, $J_{2,3}$ 5 Hz, H-2), 7 25–7 50 (*m*, H-3), 7 89 (*s*, OAc), 7 93 (*s*, 3AcO), 8 08 (*s*, NAc)

Anal Calc for $C_{17}H_{25}NO_{10}$ C, 50 6, H, 6 3, N, 3 5 Found C, 50 3, H, 6 0, N, 3 5

Preparation of an anomeric mixture of protected nucleosides **15** — To a solution of **14** (995 mg, 2 47 mmoles) in dry 1,2-dichloroethane (50 ml), bis(trimethylsilyl)-uracil (700 mg, 2 74 mmoles) and tin(IV) chloride (0 25 ml) were added under anhydrous conditions The mixture was stirred at 20° for 4 h and then poured into saturated, aqueous sodium hydrogen carbonate (100 ml) The mixture was filtered through Celite, and the aqueous phase was thoroughly extracted with ethyl acetate (10 × 50 ml) The extracts were combined and the solvent removed to give crude **15** (900 mg) A pure mixture **15** (566 mg, 51%) was obtained as a foam by column chromatography (ethyl acetate–methanol, 10 1), mass spectrum *m/e* 395 ($M^+ - CH_3CO_2H$), 344 (M^+ – base); $\nu_{max}^{CHCl_3}$ 3300 (broad, NH), 1725 (acetate), and 1665 cm^{-1} (amide)

Anal Acc mass calc for $C_{17}H_{21}N_3O_8$ ($M^+ - 60$) 395 133 Found 395 131

*1-[3-C-(R)-(1-Acetamido-2-hydroxyethyl)-3-deoxy-β-*D*-ribofuranosyl]uracil* (**16**) *and 1-[3-C-(R)-(1-acetamido-2-hydroxyethyl)-3-deoxy-α-*D*-ribofuranosyl]uracil* (**17**) — The mixture of protected nucleosides **15** (735 mg, 1 6 mmoles) was refluxed with 0 1M methanolic sodium methoxide (16 ml) for 4 h The solution was cooled, the pH was adjusted to 7 with glacial acetic acid, the solvent was removed, and the residue was chromatographed with 1 1 methanol–ethyl acetate The β-nucleoside **16** was obtained as a foam (144 mg, 27%) which crystallized from methanol as colourless needles, m p 141°, $[\alpha]_D^{20}$ +44°, ν_{max}^{KBr} 3390 (NH and OH) and 1650 cm^{-1} (amide) Electronic spectrum (methanol) log ε_{265} 3 97, log ε_{211} 3 85 O r d (*c* 1 11 × 10^{-4}, 20°, methanol) $[\Phi]_{325}$ 1350, $[\Phi]_{282}$ +14900, $[\Phi]_{270}$ 0, $[\Phi]_{251}$ −21700, $[\Phi]_{211}$ 0, a = +366 C d (*c* 1 11 × 10^{-4}, 20°, methanol) $\Delta\varepsilon$ (295) 0, (267) +7 23, (242) 0 N m r data (methanol-d_4) τ 1 75 (*d*, $J_{6,5}$ 8 Hz, H-6), 4 33 (*s*, H-1'), 4 37 (*d*, $J_{5,6}$ 8 Hz, H-5), 5 60 (*d*, $J_{2',3'}$ 5 Hz, H-2'), 7 39–7 66 (*m*, H-3'), 8 03 (*s* NAc)

Anal Calc for $C_{13}H_{19}N_3O_7 \cdot H_2O$ C, 44 9, H, 6 1, N, 12 1 Found C, 44 7, H, 6 1, N, 12 2

Compound **16** (6 mg) was also treated for 18 h with a mixture of acetic anhydride (1 ml) and pyridine (2 ml), and all solvents were then removed at 20° *in vacuo* Preparative layer chromatography of the residue with chloroform–methanol (9 1) gave a foam (4 mg) identical in chromatographic behaviour and m s to the mixture **15**

Anal Acc mass calc for $C_{17}H_{21}N_3O_8$ ($M^+ - 60$) 395 133 Found 395 133

The α-nucleoside **17** was obtained as a foam (264 mg, 50%), $[\alpha]_D^{20}$ −48°, ν_{max}^{KBr} 3380 (OH and NH) and 1665 cm^{-1} (amide) Electronic spectrum (methanol) log ε_{263} 3 84, log ε_{208} 3 87 O r d (*c* 6 91 × 10^{-4}, 20°, methanol) $[\Phi]_{325}$ 900, $[\Phi]_{285}$ −3750, $[\Phi]_{265}$ 0, $[\Phi]_{258}$ 4200, $[\Phi]_{250}$ 0, $[\Phi]_{225}$ 10400, $[\Phi]_{205}$ 4300, a = −80 C d (*c* 7 05 × 10^{-5}, 20°, methanol) $\Delta\varepsilon$ (295) 0, (274) −1 46, (260) 0, (247) 1.40, (232) 0, (*c* 7.14 × 10^{-4}, 20°, acetonitrile) $\Delta\varepsilon$ (295) 0, (276) −1 11, (267) 0, (249) 2 55, (227) 0, (*c* 2 77 × 10^{-5}, 20°, *p*-dioxane $\Delta\varepsilon$ (298) 0, (275) −1 43, (267) 0, (250) 3 85 N m r

data (methanol-d_4) τ 2 63 (*d*, $J_{6,5}$ 8 Hz, H-6), 3 77 (*d*, $J_{1',2}$ 2 Hz, H-1'), 4 36 (*d*, $J_{5,6}$ 8 Hz, H-5), 6 94–7 16 (*m*, H-3'), 8 00 (*s*, NAc)

Anal Calc for $C_{13}H_{19}N_3O_7$. C, 47.4; H, 5.8, N, 12 8. Found. C, 46.8; H, 6.1, N, 12 2

For analytical purposes, compound **17** (5 mg) was acetylated and the acetate isolated, as described for compound (**16**), to give a foam (3 mg) identical in chromatographic behaviour and m s to the mixture (**15**)

Anal Acc mass calc for $C_{17}H_{21}N_3O_8$ ($M^+ - 60$) 395 133 Found 395 131.

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