C-Nucleoside Studies. Part 23.[1] New and More Direct Synthesis of 3-(β-D-Xylofuranosyl)pyrazole

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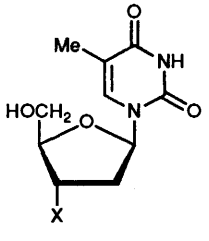
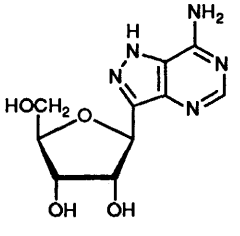
Reaction of 2,3,4-tri-*O*-benzyl-D-xylopyranose **5** with ethynylmagnesium bromide gave the D-*ido*-diol **7** with high stereoselectivity. Diol **7** was converted into its 7-*O*-pivaloyl derivative **9**, which, on treatment with toluene-*p*-sulfonyl chloride in pyridine, underwent cyclization with benzyloxy participation to yield 2,3-di-*O*-benzyl-5-*O*-pivaloyl-β-D-xylofuranosylethyne **10** in 75% yield. A similar reaction sequence involving substrate **5** and the Grignard derivative of 1,1-diethoxyprop-2-yne led to 1-(2,3-di-*O*-benzyl-5-*O*-pivaloyl-β-D-xylofuranosyl)-3,3-diethoxyprop-1-yne **14**, which, on treatment with acetic acid–dil. hydrochloric acid, followed by hydrazine, gave 3(5)-(2,3-di-*O*-benzyl-5-*O*-pivaloyl-β-D-xylofuranosyl)pyrazole **15**. Base treatment of compound **15**, followed by transfer hydrogenation, produced 3(5)-(β-D-xylofuranosyl)pyrazole **4**.

Amongst the many and varied nucleoside analogues that have been synthesized and evaluated in recent years as potential inhibitors of the retroviral reverse transcriptase of the human immunodeficiency virus (HIV) one of the most promising classes consists of cases in which the 3′-hydroxy group of the nucleoside has been replaced by a strongly electron-withdrawing substituent such as azide or fluoride,[2] as exemplified by 3′-azido-3′-deoxythymidine (AZT, **1**) and 3′-deoxy-3′-fluorothymidine **2**. The activity of such compounds against HIV reverse transcriptase has been related to the preferred conformation of the furanose ring, both in solution[3] and in the solid state.[4]



1 X = N_3
2 X = F



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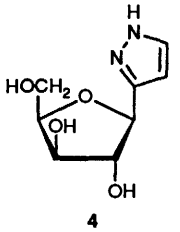

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As part of our programme of research on the synthesis of *C*-nucleoside antibiotics and their analogues, we became interested in the synthesis of nucleosides which combined the features found in the furanose ring of compounds such as **1** and **2** with the type of heterocyclic unit found in bioactive *C*-nucleosides such as formycin **3**. The β-D-xylofuranosylpyrazole **4** was envisaged as a useful potential precursor for such compounds, permitting introduction of electronegative substituents at C-3′ with inversion of configuration, and also structural modification or deoxygenation at C-2′. Furthermore, compound **4** or its sugar-modified analogues should be amenable to the very direct methods that we have recently developed[1] for the double functionalization of the pyrazole ring and the formation of the pyrazolo[4,3-*d*]pyrimidine system found in formycin **3**. Some time ago, we reported a synthesis of 3(5)-(β-D-xylofuranosyl)pyrazole **4**,[5] which was subsequently used, with some slight improvements, for the preparation of the β-D-xylofuranosyl analogue of formycin, using our earlier, less direct methods for functionalization of the pyrazole ring.[6] This route to compound **4**[5,6] suffered, however, from a number of unsatisfactory features, not least that the stereocentre destined to become C-1′ of compound **4** was initially established with the wrong stereochemistry, necessitating an inversion of configuration. In this paper we report a new and more direct route to compound **4**, using 2,3,4-tri-*O*-benzyl-D-xylopyranose **5**[7] as starting material.

It is known that compound **5** reacts with methylmagnesium iodide in diethyl ether to give the D-*ido*-diol **6** (Scheme 1) with high stereoselectivity.[8] We anticipated that, if this sterochemical result proved to be more general, a route to *C*-β-D-xylofuranosyl compounds could be developed; protection of the primary alcohol group of a diol such as **6**, followed by activation of the secondary hydroxy group, should give an intermediate capable of thermal cyclization to a five-membered ring with benzyloxy participation.[9] Our routes to pentofuranosylpyrazoles depend heavily on acetylenic intermediates for construction of the pyrazole ring,[10] and so we initially chose to investigate this approach using ethynylmagnesium bromide as nucleophile.

Therefore, tri-*O*-benzyl-D-xylopyranose **5** was treated with ethynylmagnesium bromide in tetrahydrofuran (THF) to give a diol **7**, which was converted for detailed characterization into its di-*O*-acetyl derivative **8** in 78% overall yield. Both products **7** and **8** appeared to be substantially pure diastereoisomers by NMR spectroscopy, but in the ^{1}H NMR spectra of both compounds the narrow doublet for the ethynyl proton was accompanied by a much weaker doublet at slightly lower field. Integration of these signals indicated an isomer ratio of ~12:1. By analogy with the Japanese work[8] the D-*ido*-geometry **7** is assigned to the major product, although confirmation of this was only obtained subsequently (see below).

This stereoselectivity, in which the newly created chiral centre has a *threo*-relationship with the existing chiral centre at C-2 of the hemiacetal **5**, can be rationalized in terms of the cyclic chelation model **11**, as originally proposed by

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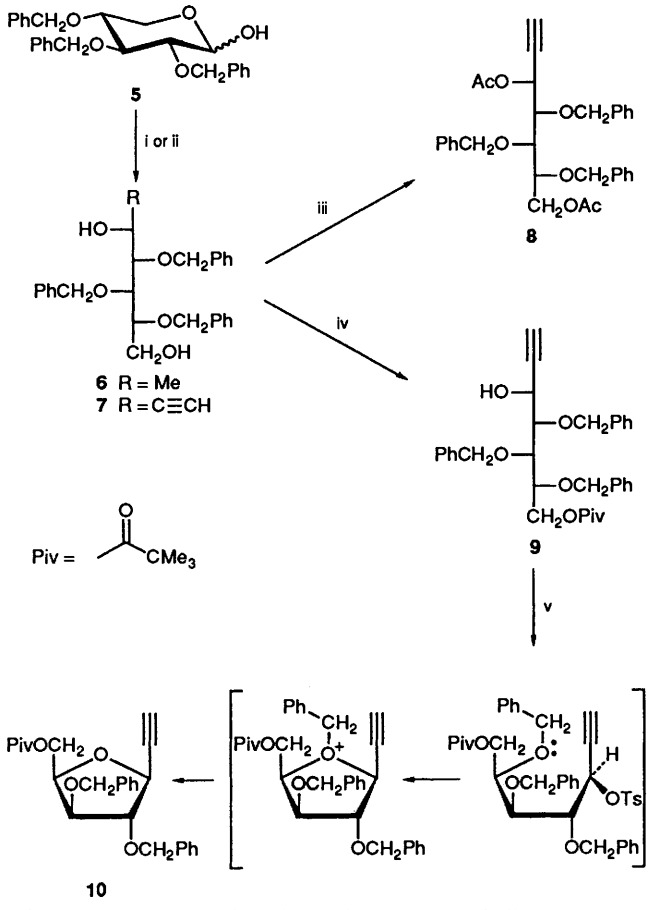
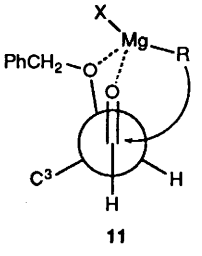


Scheme 1 *Reagents and conditions:* i, MeMgI, Et_2O; ii, HC≡CMgBr, THF; iii, Ac_2O, C_5H_5N; iv, Bu^{t}COCl, C_5H_5N; v, TsCl, C_5H_5N, 70 °C

Cram *et al.*;[11] we have earlier observed similar *threo*-selectivity in additions of Grignard reagents to 2,3,5-tri-*O*-benzyl-D-ribofuranose (although with poorer stereoselectivity in the case of alkynylmagnesium reagents),[10,12] and in the reaction of 2,3,5-tri-*O*-benzyl-D-arabinofuranose with methylmagnesium iodide.[13]



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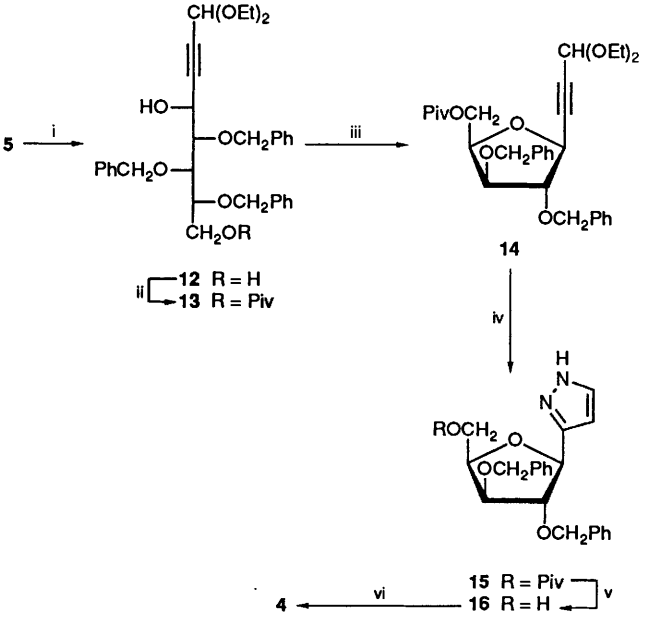
Attempts at the selective benzoylation of the primary alcohol function in diol **7** were unpromising; the reactivity of the propargylic secondary alcohol seemed to be only slightly less than that of the primary alcohol, and substantial quantities of the di-*O*-benzoyl derivative were produced except at low levels of conversion of substrate **7**. Use of the more sterically demanding pivaloyl group was more successful, however, and treatment of diol **7** with one mole equivalent of pivaloyl chloride in pyridine led to the isolation of the monopivaloyl ester **9**, as a pure epimer, in 66% yield after chromatography; a small amount (~10%) of diol was also recovered under these conditions. The correct location of the ester in compound **9** was evident from the ^{1}H NMR spectrum, which showed a downfield shift (~0.7 ppm) for the C-7 methylene group in **9**, as compared with diol **7**. We were gratified to find that treatment of compound **9** with toluene-*p*-sulfonyl chloride in pyridine at 70–80 °C led to the clean formation of a new product which was not a sulfonate, and contained only two benzyloxy groups. This product, isolated in 75% yield, has data in full support of its formulation as the (β-D-xylofuranosyl)ethyne **10**, presumably formed *via* the intermediacy of a toluene-*p*-sulfonate ester, which cyclized spontaneously with *O*-benzyl participation, as outlined in Scheme 1, under the reaction conditions.

In order to permit easy elaboration of a pyrazole ring,[10] a similar reaction sequence was carried out using the Grignard reagent derived from 3,3-diethoxyprop-1-yne.[14] Reaction of tri-*O*-benzyl-D-xylopyranose **5** with this reagent gave diol **12** (Scheme 2) in 93% yield, which appeared by NMR analysis to



Scheme 2 *Reagents and conditions:* i, BrMgC≡CCH(OEt)$_2$, THF; ii, Bu^{t}COCl, C_5H_5N; iii, TsCl, C_5H_5N, 80 °C; iv, HOAc, aq. HCl, then N_2H_4·H_2O; v, NaOMe, MeOH; vi, Pd(OH)$_2$/C, cyclohexene–toluene

be a single isomer. The mono-*O*-pivaloyl derivative **13** was prepared (66%), and, as in the simpler case above, this underwent cyclization on treatment with toluene-*p*-sulfonyl chloride in pyridine at 80 °C to yield the furanose **15** in 80% yield. Mild acid hydrolysis, followed by treatment with hydrazine hydrate, then generated the protected β-D-xylofuranosylpyrazole **15**. Treatment of compound **15** with methanolic sodium methoxide effected a slow but efficient removal of the 5′-*O*-pivaloyl group to give alcohol **16**. All of the intermediates in this sequence appeared to be homogeneous epimers by careful NMR examination. When the di-*O*-benzyl ether **16** was subjected to transfer hydrogenation, 3(5)-(β-D-xylofuranosyl)pyrazole **4** could be isolated after chromatography in 70% yield. The data obtained for compound **4** were in excellent agreement with those reported previously for material obtained by our earlier route.[5] In particular we note the sharp doublet in the ^{1}H NMR spectrum of compound **4** at δ 4.78 (J 3.17 Hz) (lit.,[5] δ 4.78, J 3.5 Hz), assignable to 1′-H. The equivalent signal in the spectrum of the α-anomer of **4** is well removed, appearing at δ 5.26;[5] no signal was observed at this position in samples of compound **4** prepared by our new route. The production of β-anomer **4** by the reaction sequence of Scheme 2 serves to confirm the D-*ido*-stereochemistry of the initial adduct **12**, and, by implication, the stereochemistry of compounds in Scheme 1.

Experimental

IR spectra were recorded on a Perkin-Elmer 1600 FTIR

spectrometer. Mass spectrometry was performed using VG updated MS9 and VG ZAB-E high-resolution EI/CI/FAB instruments. NMR spectra were recorded on a Bruker WP 200 SY spectrometer at a field strength of 200 MHz for ^1H spectra, and 50 MHz for ^{13}C spectra, with $CDCl_3$ as solvent unless otherwise stated. *J*-Values are given in Hz. Specific rotations were measured at room temperature using a Bendix-NPL 143D automatic polarimeter (path length 1 cm); units for $[\alpha]_D$-values are 10^{-1} deg cm^2 g^{-1}.

Column chromatography was carried out using Sorbsil C60; an external pressure was applied to the top of columns. Light petroleum refers to the fraction of boiling range 40–60 °C. Organic extracts were dried over anhydrous sodium sulfate.

3,7-*Di*-O-*acetyl*-4,5,6-*tri*-O-*benzyl*-1,1,2,2-*tetradehydro*-1,2-*dideoxy*-D-ido-*heptitol* **8**.—A solution of ethynylmagnesium bromide in THF (150 cm^3) was prepared from magnesium (4.0 g), ethyl bromide (16 cm^3), and excess of acetylene.[15] A solution of 2,3,4-tri-*O*-benzyl-D-xylopyranose **5** (3.36 g) in THF (50 cm^3) was added during 20 min. Acetylene was passed through the solution during the addition and for a further 1 h. The mixture was stirred overnight, concentrated to 50 cm^3, and partitioned between methylene dichloride (100 cm^3) and aq. ammonium chloride (10%; 200 cm^3). The aqueous phase was extracted with further methylene dichloride (2 × 50 cm^3). The combined organic layers were washed, dried, and evaporated to give a syrup, which was chromatographed on silica with light petroleum–diethyl ether (4:1) as eluent to give the diol **7** (3.55 g) as an oil; δ_H 2.05 (1 H, br t, *J* 6, OH), 2.50 (1 H, d, *J* 2.17, 1-H), 3.08 (1 H, d, *J* 8.5, OH), 3.6–4.0 (5 H, m), 4.52 (1 H, ddd, *J* 8.5, 2.99 and 2.35, 3-H), 4.55–4.95 (6 H, 3 AB systems, *J* ~11, C*H*$_2$Ph) and 7.3 (15 H, m, CH$_2$*Ph*).

A portion of this material (1.5 g), in a mixture of pyridine (10 cm^3) and acetic anhydride (6 cm^3) was stirred at room temperature for 3 h. Water (200 cm^3) was added, and the mixture was extracted with methylene dichloride (2 × 100 cm^3). The dried extracts were evaporated, and the residue was chromatographed on silica with light petroleum–diethyl ether (5:1) as eluent to give *diacetate* **8** (1.40 g, 78%) as an oil, $[\alpha]_D$ −31.6 (*c* 0.95, $CHCl_3$); ν_{max}(film)/cm^{-1} 3279 (≡C–H), 2122 (C≡C) and 1745 (C=O); δ_H 1.99 and 2.01 (each 3 H, s, OAc), 2.47 (1 H, d, *J* 2.1, 1-H), 3.81 (1 H, m) 3.95 (2 H, m), 4.13 (1 H, dd, *J* 12.01 and 5.89, 7-H^a), 4.29 (1 H, dd, *J* 12.02 and 3.60, 7-H^b), 4.62 (2 H, AB system, *J* 11.3, PhC*H*$_2$), 4.72 (2 H, s, PhC*H*$_2$), 4.78 (2 H, AB system, *J* 11.5, PhC*H*$_2$), 5.63 (1 H, dd, $J_{3,4}$ 6.75, $J_{3,1}$ 2.1, 3-H) and 7.3 (15 H, m, *Ph*CH$_2$); δ_C 20.55 and 20.65 (CO*Me*), 63.7 (C-7), 64.7, 72.8 (PhCH$_2$), 74.6 (×2) (PhCH$_2$), 75.2 (C-1), 76.6, 77.4, 79.0 (C-2), 79.4, 169.2 and 170.4 (*C*OMe) (Found: C, 72.1; H, 6.4. $C_{32}H_{34}O_7$ requires C, 72.43; H, 6.46%).

4,5,6-*Tri*-O-*benzyl*-1,1,2,2-*tetradehydro*-1,2-*dideoxy*-7-O-*pivaloyl*-D-ido-*heptitol* **9**.—Pivaloyl chloride (0.125 cm^3, 1 mmol) was added to a solution of diol **7** (0.446 g, 1 mmol) in dry pyridine (2 cm^3). The mixture was stirred at room temperature for 5 h, after which water (5 cm^3) was added. After 1 h, the mixture was partitioned between methylene dichloride and water. The dried organic extracts were evaporated, and the residue was chromatographed on silica, with light petroleum–diethyl ether (4:1) as eluent to give the 7-O-*pivaloyl derivative* **9** (0.353 g, 66%) as an oil, $[\alpha]_D$ −6.8 (*c* 1.18, $CHCl_3$); ν_{max}(film)/cm^{-1} 3460br (OH), 3286 (≡C–H), 2114 (C≡C) and 1728 (C=O); δ_H 1.20 (9 H, s, CMe$_3$), 2.47 (1 H, d, *J* 2.30, 1-H), 2.88 (1 H, d, *J* 8.4, OH), 3.75–3.90 (3 H, m, 4-, 5-, 6-H), 4.25–4.40 (3 H, m, 3-H and 7-H$_2$), 4.5–4.9 (6 H, m, C*H*$_2$Ph) and 7.3 (15 H, m, CH$_2$*Ph*); δ_C 27.1 (C*Me*$_3$), 38.7 (*C*Me$_3$), 62.5, 63.2 (C-7), 72.6 (PhCH$_2$), 73.9 (C-1), 75.0 and 75.1 (PhCH$_2$), 76.7, 78.2, 81.4, 83.1 (C-2) and 178.1 (CO); *m*/*z* 531 (MH$^+$), 530 (M$^+$), 475 (MH$^+$ − C$_4$H$_8$) and 439 (M$^+$ − C$_7$H$_7$) (Found: C, 74.5; H, 7.5. $C_{33}H_{38}O_6$ requires C, 74.69; H, 7.22%).

Further elution of the column with light petroleum–diethyl ether (1:1) gave recovered starting material **7** (45 mg, 10%).

2,3-*Di*-O-*benzyl*-5-O-*pivaloyl*-β-D-*xylofuranosylethyne* (2,5-*Anhydro*-3,4-*di*-O-*benzyl*-6,6,7,7-*tetradehydro*-6,7-*dideoxy*-1-*O*-*pivaloyl*-L-gluco-*heptitol*) **10**.—A solution of monoester **9** (0.746 g, 1.4 mmol) and toluene-*p*-sulfonyl chloride (0.683 g, 3.5 mmol) in pyridine (10 cm^3) was stirred at 70–80 °C for 8 h, and then at room temperature overnight. The mixture was evaporated under reduced pressure and the residue was chromatographed on silica, with light petroleum–diethyl ether (4:1) as eluent to give the *xylofuranosylethyne* **10** (0.444 g, 75%) as an oil, $[\alpha]_D$ −17.4 (*c* 2.7, $CHCl_3$); ν_{max}(film)/cm^{-1} 3285 (≡C–H), 2122 (C≡C) and 1727 (C=O); δ_H 1.20 (9 H, s, CMe$_3$), 2.59 (1 H, d, *J* 2.25, ≡CH), 4.02 (1 H, dd, *J* 4.30 and 1.87), 4.15–4.7 (9 H, m) and 7.35 (10 H, m, Ph); δ_C 27.1 (C*Me*$_3$), 38.6 (*C*Me$_3$), 62.6 (furanosyl C-5'), 71.7 and 72.1 (*C*H$_2$Ph), 72.6, 74.8 (≡CH), 79.1, 81.2 (*C*≡CH), 82.6, 87.4 and 178.1 (CO) (Found: C, 74.1; H, 7.0. $C_{26}H_{30}O_5$ requires C, 73.91; H, 7.16%).

5,6,7-*Tri*-O-*benzyl*-2,2,3,3-*tetradehydro*-2,3-*dideoxy*-D-ido-*octose Diethyl Acetal* **12**.—To a stirred solution of ethylmagnesium bromide [from magnesium (0.5 g) and ethyl bromide (2.25 cm^3)] in THF (50 cm^3) at 50–60 °C was added dropwise a solution of 3,3-diethoxyprop-1-yne[14] (2.56 g) in THF (20 cm^3). The mixture was maintained at ~60 °C for 1 h, after which a solution of 2,3,4-tri-*O*-benzyl-D-xylopyranose **5** (1.68 g) in THF (50 cm^3) was added during 15 min. After 10 h at ~60 °C and a further 24 h at room temperature, the mixture was evaporated and the residue was partitioned between chloroform (50 cm^3) and aq. ammonium chloride (10%; 100 cm^3). The organic layer was washed with brine, dried, and evaporated to give a residue, which, on chromatography on silica, with light petroleum–diethyl ether (1:1) as eluent, gave *diol* **12** (2.04 g, 93%) as an oil, $[\alpha]_D$ +0.9 (*c* 1.06, $CHCl_3$); ν_{max}(film)/cm^{-1} 3439 br (OH) and 2241 (C≡C); δ_H 1.22 (6 H, 2 t, *J* 7, OCH$_2$*Me*), 2.1 (1 H, br s, CH$_2$O*H*), 3.05 (1 H, d, *J* 7, CHO*H*), 3.5–4.0 (9 H, m), 4.5–4.9 (6 H, 3AB doublets, *J* ~11.5, C*H*$_2$Ph), 4.6 (1 H, m, C*H*OH), 5.30 (1 H, d, *J* 1.26, 1-H) and 7.3 (15 H, m, Ph); δ_C 14.9 (Me), 60.8 (O*C*H$_2$Me), 61.3 (C-8), 62.4, 72.5 (*C*H$_2$Ph), 74.9 (2 × *C*H$_2$Ph), 78.8, 78.9, 81.0 (C≡C), 81.3, 84.7 (C≡C), 91.3 (C-1); *m*/*z* (FAB) 571 (M$^+$ + Na) and 503 (M$^+$ − OEt) (Found: C, 72.0; H, 7.3. $C_{33}H_{40}O_7$ requires C, 72.24; H, 7.35%).

5,6,7-*Tri*-O-*benzyl*-2,2,3,3-*tetradehydro*-2,3-*dideoxy*-8-O-*pivaloyl*-D-ido-*octose Diethyl Acetal* **13**.—A solution of pivaloyl chloride (0.57 cm^3, 4.56 mmol) and diol **12** (2.50 g, 4.56 mmol) in pyridine (20 cm^3) was stirred at room temperature for 18 h, after which the mixture was added to a mixture of water (50 cm^3) and methylene dichloride (50 cm^3). The aqueous phase was extracted with further methylene dichloride (50 cm^3), and the dried organic layers were evaporated to give a syrup, which was chromatographed on silica, with light petroleum–diethyl ether (7:3) as eluent, to give *monoester* **13** (1.91 g, 66%) as a syrup, $[\alpha]_D$ −4.5 (*c* 1.12, $CHCl_3$); ν_{max}(film)/cm^{-1} 3447br (OH) and 1729 (C=O); δ_H 1.2 (15 H, m, CMe$_3$, OCH$_2$*Me*), 2.85 (1 H, d, *J* 5, CHO*H*), 3.4–3.9 (7 H, m), 4.3 (2 H, m, 8-H$_2$), 4.42 (1 H, br d, *J* 5, 4-H), 4.5–4.9 (6 H, 3 AB doublets, *J* ~12, C*H*$_2$Ph), 5.29 (1 H, d, *J* 1.5, 1-H) and 7.3 (15 H, m, CH$_2$*Ph*); δ_C 14.9 (CH$_2$*Me*), 27.1 (C*Me*$_3$), 38.6 (*C*Me$_3$), 60.8 (O*C*H$_2$Me), 62.4, 63.3 (C-8), 72.5, 74.9 and 75.0 (*C*H$_2$Ph), 76.6, 78.2, 81.1 (C≡C), 81.4, 84.5 (C≡C), 91.2 (C-1) and 178.0 (CO) [Found: (M$^+$ − OEt) (FAB) 587.3009. $C_{36}H_{43}O_7$ requires *m*/*z* 587.3009].

Further elution of the column led to recovery of starting material **12** (0.275 g, 11%).

1-(2,3-*Di*-O-*benzyl*-5-O-*pivaloyl*-β-D-*xylofuranosyl*)-3,3-*diethoxyprop*-1-*yne* (4,8-*Anhydro*-5,6-*di*-O-*benzyl*-2,2,3,3-*tetradehydro*-2,3-*dideoxy*-8-O-*pivaloyl*-D-gulo-*octose Diethyl Acetal*) **14**.—A solution of monoester **13** (1.99 g, 3.15 mmol) and toluene-*p*-sulfonyl chloride (2.46 g, 12.6 mmol) in pyridine (15 cm^3) was stirred at 80 °C for 5 h, and then evaporated to dryness. The residue was chromatographed on silica, with light petroleum–diethyl ether (8:1) as eluent, to yield the *xylofuranosyl alkyne* **14** (1.33 g, 80%) as an oil, $[\alpha]_D$ −26.4 (*c* 0.99, $CHCl_3$); ν_{max}(film)/cm^{-1} 2245 (C≡C) and 1729 (C=O); δ_H 1.2 (15 H, m, CMe_3, OCH_2Me), 3.45–3.80 (4 H, m, OCH_2Me), 4.02 (1 H, dd, *J* 4.3 and 1.7), 4.15–4.65 (9 H, m), 5.28 (1 H, d, *J* 1.34, 1-H) and 7.3 (10 H, m, CH_2Ph); δ_C 15.0 (OCH_2Me), 27.1 (CMe_3), 38.6 (CMe_3), 60.8 and 60.95 (OCH_2Me), 62.2 (furanosyl C-5′), 71.8 and 72.1 (CH_2Ph), 72.6, 79.1, 82.0 (C≡C), 82.7, 87.2, 91.3 (C-1) and 178.2 (CO) [Found: (M^+ − OEt) (FAB) 479.2434. $C_{29}H_{35}O_6$ requires *m/z* 479.2434].

3(5)-(2′,3′-*Di*-O-*benzyl*-5′-O-*pivaloyl*-β-D-*xylofuranosyl*)*pyrazole* **15**.—A solution of acetal **14** (1.78 g) in a mixture of glacial acetic acid (45 cm^3) and aq. hydrochloric acid (2 mol dm^{-3}; 15 cm^3) was maintained at room temperature for 0.5 h. A solution of hydrazine hydrate (3 cm^3) in acetic acid (30 cm^3) was added dropwise, and the mixture was heated under reflux for 2 h, cooled, and partitioned between water (70 cm^3) and methylene dichloride (2 × 50 cm^3). The dried organic extracts were evaporated and the residue was chromatographed on silica, with light petroleum–diethyl ether (1:1) as eluent, to yield the *pyrazole* **15** (1.03 g, 65%) as a syrup, $[\alpha]_D$ −29.5 (*c* 1.09, $CHCl_3$); ν_{max}/cm^{-1} 3317br (NH) and 1728 (C=O); δ_H 1.2 (9 H, s, CMe_3), 4.06 (1 H, dd, $J_{3',4'}$ 3.35, $J_{3',2'}$ 1.21, 3′-H), 4.14 (1 H, dd, $J_{2',1'}$ 2.50, $J_{2',3'}$ 1.26, 2′-H), 4.3–4.65 (7 H, m), 5.10 (1 H, d, $J_{1',2'}$ 2.49, 1′-H), 6.22 (1 H, br s, 4-H), 7.3 (10 H, m, Ph) and 7.49 (1 H, d, *J* 2.0, 5-H); δ_C 27.2 (CMe_3), 38.7 (CMe_3), 62.6 (C-5′), 71.9 and 72.0 (CH_2Ph), 79.5 (×2), 82.7, 86.9, 103.4 (C-4), 135.4 (C-5), 146.1 (C-3) and 178.7 (CO) (Found: C, 69.7; H, 7.1; N, 6.1. $C_{27}H_{32}N_2O_5$ requires C, 69.81; H, 6.94; N, 6.03%).

3(5)-(2′,3′-*Di*-O-*benzyl*-β-D-*xylofuranosyl*)*pyrazole* **16**.—A solution of pivalate **15** (0.8 g) in methanolic sodium methoxide (0.1 mol dm^{-3}; 30 cm^3) was stirred at room temperature for 2 days and then evaporated to dryness. Chromatography of the residue on silica, with methylene dichloride–methanol (99:1) as eluent, gave *alcohol* **16** (0.526 g, 80%) as a syrup, $[\alpha]_D$ −25.0 (*c* 1.0, $CHCl_3$); ν_{max}(film)/cm^{-1} 3280br (OH, NH); δ_H 3.90 (1 H, dd, *J* 12.2 and 4.07, 5′-H[a]), 3.97 (1 H, dd, *J* 12.2 and 4.45, 5′-H[b]), 4.15–4.3 (3 H, m), 4.49 (2 H, AB system, *J* 11.85, CH_2Ph), 4.54 (2 H, s, CH_2Ph), 5.08 (1 H, d, *J* 3.82, 1′-H), 5.7 (1 H, br s, OH), 6.25 (1 H, br s, 4-H), 7.3 (10 H, m, Ph) and 7.48 (1 H, br s, 5-H); δ_C 61.5 (C-5′), 72.0 (2 × CH_2Ph), 78.6, 81.1, 83.7, 87.6, 103.2 (C-4), 134.4 (C-5) and 147.1 (C-3) [Found: MH^+ (FAB) 381.1814. $C_{22}H_{25}N_2O_4$ requires *m/z*, 381.1814].

3(5)-(β-D-*Xylofuranosyl*)*pyrazole* **4**.—A solution of the bis-(benzyl ether) **16** (0.36 g) in a mixture of toluene (15 cm^3) and cyclohexene (8 cm^3) was heated under reflux in the presence of $Pd(OH)_2$-on-carbon (50 mg) for 3 h. After addition of ethanol (30 cm^3) the mixture was filtered through Celite, which was washed well with further ethanol. The residue obtained after evaporation of the combined filtrate and washings was chromatographed on silica, with methylene dichloride–methanol (20:1–10:1) as eluent, to give 3(5)-(β-D-xylofuranosyl)pyrazole **4** (0.132 g, 70%) as a syrup, $[\alpha]_D$ −24.8 (*c* 0.52, water) [lit.,[5] −33.1 (*c* 0.69, water)]; δ_H[$(CD_3)_2CO$ + D_2O] 3.75 (1 H, dd, *J* 12.0 and 6.50, 5′-H[a]), 3.82 (1 H, dd, *J* 12.0 and 4.15, 5′-H[b]), 4.1–4.2 (2 H, m, 3′- and 4′-H), 4.23 (1 H, dd, $J_{2',1'}$ 3.14, $J_{2',3'}$ 1.73, 2′-H), 4.78 (1 H, d, *J* 3.17, 1′-H), 6.28 (1 H, d, *J* 2.3, 4-H) and 7.53 (1 H, br d, *J* ~2, 5-H); δ_C (D_2O) 60.0 (C-5′), 76.8, 79.0, 80.9, 81.6, 103.2 (C-4), 132.2 (C-5) and 148.3 (C-3).

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