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STUDIES ON THE INTERCONVERSION OF 2,3′-ANHYDRO-1-β-D-XYLOFURANOSYLURACIL AND 2,2′-ANHYDRO-1-β-D-ARABINOFURANOSYLURACIL*

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ABSTRACT

2,3′-Anhydro-1-β-D-xylofuranosyluracil (**10**) is converted, reversibly, into 2,2′-anhydro-1-β-D-arabinofuranosyluracil (**1**) in the presence of sodium *tert*-butoxide. The reaction probably involves 2′,3′-anhydrouridine as an intermediate and equilibrium is strongly in favour of **1**. The behaviour of **1** and **10** towards sodium hydroxide and sodium methoxide is described. Reaction of 3-azido-3-deoxy-2,5-di-*O*-*p*-nitrobenzoyl-β-D-xylofuranosyl chloride with monochloromercuri-4-ethoxy-2(1*H*)-pyrimidinone afforded crystalline 1-(3-azido-3-deoxy-2,5-di-*O*-*p*-nitrobenzoyl-β-D-xylofuranosyl)uracil (**24**) in 57% yield. Alkaline methanolysis of **24** gave crystalline 1-(3-azido-3-deoxy-β-D-xylofuranosyl)uracil, which yielded 1-(3-amino-3-deoxy-β-D-xylofuranosyl)uracil (**27**) on hydrogenation. Deamination of **27** with nitrous acid gave mainly uracil (55%) and not the epoxide **5** or compounds derived from it.

INTRODUCTION

Anhydronucleosides[1] have played an important part in nucleoside chemistry, both in structure determination and in synthesis[2,3]. In the pyrimidine nucleoside series, the use of anhydro derivatives involving the C-2 carbonyl oxygen atom has enabled isomeric β-D-pentofuranosyl[4–7] and deoxy-β-D-pentofuranosyl[8–10] derivatives, as well as unsaturated nucleosides[11] and L-nucleosides[12] to be prepared. The use of pyrimidine anhydronucleosides in synthesis has been reviewed by Fox[13].

For a number of years we have studied epoxide rearrangements involving intramolecular ring-opening[14,15]. We became interested in 2′,3′-anhydrouridine (**5**), which had been proposed by Brown, Todd, and their co-workers[9] as an intermediate when 2,2′-anhydro-1-β-D-arabinofuranosyluracil (**1**) was treated with a large excess of sodium thioethoxide in *N*,*N*-dimethylformamide. The product was the ethylthio ether **6**, which was desulphurized with Raney nickel to give 3′-deoxyuridine (**7**). It

*Dedicated to Professor K. Heyns, on the occasion of his 70th birthday.

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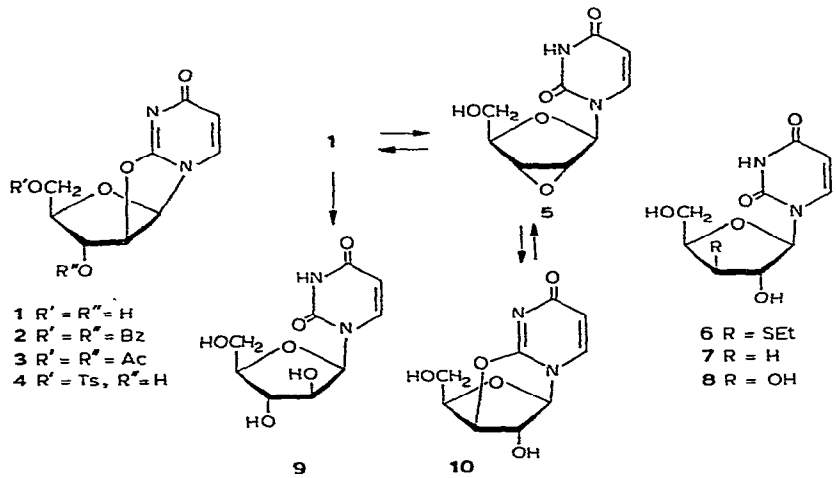
was suggested that **5** arose by nucleophilic attack of the 3′-oxyanion from **1** on C-2′, causing opening of the oxazolidine ring. The regioselectivity of attack by thioethoxide ion on the epoxide ring of **5** was that to be expected from the behaviour of other



2,3-anhydro-β-D-ribofuranosyl derivatives[16,17]. The thioether **6** has since been prepared by two other groups of investigators[18,19]. The epoxide **5** has also been proposed as an intermediate in a number of other reactions[6,22–22]. It appears to be unstable and readily converted into the 2,2′-anhydride **1**, probably by a reversible reaction whose equilibrium is strongly in favour of **1** (see also refs. 23 and 24).

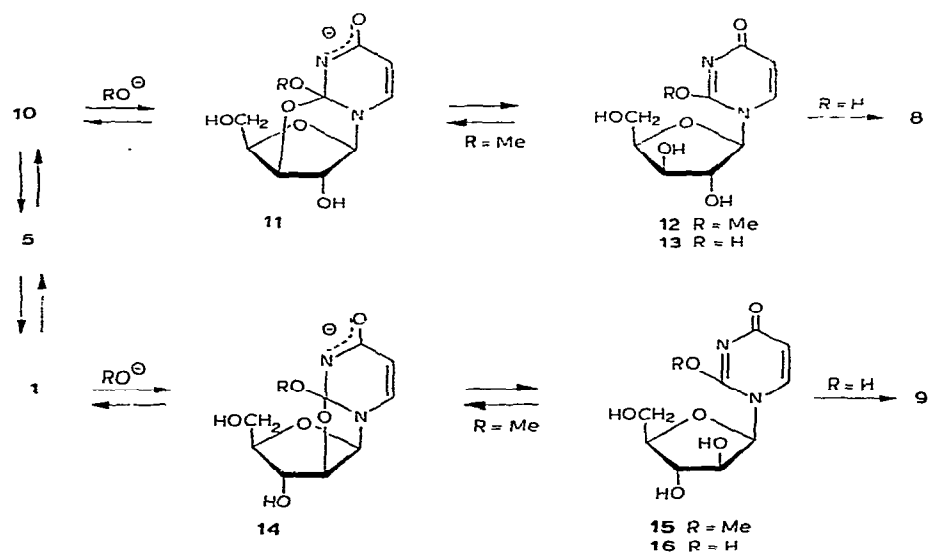
We were interested in the possibility that **5**, and hence **1**, might be formed by alkaline treatment of 2,3′-anhydro-1-β-D-xylofuranosyluracil[25,26] (**10**). Yung and Fox[26] showed that the 2′,5′-dibenzoate of **10** rearranges into the 3′,5′-dibenzoate (**2**) of **1** at the melting point, and Kowollik *et al.*[27] have found that **10** rearranges into **1** during reaction of **10** with hydrogen fluoride in 1,4-dioxane at 150° in the presence of aluminium trifluoride. We have tried, unsuccessfully, to prepare the epoxide **5** itself.

RESULTS AND DISCUSSION

When the anhydronucleoside **1** was treated with 0.01M aqueous sodium hydroxide, reaction was complete after 1 h at room temperature (change in u.v. spectrum of the solution). The product was examined by paper chromatography and electrophoresis in borate buffer[6,28] at pH 6, and shown to consist only of the arabinoside **9**. Under the same conditions, the 2,3′-anhydride **10** reacted more slowly (~40 h) and gave the xyloside **8** and arabinoside **9** in the ratio 97:3. In both of these reactions, attack by hydroxyl ion at C-2 takes place, followed by opening of the anhydride ring. In the case of **10**, a very small amount of conversion to the 2,2′-anhydride **1** took place.

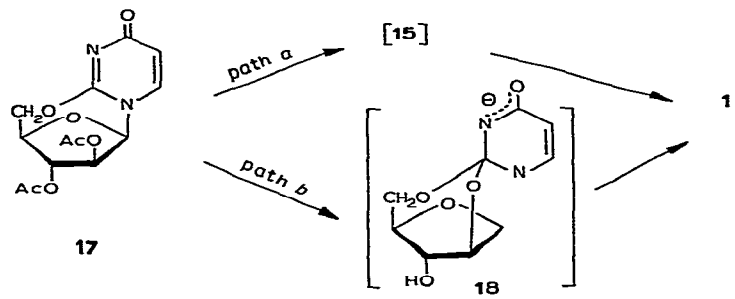
Fox and associates[6] reported that the dibenzoate (**2**) of **1**, when treated with aqueous alcoholic sodium hydroxide, gave a mixture of **8** and **9**. When we repeated this experiment, using **2** or the diacetate **3**, we found only the arabinoside **9** to have been formed. In order to prevent attack at C-2, and thereby encourage the interconversion of **10** and **1**, sodium *tert*-butoxide in *N*,*N*-dimethylformamide was used as the base. After 3 days at 100°, in the presence of 2.2 mol. equiv. of base, **10** was converted into a mixture of anhydronucleosides, nucleosides, and some uracil. Fractionation allowed the isolation of crystalline arabinoside **9** and anhydroarabinoside **1**, while chromatographic and electrophoretic evidence was obtained for the presence of unreacted **10** and the xyloside **8**. The free nucleosides clearly arose from traces of water, which are very difficult to exclude. Treatment of **1** under comparable conditions gave no indication of formation of **10** or **8**, but when the reaction was carried out at 130° some xyloside **8** was detected by electrophoresis. The interconversion of **1** and **10** has thus been established, with the equilibrium strongly in favour of **1**.

The anhydronucleosides **10** and **1** were also treated with sodium methoxide (~1 mol. equiv.) in boiling methanol. After 4 h, **10** was converted into a mixture containing **10**, **1**, **8**, **9**, and a compound with properties consistent with the structure 2-*O*-methyl-1-β-D-xylofuranosyluracil (**12**). The latter gave only **8** on alkaline hydrolysis[29], and **8**, together with a trace of uracil, on acid hydrolysis[29].

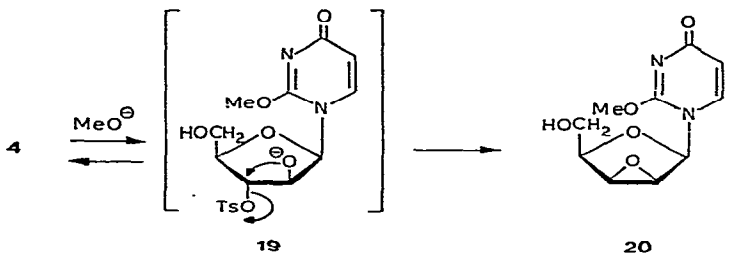


When **1** was treated with the same reagent for 1 h, it was unaffected. More prolonged reaction (48 h) gave arabinoside **9**, whose origin is discussed below, as the major product. This result must be contrasted with the lability of **1** towards aqueous alkali previously described, and may be explained by considering the sequence

1 ⇄ **14** ⇄ **15**. If this sequence is reversible, with an equilibrium strongly in favour of **1**, then no evidence for the formation of **15** would be forthcoming. When aqueous alkali is used, however, **16**, the intermediate corresponding to **15**, can readily undergo tautomeric change with formation of the arabinoside **9**. The formation of arabinoside **9** after prolonged treatment of **1** with sodium methoxide may be due to traces of water, but may also be due to nucleophilic attack by methoxide ion on the methyl group in **15**, present in very small equilibrium concentration.



Hirata[30] found that treatment of the 2,5′-anhydride **17** with methanol containing triethylamine gave **1**, either *via* **15** (path *a*)[29,30], or directly *via* the intermediate **18** (path *b*)*. Hirata[31] also showed that the 2-*O*-methyl derivative **20**



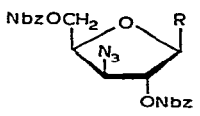
resulted when the sulphonate **4** was treated with sodium methoxide in methanol at room temperature. In this case, although the methoxyl group in **19** is probably unstable, it is "trapped" by formation of the D-*lyxo* epoxide **20**.

A similar argument applies to the ring-opening sequence **10** ⇄ **11** ⇄ **12**. This is probably reversible, but with aqueous alkali, **13**, the intermediate corresponding to **12**, is converted irreversibly into the D-xylofuranoside **8**.

We wished to synthesise the D-*ribo* epoxide **5**. Methods involving the treatment of a D-*arabino* 2′-sulphonate or a D-*xylo* 3′-sulphonate with base were clearly unsuitable. In a previous paper[32] we showed that treatment of methyl 3-amino-3-

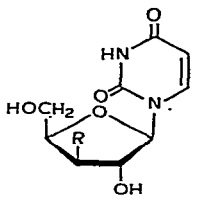
*We are grateful to referees who have pointed out this possibility.

deoxy-β-D-xylofuranoside with nitrous acid under mild conditions gave methyl 2,3-anhydro-β-D-ribofuranoside in 63% yield. It was hoped that a similar reaction could be carried out in the uracil series, and we therefore prepared the 3′-amino-3′-deoxy nucleoside **27**.



21 R = OMe
22 R = OAc
23 R = Cl
24 R = Uracil-1-yl
25 R = OH (α,β)

Nbz = p-$NO_2C_6H_4CO$

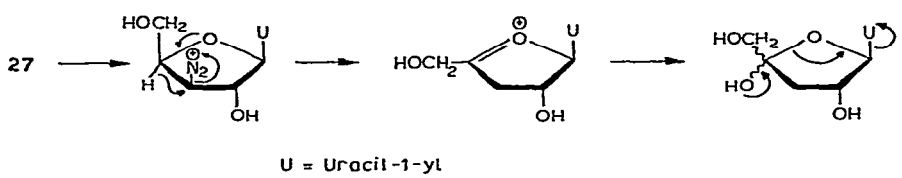


26 R = N_3
27 R = NH_2

The D-*xylo* azide[32] **21** was converted, by acetolysis, into the crystalline β-acetate **22** in 80% yield. The β-D configuration was assigned[33] from the ^{1}H-n.m.r. spectrum by comparison with that of the other anomer present in the mother liquors. When **22** was treated with hydrogen chloride in dichloromethane and ether, the crystalline chloride **23** was isolated in 77% yield. Attention to detail was necessary in order to avoid contamination of **23** with unreacted **22**, which had very similar solubility properties.

The pentosyl chloride **23** was treated with monochloromercuri-4-ethoxy-2(1*H*)-pyrimidinone[34] in boiling xylene to give the crystalline, blocked nucleoside **24** (57%) together with the free sugar **25** (13%). It is noteworthy that the uracil derivative **24**, rather than the 4-ethoxy compound, was obtained directly from the processed reaction mixture. Alkaline methanolysis of the ester groups afforded crystalline 1-(3-azido-3-deoxy-1-β-D-xylofuranosyl)uracil (**26**) (81%). Hydrogenolysis of **26** gave the chromatographically homogeneous amine **27** which did not crystallise.

Deamination of **27** in aqueous acetic acid gave uracil (55%) as the only identified product. There was no evidence for the presence of **5** or the derived com-



U = Uracil-1-yl

Scheme 1

pounds **1** and **9**. A possible mechanism for the formation of uracil is shown in Scheme 1 (*cf.* ref. 35). The conformation of **27** probably differs from that of methyl .

3-amino-3-deoxy-β-D-xylofuranoside[32], owing to the lack of anomeric effect in **27** and the greater steric bulk of a uracil residue. In reactions of low activation energy, such as deaminations, ground-state conformations can play an important role in determining the products[32,36].

Recently, Ueda *et al.*[37] have prepared the episulphide corresponding to **5** and have found it to be stable towards methanolic sodium methoxide at room temperature. Although this may seem surprising, it is known that 2,3-anhydrohexoses and their glycosides easily undergo intramolecular rearrangement[38], whereas the corresponding episulphides are more stable[39].

TABLE I

PAPER CHROMATOGRAPHY AND ELECTROPHORESIS OF URACIL DERIVATIVES

Compound	R_F *values*		*Mobility (cm)*[a]
	Solvent A	*Solvent* B	
1	0.13	0.40	
8	0.32	0.38	+7.2
9	0.34	0.40	−6.4
10	0.10	0.37	
12	0.16	0.44	+7.3
26	0.77	0.52	
Uracil	0.40	0.43	−6.5
Uridine	0.25	0.35	+13.3

[a]Sodium borate buffer (pH 6.00–6.05) at 1200 v for 5 h (*cf.* refs. 5 and 25).

EXPERIMENTAL

General methods.— See ref. 32. U.v. spectra were recorded with a Unicam SP800 spectrophotometer at 1-cm path length. The following solvents were used for paper chromatography (p.c.): (*A*) 2-butanone saturated with water (pre-equilibration of the paper with solvent vapour was desirable); (*B*) 1-butanol–acetic acid–water (5:2.3, v/v); and (*C*) ethyl acetate–pyridine–water–acetic acid (5:5:3:1, v/v) in the trough and ethyl acetate–pyridine–water (40:11:6, v/v) in the tank[40].

Paper electrophoresis of nucleosides was carried out[28] on Whatman 3MM paper in sodium borate buffer solution (pH 6.00–6.05) in a Shandon water-cooled apparatus at 1200 v for 5 h. Unless stated otherwise, identification of **8** and **9** was made by comparison with the authentic compounds by use of p.c., electrophoresis, and u.v. spectra.

2,2′-Anhydro-1-β-D-arabinofuranosyluracil[41] (**1**) and 2,3′-anhydro-1-β-D-xylofuranosyluracil[26] (**10**) were prepared from uridine by the methods cited.

Reactions of anhydronucleosides **1** *and* **10** *under basic conditions. — Reaction of* **1** *with 0.01M sodium hydroxide.* Compound **1** (17.9 mg) in 0.01M sodium hydroxide (500 ml) was kept at room temperature for 1 h, the time taken for a sample to show a constant u.v. spectrum (λ_{max} 263 nm). The solution was de-ionised with Dowex 50 (H^+) resin, the eluate evaporated to dryness, and the residue crystallised from ethanol to give the arabinoside **9**, m.p. 217–219°, indistinguishable from an authentic sample. Examination of the mother liquors by p.c. and electrophoresis revealed only **9**.

Reaction of **10** *with 0.01M sodium hydroxide.* A similar reaction using **10** (18.2 mg) in 0.01M aqueous sodium hydroxide (500 ml) required 40 h for completion. Isolation of the product using Dowex 50 (H^+) resin afforded a residue that was dissolved in water (0.5 ml) and subjected to preparative p.c. (solvent *A*). A trace of starting material (~5%) was present and the free nucleoside product (R_F 0.33) was eluted and examined by electrophoresis. The major product was the xyloside **8** together with **9**, in the ratio 97:3. Identification was made by comparison with authentic[6] **8**.

Reactions of **2** *and* **3** *with aqueous, alcoholic sodium hydroxide.* The dibenzoate **2** (12 mg) in a mixture of ethanol and 1.1M sodium hydroxide[6] (3:2, 1.6 ml) was heated under reflux for 30 min. After being cooled, the mixture was neutralised with Dowex 50 (H^+) resin, the resin removed by filtration, and the residue examined by p.c. (solvent *A*) and electrophoresis. Only **9** could be detected (λ_{max} 263 nm).

A similar reaction using the diacetate[4,2] **3** (12.5 mg) gave **9** as the only product.

Reaction of **1** *with sodium* tert-*butoxide in* N,N-*dimethylformamide.* Compound **1** (30 mg) in *N,N*-dimethylformamide (1.5 ml) containing sodium *tert*-butoxide (32 mg, 2.5 mol. equiv.) was heated at 130° for 2 days. The solvent was removed by evaporation and Dowex 50 (NH_4^+) resin and water (5 ml) were added to the residue. After filtration from resin, the filtrate was examined by p.c. (solvent *A*). Anhydronucleoside, nucleoside, and a trace of uracil were detected. The remainder was subjected to preparative p.c., followed by elution of each area. The nucleosides were shown, by electrophoresis, to be a mixture of **9** and **8** (8:1). The anhydronucleosides were subjected to acid hydrolysis (0.05M sulphuric acid, 4 h, 100°). Electrophoresis showed the presence of **9** and a trace of **8**.

Reaction of **10** *with sodium* tert-*butoxide in* N,N-*dimethylformamide.* Compound **10** (90 mg) in *N,N*-dimethylformamide (5 ml) containing sodium *tert*-butoxide (85 mg, 2.2 mol. equiv.) was heated at 100° for 2 days. After evaporation to dryness, the mixture was treated with Dowex 50 (NH_4^+) resin and water (15 ml). The filtrate after removal of the resin was evaporated to give a residue that crystallised from ethanol to give **9** (43 mg, 45%), m.p. 217–218°, indistinguishable from an authentic sample (i.r., mixed m.p., p.c., and electrophoresis). The mother liquors were evaporated to dryness, and the residue dissolved in water (0.5 ml). Preparative p.c. (solvent *A*) showed the presence of four components, *viz.*, two anhydronucleosides, free nucleoside, and uracil (λ_{max} 259 nm). Paper electrophoresis of the eluted nucleoside area showed **9** and **8** in the ratio 3:1. The band corresponding to **1** was eluted with water to give, after evaporation, a residue (18 mg) that crystallised from ethanol,

yielding **1** (7 mg, 8%), m.p. 230–234°, indistinguishable from an authentic sample (i.r., u.v., mixed m.p., and hydrolysis with acid to give **9**).

Reaction of **10** *with sodium methoxide in methanol.* Compound **10** (40 mg) was heated under reflux in dry methanol (3 ml) containing sodium methoxide (from 4.5 mg of Na, 1.1 mol. equiv.) for 4 h. The cool reaction mixture was passed through a short column of Amberlite IRC 50 (H^+) resin. The neutral eluate was examined by p.c. in solvent *A*, which showed **10**, **1** (both confirmed by u.v. spectra), free nucleoside, and probably 2-*O*-methyl-1-β-D-xylofuranosyluracil (**12**) in the approximate ratio 2:1:2:4. The free nucleoside spot was eluted with water and examined electrophoretically; **9** and **8** were present (1:2). The u.v. spectrum of suspected **12** in water showed λ_{max} 299, 252, and 270 (sh); λ_{min} 239 nm; (2-*O*-methyluridine[29] shows λ_{max} 229, 249; λ_{min} 237.5 nm). Hydrolysis in dilute, aqueous alkali yielded only **8**, and hydrolysis in dilute aqueous acid gave **8** and a trace of uracil.

Reaction of **1** *with sodium methoxide in methanol.* Compound **1** (20 mg) in methanol (1.1 ml) containing sodium methoxide (from 2.2 mg of Na, 1.1 mol. equiv.) was heated under reflux for 1 h. On cooling, **1** crystallised out and was identified (p.c., u.v.) as such. Examination of the mother liquors by p.c. showed the presence only of **1**.

A similar reaction using **1** (33 mg), methanol (3 ml), and sodium (9 mg) was heated under reflux for 48 h. After being cooled, the solution was passed through Amberlite CG 50 (H^+) resin and the filtrate evaporated to dryness. From aqueous methanol, **9** crystallised, m.p. 221°; its identity was confirmed by p.c. and electrophoresis.

1-O-*Acetyl-3-azido-3-deoxy-2,5-di*-O-p-*nitrobenzoyl-β*-D-*xylofuranose* (**22**). — The methyl glycoside[32] **21** (2.60 g) was dissolved in glacial acetic acid (20 ml) and acetic anhydride (2.15 ml). To the ice-cold solution was added, dropwise, sulphuric acid (96%, 0.69 ml) with ice-cooling, keeping the temperature below 10°. After 22 h at room temperature, crystals had separated. The reaction mixture was diluted with ice-water (100 ml) and extracted with chloroform (3 × 40 ml). The combined extracts were washed with aqueous sodium hydrogencarbonate and water, dried (sodium sulfate), and the filtered solution evaporated to dryness. The syrupy residue was crystallised twice from benzene–ether to give the acetate **22** (2.21 g, 80%), m.p. 155–157°, $[\alpha]_D^{21}$ −9° (*c* 0.8, chloroform); n.m.r. (60 MHz, $CDCl_3$): τ 1.80 (s, 8 H, Ar), 3.63 (s, 1 H, H-1), 4.40 (d, 1 H, $J_{2,3}$ 1.0 Hz, H-2), 5.33 (m, 4 H), and 7.84 (s, 3 H, OAc).

Anal. Calc. for $C_{21}H_{17}N_5O_{11}$: C, 48.90; H, 3.30; N, 13.58. Found: C, 48.87; H, 3.60; N, 13.52.

The n.m.r. spectrum (60 MHz, $CDCl_3$) of the evaporated mother liquors (0.48 g, 17%) showed, by quantitative integration of the H-1 and acetyl signals, a ratio of α to β acetates of 2:1. N.m.r. data for α anomer: τ 3.36 (d, $J_{1,2}$ 4.5 Hz, H-1) and 7.93 (s, OAc); the H-1 signals from 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-D-xylofuranose are a singlet (τ 3.55) for the β anomer and a "well-defined" doublet (τ 3.26) for the α anomer[33].

3-Azido-3-deoxy-2,5-di-O-p-*nitrobenzoyl-β*-D-*xylofuranosyl chloride* (**23**). — The acetate **22** (7.0 g) was dissolved in dry dichloromethane (65 ml) saturated at 0° with dry hydrogen chloride. After 48 h at 4°, dry ethereal hydrogen chloride (15 ml) was added and the solution stored overnight at 4°. This procedure was repeated until 60 ml of ethereal hydrogen chloride had been added over a period of 4 days, during which crystals separated out. The crystals (3.80 g) were filtered off and washed with dry ether. The mother liquors afforded a further 1.34 g (from benzene–ether); yield 5.14 g (77%), m.p. 137–139°, $[\alpha]_D^{21}$ −22° (*c* 0.7, chloroform); n.m.r. (60 MHz, $CDCl_3$): τ 1.67 (8 H, Ar), 3.73 (s, 1 H, H-1), 4.10 (s, 1 H, H-2), 5.14 (m, 4 H) (*cf.* ref. 33).

Anal. Calc. for $C_{19}H_{14}ClN_5O_9$: C, 46.40; H, 2.85; Cl, 7.22; N, 14.22. Found: C, 46.59; H, 2.85; Cl, 7.20; N, 14.41.

1-(3-Azido-3-deoxy-2,5-di-O-p-*nitrobenzoyl-β*-D-*xylofuranosyl)uracil* (**24**). — To an azeotropically dried suspension of monochloromercuri-4-ethoxy-2(1*H*)-pyrimidinone[34] (3.05 g) in xylene (120 ml), preheated to 100°, was added the pentosyl chloride **23** (4.0 g). The mixture was stirred at the boiling point. Complete solution occurred after 10 min and boiling was continued for a further 35 min. The solution was cooled and poured into light petroleum (500 ml). The precipitate was filtered off and dissolved in chloroform, and the solution washed with 30% aqueous potassium iodide, followed by water. The dried (sodium sulfate) chloroform solution was evaporated to give a viscous, yellow solution, which was crystallised from the minimum volume of chloroform; yield 2.63 g (57%) of pale-yellow crystals, m.p. 153–157°. Recrystallisation from methanol afforded analytically pure **24**, m.p. 158–160°, $[\alpha]_D^{21}$ −55.5° (*c* 0.9, pyridine).

Anal. Calc. for $C_{23}H_{17}N_7O_{11}$: C, 48.65; H, 3.00; N, 17.29. Found: C, 48.44; H, 3.16; N, 17.43.

The mother liquors were shown, by t.l.c., to contain another major component that was less polar than **24**. Chromatography on two silica gel columns using chloroform and then benzene–ether as eluents gave **25** (485 mg, 13%), m.p. 149–151° (from ethanol), which was reactive towards aniline phthalate[43] on t.l.c.; ν_{max}^{KBr} 3420 (OH), 2138 (N_3), 1738 (C=O), 1723, 1528, and 1356 cm^{-1} (NO_2).

Anal. Calc. for $C_{19}H_{15}N_5O_{10}$: C, 48.15; H, 3.20; N, 14.80. Found: C, 48.08; H, 3.36; N, 14.94.

Acetylation of **25** with acetic anhydride and pyridine afforded **22** and its α anomer in the ratio 3:2 (by n.m.r. spectrum and t.l.c.).

1-(3-Azido-3-deoxy-β-D-*xylofuranosyl)uracil* (**26**). — Compound **24** (1.0 g) was heated in dry methanol (60 ml) containing sodium methoxide (from 32 mg of Na) for 20 min under reflux, and the cooled solution evaporated to dryness. The residue was triturated with water (15 ml) and pale-yellow crystals of methyl *p*-nitrobenzoate (583 mg, 91%, m.p. 94–95°) were filtered off. The aqueous filtrate was neutralised by passing through a short column of Dowex 50 (NH_4^+) resin and evaporated to give a colourless syrup, from which **26** (383 mg, 81%) crystallised on treatment with ethanol. After recrystallisation from ethanol, **26** had m.p. 192–194°, $[\alpha]_D^{21}$ −84.5° (*c* 1.0, methanol); λ_{max}^{MeOH} 264 nm (ε 9840), λ_{min} 233 nm (ε 2690); ν_{max}^{KBr} 2127 cm^{-1} (N_3);

n.m.r. (90 MHz, D_2O): τ 2.48 (d, 1 H, $J_{5,6}$ 8.0 Hz, H-6), 3.78 (d, 1 H, $J_{1',2'}$ 6.5 Hz, H-1'), 4.16 (d, 1 H, $J_{5,6}$ 8.0 Hz, H-5), 4.84 (m, 1 H, H-4'), 5.60 (m, 2 H, H-2', H-3'), and 6.17 (m, 2 H, H-$5'_a$,$5'_b$).

Anal. Calc. for $C_9H_{11}N_5O_5$: C, 40.15; H, 4.09; N, 26.10. Found: C, 40.30; H, 3.85; N, 25.96.

*1-(3-Amino-3-deoxy-β-*D*-xylofuranosyl)uracil* (**27**). — The azide **26** (150 mg) in ethanol (30 ml) was hydrogenated at atmospheric pressure over 5% palladium-on-charcoal (35 mg). The catalyst was removed by filtration and the filtrate evaporated to give a syrup (133 mg, 97%), which was homogeneous on chromatography in solvent *C* (R_{GlcN} 1.36), detection by u.v. lamp and by ninhydrin[44] (orange spot), $[\alpha]_D^{21}$ −31.5° (*c* 1.0 methanol); λ_{max}^{EtOH} 261 nm, λ_{max}^{EtOH} 236.5 nm.

Deamination of **27**. — A solution of **27** (30 mg) in 25% aqueous acetic acid (v/v, 1.2 ml) was treated with sodium nitrite (10 mg) and stored at 4° overnight. The solution was evaporated to dryness, and the residue dissolved in water (20 ml) and passed through a short column of Amberlite Monobed MB1 ion-exchange resin (p.c. showed no alteration to products). Evaporation of the eluate followed by trituration of the residue under water (2 ml) afforded crystals of uracil (7 mg, 55%), indistinguishable from an authentic sample (m.p., u.v., i.r., and p.c.). In the mother liquors was evidence for two unidentified compounds, one a reducing sugar (reactive to aniline phthalate) and the other a nucleoside derivative.

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