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Azido-(Amino-)furanosyl Nucleosides and their Phosphoramidates

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The ring-opening of 2,2′-anhydro-1-[5-azido- **5** and 5-benzamido- **3** 5-deoxy-3-*O*-methylsulfonyl-β-D-arabinofuranosyl]uracil by the ion exchanger Dowex 50 (H^+) afforded the corresponding 1-[5-azido- **8** and 5-benzamido- **12** 5-deoxy-3-*O*-methylsulfonyl-β-D-arabinofuranosyl]uracil. Hydrogenolysis of the azido nucleosides over Pd-black in the presence of benzoic acid anhydride led to the corresponding benzamido nucleosides in high yields. The 5′-azido-2′,3′-oxirane **10** on reaction with ethanolic ammonia generated 1-(3-amino-5-azido-3,5-dideoxy-β-D-arabinofuranosyl)uracil **15** and 1-(2-amino-5-azido-2,5-dideoxy-β-D-xylofuranosyl)uracil **16** in a ratio 2:1. The 5′-*O*-mesyl-2′,3′-oxirane **25**, on being treated with NaN_3 in DMF at 100 °C, afforded 2′,5′-anhydro-1-(3-azido-3-deoxy-β-D-arabinofuranosyl)uracil **26** (54.5%), 3′,5′-diazido-β-D-arabinofuranosyl **27** (20.6%) and 2′,5′-diazido-β-D-xylofuranosyl **28** (5.4%). The hydrogenolysis of **5** over Pd-black proceeded into 2,5′-imino-1-(3-*O*-methylsulfonyl-β-D-arabinofuranosyl)uracil **32** which, as the 5′-benzamido derivative **36**, was transformed into **3**. The 5′-azido compound **5** and **10** on reaction with triphenyl phosphite in aqueous dioxane gave the respective 5′-diphenylphosphoramidate **38** and **39**. Similarly, the 3′-azido compound **22** was converted into 3′-diphenylphosphoramidate **40**.

Appropriately activated uridine may undergo intramolecular transformation to give arabino-, lyxo- and xylo-furanosyl stereoisomers.[1–3] Recently, we described synthesis of 5′-azido-(5′-amino-)-5′-deoxyuridine and its furanosyl stereoisomers as well as 5′-*N*-aminoacyl- and 5′-*N*-peptidyl-5′-amino-5′-deoxy-5,6-dihydrouridine.[4] Here, we extend our work on stereoisomeric azido-, amino-, phosphoramido pyrimidine nucleosides, and their intramolecular cyclisations.

Current interest in azido nucleoside chemistry stems from the antiviral activity[5,6] of 3′-azido-3′-deoxythymidine (AZT).[7] However, the increasing resistance of human immunodeficiency virus (HIV) to AZT stimulated syntheses of a number of novel azido nucleosides. For this purpose the silyl (Hilbert–Johnson)[8,9] coupling of azido furanose with nucleic acid bases, the ring-opening of 1-(3,5-anhydro-β-D-xylofuranosyl)uracil by LiN_3[10] and the nucleophilic substitution of 5′-*O*-sulfonyluridine by NaN_3,[11,12] have most frequently been exploited.

Recently, we showed that the intramolecular transformations of 5′-benzamido-5′-deoxy-2′,3′-di-*O*-methylsulfonyluridine **1** when heated under reflux in water gave 1-(5-benzamido-5-deoxy-β-D-lyxofuranosyl)uracil[4] **2** (Scheme 1). We also reported that transformations of **1** on treatment with potassium phthalimide in dioxane stopped at 2,2′-anhydro-1-(5-benzamido-5-deoxy-3-*O*-methylsulfonyl-β-D-arabinofuranosyl)-uracil **3**. We report here transformations of 2′,3′,5′-tri-*O*-methylsulfonyluridine[1] **4** on reaction with NaN_3–DMF to yield 2,2′-anhydro-1-(5-azido-5-deoxy-3-*O*-methylsulfonyl-β-D-arabinofuranosyl)uracil **5**.

The arabinofuranosyl configuration of **5** was confirmed by the characteristic ^1H NMR spectral data, particularly by the coupling constant, $J_{1',2'}$ 5.9 †[4,13] (Table 1). The UV absorbancy of **5** at λ_{max}/nm 245 indicated also its quinone-like structure.

The 2,2′-anhydro compound **5** when heated under reflux in water or dilute hydrochloric acid gave 1-(5-azido-5-deoxy-β-D-lyxofuranosyl)uracil **6**, characterized as its 2′,3′-*O*-isopropylidene derivative **7**. In contrast to the specific rotation of the 2,2′-anhydro compound **5**, $[\alpha]_D^{27}$ −37 † (*c* 1, DMF), the lyxofuranosyl stereoisomer **6**, $[\alpha]_D^{24}$ +163 (*c* 0.86, MeOH), and **7**, $[\alpha]_D^{22}$ +158 (*c* 1.15, MeOH), were significantly dextrorotatory.

† *J* Values in Hz and $[\alpha]_D$ values in units of 10^{-1} deg cm^2 g^{-1} throughout.

The ring-opening of **5**, on treatment with the ion exchanger Dowex 50 (H^+),[2] afforded 1-(5-azido-5-deoxy-3-*O*-methylsulfonyl-β-D-arabinofuranosyl)uracil **8**. The latter, on mesylation, gave the respective 2′-*O*-mesyl derivative **9**. Furthermore, treatment of **5** with aqueous NaOH gave 1-(5-azido-5-deoxy-2,3-epoxy-β-D-lyxofuranosyl)uracil **10**. Similarly, treatment of **5** with NaOMe–MeOH afforded 1-(5-azido-5-deoxy-2,3-epoxy-β-D-lyxofuranosyl)-2-*O*-methyluracil **11** through an $^-$OMe attack at the C-2 position of **5**, followed by the C(2)–O–C(2′) ring-opening and $^-$O–C(2′), C(3′) cyclisation.[14] As expected, the anomeric H–C(1′) in the ^1H NMR spectra of the 2′,3′-oxiranes **10** and **11** exhibited the singlet-like signals at δ_H 6.1.

In analogy to the stereochemically controlled ring-opening of the azido compound **5** to give **8** (Scheme 1, pathway vi), the benzamido derivative **3** afforded 1-(5-benzamido-5-deoxy-3-*O*-methylsulfonyl-β-D-arabinofuranosyl)uracil **12**. The combined hydrogenolysis–benzoylation of the azido compounds **5** and **10** over Pd-black in the presence of benzoic acid anhydride smoothly proceeded to give the 5′-benzamido 2,2′-anhydro compound **3** (84.3%) and 1-(5-benzamido-5-deoxy-2,3-epoxy-β-D-lyxofuranosyl)uracil **14** (97%), respectively. It should be pointed out that hydrogenolysis of the 5′-azido compound **10**, followed by the benzoylation of the resulting 1-(5-amino-5-deoxy-2,3-epoxy-β-D-lyxofuranosyl)uracil **13** afforded the 5′-benzamido compound **14** in lower yield than that obtained from the above described hydrogenolysis–benzoylation of the 5′-azido compound **10**.

For the reason we shall deal with below, treatment of the 2′,3′-oxirane **10** with ammonia in ethanol[15] generated 1-(3-amino-5-azido-3,5-dideoxy-β-D-arabinofuranosyl)uracil **15** and 1-(2-amino-5-azido-2,5-dideoxy-β-D-xylofuranosyl)-uracil **16** in a 2:1 ratio (established by their ^1H NMR spectra). These stereoisomers were separated as 1-(5-azido-3-benzamido-3,5-dideoxy-β-D-arabinofuranosyl)uracil **17**, R_f 0.19 (47%), and 1-(5-azido-2-benzamido-2,5-dideoxy-β-D-xylofuranosyl)-uracil **18**, R_f 0.15 (36%), characterized also as the 2′-*O*-acetyl **19** and 3′-*O*-acetyl derivative **20**, respectively (Scheme 2).

The 5′-benzamido-2′,3′-oxirane **14** on reaction with NaN_3–DMF gave 1-(3-azido-5-benzamido-3,5-dideoxy-β-D-arabinofuranosyl)uracil **21** (78%), characterized as its 2′-*O*-acetyl derivative **22**. Comparing the ^1H NMR spectra of the 2′-hydroxy compound **21** with that of the 2′-acetoxy derivative **22**,

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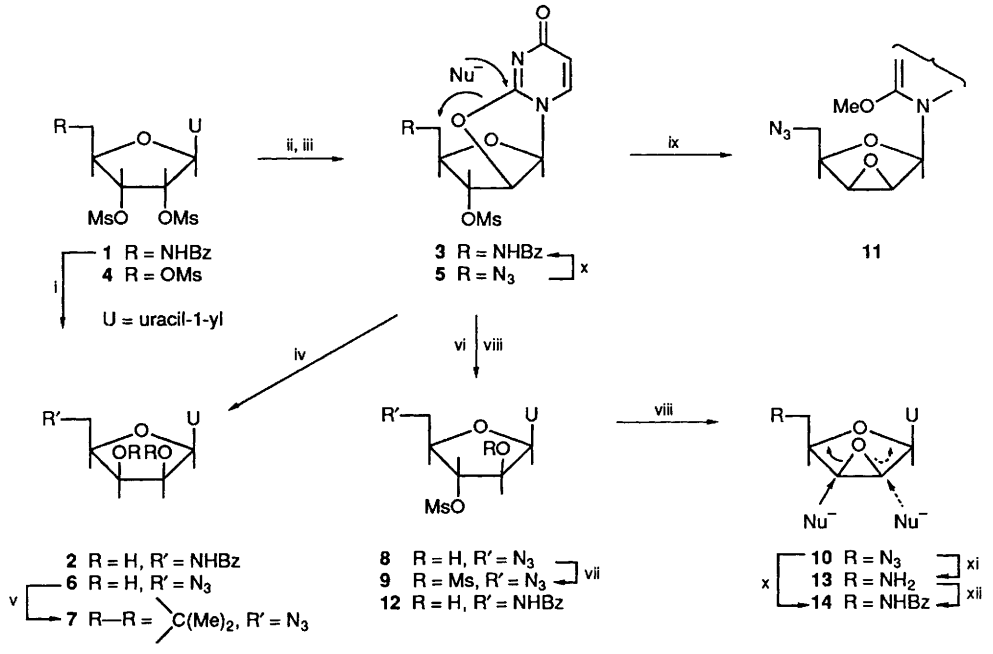
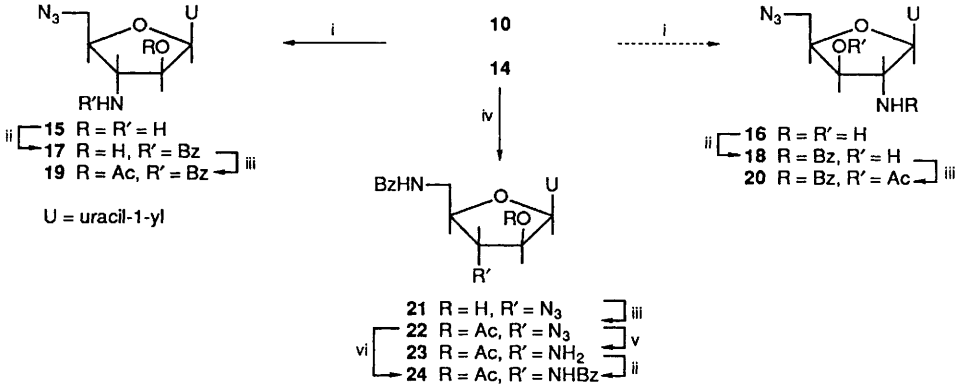
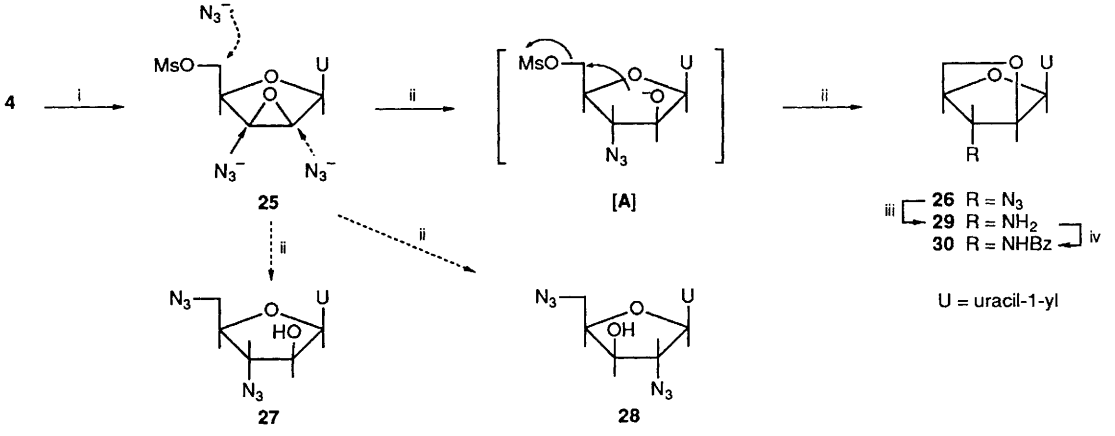


Scheme 1 *Reagents and conditions:* i, H_2O, heat; ii, Pht–K–dioxane; iii, NaN_3–DMF; iv, H_2O or HCl–H_2O; v, Me_2CO–$CuSO_4$–H_2SO_4; vi, Dowex 50(H^+)–Me_2CO–H_2O; vii, MsCl–py; viii, NaOH–H_2O; ix, NaOMe–MeOH; x, [H_2]–Pd black–Bz_2O–MeOH; xi, [H_2]–Pd black–EtOH; xii, Bz_2O–py



Scheme 2 *Reagents and conditions:* i, NH_3–EtOH; ii, Bz_2O–py; iii, Ac_2O–py; iv, NaN_3–DMF; v, [H_2]–Pd black–EtOH; vi, [H_2]–Pd black–Bz_2O–MeOH



Scheme 3 *Reagents and conditions:* i, NaOH–H_2O; ii, NaN_3–DMF; iii, [H_2]–Pd black–EtOH; iv, Bz_2O–py

the latter showed the expected downfield resonances for the 2′-H (0.86 ppm) and 3′-H (0.43 ppm) (Table 1). Moreover, the ^{13}C NMR spectrum of **22** (Table 2) confirmed the so-called β-acetyl effect[16] by exhibiting a downfield C-2′ shift (1.2 ppm) and an upfield C-3′ shift (2.3 ppm).

Hydrogenolysis of the 3′-azido isomer **22** over Pd-black in ethanol yielded 1-(2-*O*-acetyl-3-amino-5-benzamido-3,5-dideoxy-β-D-arabinofuranosyl)uracil **23** which, on benzoylation, yielded the 3′,5′-dibenzamido compound **24** (81%). The latter was prepared by hydrogenolysis–benzoylation of the azido compound **22** in 92% yield.

Treatment of 1-(5-*O*-methylsulfonyl-2,3-epoxy-β-D-lyxo-

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Table 1 ^{1}H NMR chemical shifts (δ_H), and coupling constants, given in parentheses, for the 1-(furanos-1′-yl)uracil isomers[a,b,c,d,e,f,g,h]

Compound	Solvent*	6-H d	1′-H d	5-H d	2′-H	3′-H	4′-H	5′-H_A dd	5′-H_2 5′-H_B dd
					Data for arabino-, lyxo- and xylo-isomers				
6	A	7.83 (8.2)	6.07 (6.5)	5.55 (8.2)	4.40dd (6.5, 4.7)	4.08 —	3.91		3.57d (6.2)
7[i]	B	7.49 (8.2)	5.85 (3.2)	5.73 (8.2)	4.93 —	4.72	3.93sext (3.2, 6.2)		3.65d (6.2)
8	A	7.52 (8.2)	6.06 (4.1)	5.60 (8.2)	4.88dd (4.1, 3.2)	4.43dd (3.2, 4.7)	4.29–4.07		3.68d (5.6)
9	C	7.55 (8.2)	6.25 (5.0)	5.76 (8.2)	5.48dd (5.0, 3.2)	5.31dd (3.2, 5.3)	4.34sext (5.3, 4.1)		3.84–3.76
12	A	7.70 (8.2)	6.48 (3.8)	5.53 (8.2)	5.02t (2.1)	4.44 —	4.18		3.82–3.64
19	D	7.88 (8.2)	6.27 (5.6)	5.75 (8.2)	5.67dd (5.6, 4.1)	4.82 —	4.60		3.78–3.66
20[j]	D	7.76 (8.2)	6.46 (5.3)	5.71 (8.2)	5.73–5.62	5.80sext (4.1, 7.3)	4.38–4.21		3.85–3.74
21	D	7.77 (8.2)	6.11 (4.7)	5.55 (8.2)	4.49 br s	4.29	—		3.81
22	D	7.77 (8.2)	6.21 (4.9)	5.63 (8.2)	5.35dd (4.9, 3.5)	4.48dd (3.5, 5.6)	4.14dd (5.6, 10.4)		3.97–3.84
24	A	7.74 (8.2)	6.32 (4.9)	5.61 (8.2)	5.46dd (4.9, 3.5)	4.52sext (3.5, 6.7)	4.33–4.14		3.80–3.68
40[k]	D	7.73 (8.2)	6.29 (4.7)	5.59 (8.2)	5.41t (4.7)	4.38	4.02		3.86–3.65
					Data for imino nucleosides				
32	A	7.41 (7.6)	5.83 (6.7)	5.60 (7.6)	4.91d (2.3)	4.56 —	4.49	3.47 (14.2, 3.1)	3.21 (14.2, 1.8)
33	A	7.39 (7.6)	6.16 (6.7)	5.61 (7.6)	5.36dd (6.7, 1.8)	5.19d (1.8)	4.73–4.58	3.52 (16.2, 2.9)	3.26 (16.2, 1.8)
34	A	7.95 (7.6)	6.39 (7.3)	6.08 (7.6)	5.49d (7.3)	4.85 s br	4.77d (2.6)	4.99 (14.6, 2.6)	3.22 (14.6, 1.8)
35	C	7.28 (7.6)	6.15 (6.8)	5.68 (7.6)	5.84dd (6.8, 1.5)	5.44d (1.5)	4.81 s br	4.06 (14.5, 2.9)	3.47 (14.5, 1.8)
37[l]	A	7.94 (7.6)	6.64 (6.5)	5.89 (7.5)	5.71 —	5.68	4.97 s br	4.79 (14.5, 2.9)	3.50 (14.5, 1.8)

[a] Me(Ms) of (**8, 9, 12, 32–37**) at 3.43–3.13 (s). [b] *N*- and *O*-Benzoyl of (**12, 19–22, 24, 35, 37, 40**) at 8.01–7.71 and 7.64–7.28. [c] H–N(3) of (**6, 8, 9, 12, 19–22, 24, 40**) at 11.21–9.41 (br s), D_2O-exchangeable. [d] 5′-NH of (**19, 21, 22, 24, 32, 33, 35, 40**) at 8.56–6.62, D_2O-exchangeable. [e] 3′-NH of (**19, 24, 40**) at 8.85–5.82, D_2O-exchangeable. [f] 2′-OH and 3′-OH of (**6, 8, 12, 21, 32**) at 6.62–4.07, D_2O-exchangeable. [g] Me(Ac) of (**19, 20, 22, 24, 33, 34, 40**) at 2.29–1.83 (s). [h] Two dimensional spectra of (**34, 35, 37**) on JEOL Varian Gemini-300 instrument. [i] $(Me)_2$ at 1.47 and 1.32. 2′-NH at 8.41–8.34, D_2O-exchangeable. [k] $NPO(OPh)_2$ at 7.46–7.06. [l] NCOPh at 7.52–6.70.
* A = [$^2H_6$]-DMSO, B = C^2HCl_3, C = C^2H_3CN, D = [$^2H_6$]acetone.

furanosyl)uracil[17] **25** with NaN_3 at 100 °C afforded 2′,5′-anhydro-1-(3-azido-3-deoxy-β-D-arabinofuranosyl)uracil **26** (54.5%), most probably *via* the intermediacy of [**A**] (Scheme 3). This reaction (depicted by dotted lines) led also to 1-(3,5-diazido-3,5-dideoxy-β-D-arabinofuranosyl)uracil **27** (20.6%), R_f 0.43, and in lesser extent to 1-(2,5-diazido-2,5-dideoxy-β-D-xylofuranosyl)uracil **28**, R_f 0.42. The hydrogenolysis of **26** over Pd-black–EtOH gave the corresponding 3′-amino compound **29**, characterized as its 3′-benzamido derivative **30**. The ^{13}C NMR spectra of the 2′,5′-oxolanes **26**, **29** and **30** exhibited C-5′ downfield shifts (11 ppm) as recorded in the 2,5′-anhydro series.[18]

The hydrogenolysis of the 5′-azido-2,2′-anhydro compound **5** over Pd-black in ethanol afforded 2,2′-anhydro-1-(5-amino-5-deoxy-3-*O*-methylsulfonyl-β-D-arabinofuranosyl)uracil **31** which spontaneously rearranged into the hitherto unknown 2,5′-imino-1-(3-*O*-methylsulfonyl-β-D-arabinofuranosyl)-uracil **32** (94%) (Scheme 4).

While the imino compound **32** on reaction with acetic anhydride yielded 2,5′-imino-1-(2-*O*-acetyl-3-*O*-methylsulfonyl-β-D-arabinofuranosyl)uracil **33** (79.6%), on reaction with acetyl chloride it gave 5′-*N*-acetyl-2,5′-imino-1-(2-*O*-acetyl-3-*O*-methylsulfonyl-β-D-arabinofuranosyl)uracil **34** (85%). The benzoylation of **32** with benzoic acid anhydride afforded 2,5′-imino-1-(2-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-arabinofuranosyl)uracil **35** (53.7%) and 5′-benzamido-2,2′-anhydro compound **3** (33.7%) (Scheme 1). The latter was unexpectedly formed by an intamolecular $^-$O-C(2′) attack at the C-2 position of the 5′-benzamido-2,5′-imino intermediate **36**. The structure of the 2′-*O*-benzoyl derivative **35** was supported by its facile hydrolysis into the hydroxy compound **32**.

It is worth noting that compound **32** on reaction with benzoyl chloride afforded the 2,2′-anhydro compound **3** (74%) which then partly cleaved to give up 5′-benzamido-3′-*O*-mesyl compound **12** (Scheme 1). Such a rearrangement was prevented when the β-oriented 2′-hydroxy group was blocked as in 5′-*N*-benzoyl-2,5′-imino-1-(2-*O*-benzoyl-3-*O*-methylsulfonyl-β-D-arabino-furanosyl)uracil **37**. The latter was easily prepared from the 2′-*O*-benzoyl derivative **35** on reaction with benzoyl chloride. The aromatic protons of the *N*,*O*-dibenzoyl derivative **37**, were clearly assigned by two-dimensional (COSY) ^1H NMR spectrum showing the *O*-benzoyl signals at δ_H 7.96–7.93, 7.81–7.63, 7.61–7.56 and *N*-benzoyl signals at δ_H 7.52–7.50, 7.25–7.21, 6.74–6.70 for *meta*-(2H), *para*-(1H) and *ortho*-(2H), respectively.

Phosphorylation of the azido nucleosides facilitated the regioselective phosphorodiamido bond formation. Thus, the 5′-azido compounds **5** and **10** on reaction with triphenyl phosphite in dioxane–water[19,20] afforded 2,2′-anhydro-1-(5-deoxy-5-diphenylphosphoramido-β-D-arabinofuranosyl)-uracil **38** (89.3%) and 1-(5-deoxy-5-diphenylphosphoramido-2,3-epoxy-β-D-lyxofuranosyl)uracil **39** (78%); respectively

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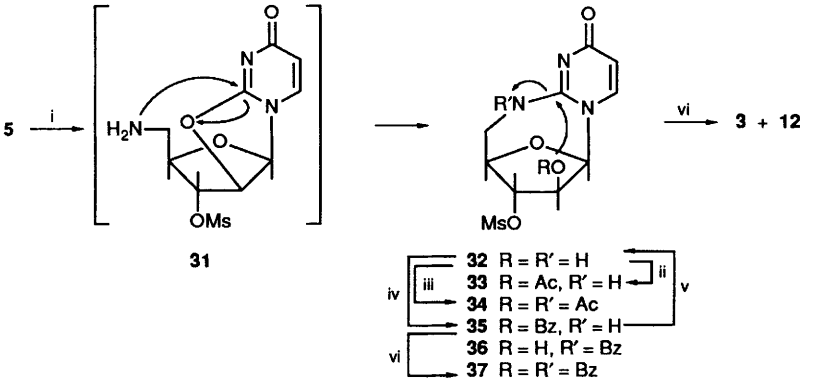
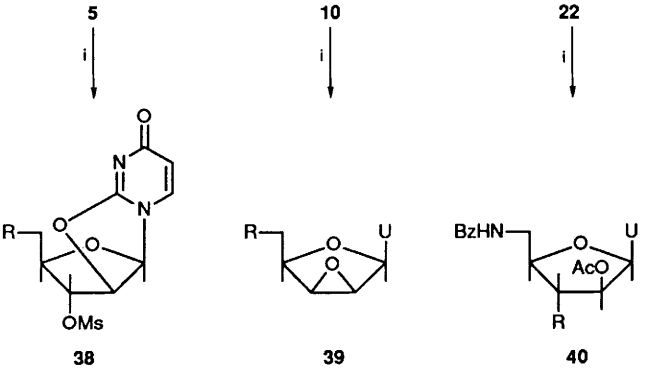
Table 2 ^{13}C NMR spectroscopic data [δ_C (ppm)] for the 1-(furanos-1′-yl)uracil isomers[a,b,c,d,e]

Compound	Solvent*	C-4 (s)	C-2 (s)	C-6 (d)	C-5 (d)	C-1′ (d)	C-4′ (d)	C-2′ (d)	C-3′ (d)	C-5′ (t)
					Arabino-, lyxo- and xylo-isomers					
6	A	162.9	150.5	142.2	99.8	83.2	77.3	70.3	69.2	49.9
7[f]	D	163.1	150.3	142.0	100.3	84.8	80.1	78.9	77.7	49.7
8	C	164.7	151.6	143.2	101.9	86.1	84.4	74.6	80.4	51.8
9	C	164.1	151.2	142.3	102.9	84.5	81.3	80.0	80.6	51.2
12	A	163.3	150.5	142.6	100.3	85.7	84.7	72.9	80.8	40.9
19	D	163.5	151.5	140.9	103.4	87.7	79.1	76.4	61.0	50.9
20	D	163.3	150.9	141.9	102.1	84.1	80.4	57.4	76.9	52.7
21	D	163.4	150.8	142.7	100.7	85.7	79.9	74.9	68.1	41.6
22	D	163.0	150.3	141.8	101.2	84.2	80.2	76.1	65.8	41.0
24	A	162.9	150.0	141.7	100.9	83.5	79.7	75.9	56.7	41.2
40	D	163.6	150.3	142.2	101.1	83.8	80.7	77.3	58.1	41.0
					2,2′-Anhydro compounds					
3	A	172.1	159.8	137.4	109.7	90.5	84.1	86.7	82.1	40.9
5	A	171.1	159.7	136.8	109.2	90.1	83.9	86.3	81.9	51.2
38	A	170.8	159.3	136.8	109.0	89.7	84.6	86.1	81.0	42.2
					Oxiranes					
10	A	162.6	149.9	140.7	101.8	80.6	75.4	55.4	55.1	49.7
11[g]	D	169.5	155.8	138.7	108.4	83.4	76.8	56.1	55.9	50.5
14	A	163.3	150.6	141.3	101.9	81.2	75.6	56.1	55.9	39.2
39	A	163.0	150.7	141.3	101.9	81.0	76.7	56.3	55.5	40.7
					Oxolanes					
26	A	163.2	150.5	140.6	100.6	89.1	79.6	75.6	65.2	72.6
29	A	163.4	150.6	141.1	100.3	89.8	81.8	77.6	59.6	72.8
30	A	163.4	150.6	140.9	100.5	89.4	79.5	75.9	58.2	72.2
					Imino nucleosides					
32	A	169.9	158.7	143.7	107.2	93.8	87.8	77.7	81.4	47.7
33	A	169.2	158.1	143.1	107.4	91.7	83.7	78.1	81.1	47.3
34	B	169.4	152.1	143.9	111.2	93.9	82.4	79.2	82.1	45.7
35	D	170.1	160.3	143.9	108.7	93.9	85.4	79.2	83.4	48.4
37	A	171.9	153.6	145.3	108.9	92.9	83.2	79.7	82.2	47.5

[a] CO(amide) and CO(ester) of (**3**,**12**,**14**,**19**–**22**, **24**, **30**, **33**, **35**, **37**, **40**) at 171.1–166.2. [b] Aromatic C-atoms of (**3**, **12**, **14**, **19**–**22**, **24**, **30**, **35**, **37**, **40**) at 135.1–127.3. [c] Me(Ms) of (**3**,**5**,**8**,**9**,**12**,**32**–**35**,**37**, **38**) at 38.9–37.6 (q). [d] Me(OAc) of (**19**, **20**, **22**, **24**, **33**, **34**, **40**) at 20.8–19.5 (q) and Me(NAc) of **34** at 23.9 (q). [e] $PO(OPh)_2$ of (**38**–**40**) at 150.6 and 129.9–120.2. [f] O–C–O at 113.2 (s), Me_2 at 25.0 (q) and 23.6 (q). [g] Me–O–C(2) at 55.1 (q).
* A = [$^2H_6$]-DMSO, B = C^2HCl_3, C = C^2H_3CN, D = [$^2H_6$]acetone.



Scheme 4 *Reagents and conditions:* i, [H_2]–Pd black–EtOH; ii, Ac_2O–py; iii, AcCl–py; iv, Bz_2O–py; v, NaOH–H_2O; vi, BzCl–py



Scheme 5 *Reagents and conditions:* i, $(PhO)_3P$–dioxane–H_2O

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(Scheme 5); both exhibited characteristic ^{13}C NMR spectra[21] (Table 2).

The 2-*O*-acetyl-3-azido-5′-benzamido-arabinofuranosyl compound **22** was analogously converted into 1-(2-*O*-acetyl-3-benzamido-3,5-dideoxy-3-diphenylphosphoramido-β-D-arabinofuranosyl)uracil **40** in 83% yield.

The ^1H and ^{13}C NMR spectral characteristics of all the reported compounds (Tables 1 and 2), together with their optical rotations (see Experimental section), IR (in particular, for the azido compounds with characteristic ν_{max}/cm^{-1} ~2100), UV (in particular for the 2,5′- and 2,2′-anhydro as well as 2-OMe compound with λ_{max}/nm ~245) and elemental analyses agreed with the proposed structures presented in this paper.

Experimental

M.p.s, uncorrected, were determined on a Kofler hot-stage apparatus. IR spectra were obtained for KBr pellets on a Perkin-Elmer 782 spectrophotometer. UV spectra were taken for solutions in ethanol on a Perkin-Elmer double-beam spectrophotometer model 124. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX90Q and JEOL FX 100Q spectrometers with tetramethylsilane as the internal standard. Multiplicities s, d, t and q refer to off-resonances decoupled spectra. Optical rotations were measured in methanol, unless otherwise stated, on a Zeiss–Winkel 179707 apparatus. The silica gel (Merck HF_{254}, type 60) for TLC was activated at 110 °C for 60 min. R_f Values of the products were determined by developments in CH_2Cl_2–MeOH, 10:1 and located by UV illumination and a ninhydrin spray. Removal of the solvents under reduced pressure. DMF (dimethylformamide) and pyridine were dried and distilled over CaH_2 and stored over molecular sieves (4 Å). Mass spectra were recorded on a SHIMADZU GC-MS QP-1000 spectrometer; electron impact, ionizing voltage 70 eV.

General Procedure for the Hydrogenolysis–Benzoylation of the Azides **5**, **10** *and* **22**.—To a solution of the azide (0.34–1.31 mmol) in methanol (7–35 cm^3) Pd-black (7–28 mg) and benzoic acid anhydride (0.43–1.71 mmol) were added. The suspension was stirred in a H_2 atmosphere at 0.35 MPa at room temperature for 24 h. The catalyst was filtered off and the filtrate evaporated to dryness. The residue was triturated with diethyl ether and recrystallized from methanol to give compounds **3**, **14** and **24**.

2,2′-*Anhydro*-1-(5-*benzamido*-5-*deoxy*-3-O-*methylsulfonyl*-β-D-*arabinofuranosyl*)*uracil* **3**. From **5**, 84.3%; R_f 0.17; m.p. 194–200 °C; identical (mixed m.p., NMR and IR spectra) with an authentic specimen (ref. 4).

1-(5-*Benzamido*-5-*deoxy*-2,3-*epoxy*-β-D-*lyxofuranosyl*)*uracil* **14**. From **10**: 97%; R_f 0.36; m.p. 186–188 °C; identical (mixed m.p., NMR and IR spectra) with an authentic specimen (ref. 4).

1-(2-O-*Acetyl*-3,5-*dibenzamido*-3,5-*dideoxy*-β-D-*arabinofuranosyl*)*uracil* **24**. From **22**: 92%; R_f 0.39; m.p. 264–265 °C (Found: C, 60.8; H, 4.75; N, 11.25. $C_{25}H_{24}N_4O_7$ requires C, 60.95; H, 4.9; N, 11.4%); $[\alpha]_D^{22}$ +46 (*c* 1 in DMF); λ_{max}/nm 227 (log ε 4.22); λ_{infl}/nm 262 (log ε 3.98); λ_{min}/nm 246 (log ε 4.06); ν_{max}/cm^{-1} 3271, 3063, 1750, 1717, 1706, 1690, 1639, 1534, 1268, 1226, 1218, 1210, 1114, 822, 803, 715 and 694.

General Procedure for the Azidolysis of the Mesylate **4**[1] *and Oxiranes* **14**,[4] **25**.[17]—To a solution of mesylate or oxirane (1 mmol) in DMF (40 cm^3) sodium azide (2 mmol) was added. The mixture was stirred at 100 °C for 1 h for **4**, 2 h for **25** or for 1 day for **14** and then cooled. A precipitate was filtered off and the filtrate evaporated to dryness. The residue was crystallized from water as in the case of the azide **5** and purified by TLC [CH_2Cl_2–MeOH (10:0.5), two developments] as in the case of the azido compounds **21** and **26**.

2,2′-*Anhydro*-1-(5-*azido*-5-*deoxy*-3-O-*methylsulfonyl*-β-D-*arabinofuranosyl*)*uracil* **5**. From **4**: 93%; R_f 0.20; m.p. 155–156 °C (from MeOH) (Found: C, 36.2; H, 3.6; N, 21.25. $C_{10}H_{11}N_6O_5S$ requires C, 36.45; H, 3.35; N, 21.25%); $[\alpha]_D^{27}$ −37.5 (*c* 1 in DMF); λ_{max}/nm 245 (log ε 3.99); ν_{max}/cm^{-1} 2154, 2113, 1664, 1637, 1613, 1528, 1495, 1362, 1284, 1179, 1094, 961 and 829; $\delta_H([^2H_6]\text{-DMSO})$ 7.85 (1 H, d, *J* 7.6, 6-H), 6.44 (1 H, d, *J* 5.9, 1′-H), 5.89 (1 H, d, *J* 7.6, 5-H), 5.64 (1 H, d, *J* 5.9, 2′-H), 5.38 (1 H, m, 3′-H), 4.64–4.49 (1 H, m, 4′-H), 3.60 (1 H, dd, *J* 13.5 and 4.4, 5′-H_A), 3.37 (3 H, s, MsMe), 3.36 (1 H, dd, *J* 13.5 and 6.7, 5′-H_B).

1-(3-*Azido*-5-*benzamido*-3,5-*dideoxy*-β-D-*arabinofuranosyl*)-*uracil* **21**. From **14**: 78%; R_f 0.31; m.p. 115–117 °C (from acetone–hexane) (Found: C, 51.35; H, 4.7; N, 22.35. $C_{16}H_{16}N_6O_5$ requires C, 51.6; H, 4.45; N, 22.55%); $[\alpha]_D^{14}$ −117 (*c* 1.02 in MeOH); λ_{max}/nm 218.5 and 260 (log ε 4.13 and 4.03), λ_{min}/nm 246 (log ε 3.99); ν_{max}/cm^{-1} 3314br, 3104, 3054, 2924, 2109, 1719, 1684br, 1634infl, 1534, 1459, 1270, 1069, 797, 707 and 688.

1-(2,5-*Anhydro*-3-*azido*-3-*deoxy*-β-D-*arabinofuranosyl*)*uracil* **26**. From **25**: 54.5%; R_f 0.45; m.p. 227–229 °C (from MeOH) (Found: C, 43.2; H, 3.85; N, 27.65. $C_9H_9N_5O_4$ requires C, 43.05; H, 3.6; N, 27.9%); $[\alpha]_D^{28}$ +238 (*c* 0.5 in MeOH); λ_{max}/nm 264.5 (log ε 3.89); ν_{max}/cm^{-1} 3126, 3011, 2892, 2110, 1714, 1689, 1674, 1468, 1397, 1267, 1058 and 1016; $\delta_H([^2H_6]\text{-DMSO})$ 11.27 (1 H, br s, 3-NH), 7.78 (1 H, d, *J* 8.2, 6-H), 5.92 (1 H, s, 1′-H), 5.59 (1 H, d, *J* 8.2, 5-H), 4.82 (1 H, s, 2′-H), 4.65 (1 H, d, *J* 2.6, 3′-H), 4.52 (1 H, q, *J* 2.6 and 0.9, 4′-H), 4.07 (1 H, d, *J* 12.9, 5′-H_A) and 3.97 (1 H, d, *J* 12.9, 5′-H_B).

1-(5-*Azido*-5-*deoxy*-β-D-*lyxofuranosyl*)*uracil* **6**.—(a) A solution of the 2,2′-anhydro compound **5** (100 mg, 0.3 mmol) in water (4 cm^3) was heated under reflux for 3 h and then evaporated to dryness. The residue crystallized from ethyl acetate to give the lyxofuranosyl isomer **6** (76 mg, 94%); R_f 0.18; m.p. 139–141 °C (Found: C, 40.25; H, 4.4; N, 26.0. $C_9H_{11}N_5O_5$ requires C, 40.15; H, 4.1; N, 26.0%); $[\alpha]_D^{24}$ +163 (*c* 0.86 in MeOH); λ_{max}/nm 259 (log ε 3.93); ν_{max}/cm^{-1} 3423, 3232, 3110, 2110, 1702, 1677, 1475, 1276, 1110, 1064 and 813.

(b) A solution of compound **5** (200 mg, 0.61 mmol) in 0.1 mol dm^{-3} aq. HCl (5 cm^3) was heated under reflux for 1 h and then evaporated to dryness. The residue was purified by preparative TLC [CH_2Cl_2–MeOH (10:0.6), two developments] to give **6** (145 mg, 90%), m.p. 138–140 °C (from ethyl acetate); identical (mixed m.p., NMR and IR spectra) with those obtained under (a).

1-(5-*Azido*-5-*deoxy*-2,3-O-*isopropylidene*-β-D-*lyxofuranosyl*)-*uracil* **7**.—A suspension of the lyxofuranosyl compound **6** (70 mg, 0.26 mmol) and dry cuprous sulfate (126 mg, 0.77 mmol) in acetone (4 cm^3) and sulfuric acid (2.4 × 10^{-3} cm^3) was heated at 37 °C for 45 h. The resulting precipitate was filtered off (Celite column) and the filtrate treated with dry calcium hydroxide (62 mg, 0.84 mmol). This mixture was stirred at room temperature for 1 h after which the resulting precipitate was filtered off and the filtrate evaporated to dryness. The residue was subjected to preparative TLC [CH_2Cl_2–MeOH (10:0.6), two developments] to give the acetonide **7** (74 mg, 92.5%); R_f 0.39; m.p. 112–115 °C (from MeOH) (Found: C, 46.5; H, 5.15; N, 22.6. $C_{12}H_{15}N_5O_5$ requires C, 46.6; H, 4.9; N, 22.65%); $[\alpha]_D^{22}$ +158 (*c* 1.15 in MeOH); λ_{max}/nm 260 (log ε 3.99); ν_{max}/cm^{-1} 3549, 3474, 3429, 2103, 1714infl, 1694br, 1625, 1458, 1386, 1285, 1210, 1112 and 880.

1-(5-*Azido*-5-*deoxy*-3-O-*methylsulfonyl*-β-D-*arabinofuranosyl*)*uracil* **8**—To a solution of compound **5** (200 mg, 0.61

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mmol) in acetone–water (1:1; 50 cm^3) the ion exchanger Dowex 50 (H^+) (640 mg) was added. The mixture was stirred at room temperature for 72 h and then filtered. The filtrate was evaporated to dryness and the residue crystallized from dichloromethane–diethyl ether–hexane to give the ring-opened product **8** (174 mg, 82.5%); R_f 0.3; m.p. 83–84 °C (Found: C, 34.4; H, 3.95; N, 19.9. $C_{10}H_{13}N_5O_7S$ requires C, 34.6; H, 3.75; N, 20.15%); $[\alpha]_D^{23}$ +215 (*c* 0.91 in MeOH); λ_{max}/nm 258 (log ε 4.08); ν_{max}/cm^{-1} 3480infl, 3247br, 3032, 2111, 1694br, 1630infl, 1469, 1360, 1281, 1177, 966, 843 and 812.

1-(5-*Azido*-5-*deoxy*-2,3-*di*-O-*methylsulfonyl*-β-D-*arabinofuranosyl*)*uracil* **9**.—A solution of the arabinofuranosyluracil **8** (160 mg, 0.46 mmol) in pyridine (5 cm^3) was treated with methanesulfonyl chloride (75.5 mg, 0.66 mmol) at room temperature for 24 h. The solvent was coevaporated with toluene and the residue washed with ice–water. It was then subjected to preparative TLC [CH_2Cl_2–MeOH (10:0.6), two developments] to give the 2′-*O*-mesyl compound **9** (147 mg, 75%); R_f 0.42; m.p. 80–82 °C (from dichloromethane–diethyl ether–hexane) (Found: C, 31.25; H, 3.7; N, 16.6. $C_{11}H_{15}N_5O_9S_2$ requires C, 31.05; H, 3.55; N, 16.45%); $[\alpha]_D^{26}$ +103 (*c* 0.75 in MeOH); λ_{max}/nm 253.5 (log ε 3.98); ν_{max}/cm^{-1} 3440br, 3214, 3032, 2113, 1695br, 1632, 1463, 1365, 1288, 1179, 968, 879 and 821.

1-(5-*Azido*-5-*deoxy*-2,3-*epoxy*-β-D-*lyxofuranosyl*)*uracil* **10**.—A solution of compound **5** (300 mg, 0.91 mmol) in 0.48 mol dm^{-3} NaOH (3.79 cm^3, 1.82 mmol) was kept at room temperature for 30 min. The mixture was neutralized with 0.65 mol dm^{-3} aq. HCl. The crystalline precipitate was filtered off and washed with methanol. It afforded the oxirane **10** (210 mg, 92%); R_f 0.42; m.p. 186–188 °C (from MeOH) (Found: C, 43.1; H, 3.75; N, 28.15. $C_9H_9N_5O_4$ requires C, 43.05; H, 3.6; N, 27.9%); $[\alpha]_D^{24}$ +116 (*c* 0.56 in MeOH); λ_{max}/nm 259 (log ε 3.93); ν_{max}/cm^{-1} 3125, 3003, 2807, 2131, 2092, 1695, 1682, 1469, 1388, 1260, 1120, 1083, 851, 828 and 800; $\delta_H([^2H_6]$-DMSO) 11.12 (1 H, br s, 3-NH), 7.64 (1 H, d, *J* 8.2, 6-H), 6.08 (1 H, s, 1′-H), 5.64 (1 H, d, *J* 8.2, 5-H), 4.29–3.99 (3 H, m, 2′-, 3′- and 4′-H) and 3.60 (2 H, d, *J* 5.9, 5′-H_2).

1-(5-*Azido*-5-*deoxy*-2,3-*epoxy*-β-D-*lyxofuranosyl*)-2-O-*methyluracil* **11**.—A solution of compound **5** (200 mg, 0.61 mmol) in methanolic 0.35 mol dm^{-3} sodium methoxide (3.5 cm^3, 1.22 mmol) was set aside at room temperature for 30 min. The solution was neutralized with 0.65 dm^{-3} aq. HCl to give a crystalline product, identified as the oxirane **10** (49 mg, 32%), m.p. 185–188 °C; identical (mixed m.p., NMR and IR spectra) with an authentic specimen. The mother liquor was evaporated to dryness and the oily residue purified by preparation TLC [CH_2Cl_2–MeOH (10:0.6), two developments] to give the 2-*O*-methyloxirane **11** (108 mg, 66.7%); R_f 0.40 (Found: C, 45.4; H, 4.45; N, 26.3. $C_{10}H_{11}N_5O_4$ requires C, 45.25; H, 4.2; N, 26.4%); $[\alpha]_D^{24}$ +51 (*c* 0.36 in MeOH); λ_{max}/nm 242.5 (log ε 4.14); ν_{max}/cm^{-1} 2103, 1650, 1524, 1454, 1384, 1240, 1101 and 828; $\delta_H([^2H_6]$-DMSO) 7.77 (1 H, d, *J* 7.9, 6-H), 6.18 (1 H, s, 1′-H), 5.84 (1 H, d, *J* 7.9, 5-H), 4.43–4.07 (3 H, m, 2′-, 3′- and 4′-H), 3.96 (3 H, s, 2-Me), 3.70 (2 H, d, *J* 5.9, 5′-H_2).

1-(5-*Benzamido*-5-*deoxy*-3-O-*methylsulfonyl*-β-D-*arabinofuranosyl*)*uracil* **12**.—To a solution of the 2,2′-anhydro-5′-benzamido compound **3** (100 mg, 0.25 mmol) in acetone–water 1:1 (20 cm^3) the ion exchanger Dowex 50 (H^+) (260 mg) was added. This suspension was stirred at room temperature for 72 h and filtered. The filtrate was evaporated to dryness and the residue crystallized from methanol–diethyl ether to give the ring-opened product **12** (89 mg, 84%); R_f 0.27; m.p. 174–176 °C (Found: C, 48.05; H, 4.6; N, 10.0. $C_{17}H_{19}N_3O_8S$ requires C, 48.0; H, 4.5; N, 9.9%); $[\alpha]_D^{28}$ +161 (*c* 1.09 in MeOH); λ_{max}/nm 219 and 260 (log ε 4.10 and 4.00); λ_{min}/nm 244 (log ε 3.96); ν_{max}/cm^{-1} 3394, 3313, 3107, 3019, 1722, 1695, 1630, 1542, 1454, 1354, 1280, 1180, 965 and 847.

1-(3-*Amino*-5-*azido*-3,5-*dideoxy*-β-D-*arabinofuranosyl*)*uracil* **15** *and* 1-(2-*Amino*-5-*azido*-2,5-*dideoxy*-β-D-*xylofuranosyl*)*uracil* **16**.—A solution of the oxirane **10** (200 mg, 0.79 mmol) in 15% ethanolic ammonia (7 cm^3) was heated in a pressure vessel at 130 °C for 5 h and then evaporated to dryness. It afforded the arabinofuranosyl **15**, R_f 0.05, and xylofuranosyl isomer **16**, R_f 0.04, in a ratio 2:1 (established by ^1H NMR spectra), used for further experiments.

General Procedure for the Hydrogenolysis of Azides **10**, **22**, **26** *and* **5**.—To a solution of the azides (0.4 mmol) in ethanol (30 cm^3) Pd-black (9 mg) was added and stirred in a H_2 atmosphere at 0.35 MPa at room temperature for 18 h. The catalyst was filtered off and the filtrate evaporated to dryness as in the case of the amino compounds **13** and **23** (used for further experiment). The residue was recrystallized from methanol as in the case of the amino compound **29** and rearranged imine **32**.

1-(5-*Amino*-5-*deoxy*-2,3-*epoxy*-β-D-*lyxofuranosyl*)*uracil* **13**. From **10**: 99%; R_f 0.03.

1-(2-O-*Acetyl*-3-*amino*-5-*benzamido*-3,5-*dideoxy*-β-D-*arabinofuranosyl*)*uracil* **23**. From **22**: 98%; R_f 0.13.

1-(3-*Amino*-2,5-*anhydro*-3-*deoxy*-β-D-*arabinofuranosyl*)*uracil* **29**. From **26**: 82%; R_f 0.09; m.p. 244–246 °C (Found: C, 47.75; H, 5.15; N, 18.4. $C_9H_{11}N_3O_4$ requires C, 48.0; H, 4.9; N, 18.65%); $[\alpha]_D^{25}$ +337 (*c* 0.23 in MeOH); λ_{max}/nm 264 (log ε 3.93); ν_{max}/cm^{-1} 3388, 3318, 3103, 3023, 2993, 1772, 1708, 1683infl, 1665, 1650infl, 1601, 1463, 1414, 1382, 1272, 1262, 1095 and 963; $\delta_H([^2H_6]$-DMSO) 7.91 (1 H, d, *J* 8.2, 6-H), 6.25 (1 H, s, 1′-H), 5.69 (1 H, d, *J* 8.2, 5-H), 4.51 (1 H, s, 2′-H), 4.29 (1 H, q, *J* 2.4 and 1.2, 4′-H), 4.04 (2 H, br s, 5′-H_2), 3.77 (1 H, d, *J* 2.4, 3′-H).

2,5′-*Imino*-1-(2-O-*methylsulfonyl*-β-D-*arabinofuranosyl*)*uracil* **32**. From **5**, 94%; R_f 0.05; m.p. 201–203 °C (Found: C, 39.4; H, 4.4; N, 13.65. $C_{10}H_{13}N_3O_6S$ requires C, 39.6; H, 4.3; N, 13.85%); $[\alpha]_D^{33}$ −73 (*c* 0.85 in DMF); λ_{max}/nm 215.5 (log ε 4.38); λ_{max}/cm^{-1} 3550infl, 3480, 3429, 3240infl, 2899, 1649, 1611, 1532, 1496, 1453, 1342, 1178, 997 and 972.

General Procedure for the Benzoylation of Amines **13**, **15** + **16**, **23**, **29** *and the Imine* **32**.—To a solution of amine (0.4 mmol) or imine (0.16 mmol) in pyridine (5 cm^3) benzoic acid anhydride (0.44 mmol) was added and the mixture kept at room temperature (45 min in the case of the amino compounds and 6 h in the case of the imino compound). The solvent was coevaporated with toluene. The residue was washed with diethyl ether and subjected to preparative TLC [CH_2Cl_2–MeOH (10:0.5), three developments].

1-(5-*Benzamido*-3-*deoxy*-2,3-*epoxy*-β-D-*lyxofuranosyl*)*uracil* **14**. From **13**: 92%; m.p. 186–188 °C; identical (mixed m.p., NMR and IR spectra) with a specimen obtained by the hydrogenolysis–benzoylation of the azido compound **10**.

1-(5-*Azido*-3-*benzamido*-3,5-*dideoxy*-β-D-*arabinofuranosyl*)-*uracil* **17** and 1-(5-*Azido*-2-*benzamido*-2,5-*dideoxy*-β-D-*xylofuranosyl*)*uracil* **18**. From a mixture of the amino compound **15** and **16**: 47% of **17**; R_f 0.19, and 36% of **18**; R_f 0.15; both used for further experiments.

1-(2-O-*Acetyl*-3,5-*dibenzamido*-3,5-*dideoxy*-β-D-*arabinofuranosyl*)*uracil* **24**. From **23**: 81%; R_f 0.39; m.p. 264–265 °C (from MeOH); identical (mixed m.p., NMR and IR spectra) with a specimen obtained by the hydrogenolysis–benzoylation of the azido compound **22**.

1-(2,5-*Anhydro*-3-*benzamido*-3-*deoxy*-β-D-*arabinofuranosyl*)-*uracil* **30**. From **29**: 76%; R_f 0.26; m.p. 263–265 °C (from MeOH) (Found: C, 58.5; H, 4.45; N, 12.95. $C_{16}H_{15}N_3O_5$ requires C, 58.35; H, 4.6; N, 12.75%); $[\alpha]_D^{25}$ +92 (*c* 0.45 in MeOH);

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λ_{max}/nm 220 and 261.5 (log ε 4.16 and 4.12); λ_{min}/nm 245 (log ε 4.06); ν_{max}/cm^{-1} 3312, 3262, 3012, 2957, 1707, 1689, 1685, 1632, 1527, 1456, 1280, 1262, 1039, 921 and 859; δ_H([$^2H_6$]-DMSO) 11.37 (1 H, br s, 3-NH), 9.07–9.03 (1 H, m, 3′-NH), 7.98–7.87 and 7.58–7.41 (2 + 3 H, 2 × m, ArH), 7.86 (1 H, d, *J* 7.9, 6-H), 5.99 (1 H, s, 1′-H), 5.61 (1 H, d, *J* 7.9, 5-H), 4.91 (1 H, s, 2′-H), 4.70 (1 H, d, *J* 2.6, 3′-H), 4.34 (1 H, t, *J* 2.6, 4′-H) and 4.04 (2 H, br s, 5′-H_2).

2,5′-*Imino*-1-(2-O-*benzoyl*-3-O-*methylsulfonyl*-β-D-*arabinofuranosyl*)*uracil* **35**. From **32**: 53.7%; R_f 0.30; m.p. 148–150 °C (from dichloromethane–diethyl ether–hexane) (Found: C, 49.85; H, 4.35; N, 10.4. $C_{17}H_{17}N_3O_7S$ requires C, 50.1; H, 4.2; N, 10.3%); $[\alpha]_D^{33}$ +32 (*c* 0.55 in MeOH); λ_{max}/nm 222.5 (log ε 4.43); ν_{max}/cm^{-1} 3393, 3156, 3022, 2935, 1735, 1661, 1497, 1409, 1354, 1262, 1176, 1114, 965, 870 and 826. The by-product **3** was isolated in 33.7% yield; identical (NMR and IR spectra) with an authentic specimen.

General Procedure for the Acetylation of Secondary Alcohols **17**, **18**, **21** *and Imine* **32**.—To a solution of alcohol or imine (0.19 mmol) in pyridine (7 cm^3) acetic anhydride (0.39 mmol) was added and the mixture kept at room temperature for 24 h as in the case of alcohols or 2 h as in the case of the imino compound. The solvent was coevaporated with toluene. The residue was purified by preparative TLC [CH_2Cl_2–MeOH (10:0.6)].

1-(2-O-*Acetyl*-5-*azido*-3-*benzamido*-3,5-*dideoxy*-β-D-*arabinofuranosyl*)*uracil* **19**. From **17**: 62%; R_f 0.24; m.p. 184–186 °C (from MeOH) (Found: C, 52.1; H, 4.65; N, 20.1. $C_{18}H_{18}N_6O_8$ requires C, 52.15; H, 4.4; N, 20.3%); $[\alpha]_D^{22}$ −67 (*c* 0.93 in DMF); λ_{max}/nm 224 and 255 (log ε 3.78 and 3.74); λ_{min}/nm 244 (log ε 3.72); ν_{max}/cm^{-1} 3317, 3178, 3053, 2089, 1746, 1696, 1674, 1622, 1537, 1468, 1420, 1258, 1223, 1212, 1043, 859, 802 and 714.

1-(3-O-*Acetyl*-5-*azido*-2-*benzamido*-2,5-*dideoxy*-β-D-*xylofuranosyl*)*uracil* **20**. From **18**: 67%; R_f 0.24; m.p. 125–127 °C (from acetone) (Found: C, 52.25; H, 4.3; N, 20.15. $C_{18}H_{18}N_6O_8$ requires C, 52.15; H, 4.4; N, 20.3%); $[\alpha]_D^{21}$ +272 (*c* 1.19 in MeOH); λ_{max}/nm 219.9 and 256.8 (log ε 4.03 and 3.95); λ_{min}/nm 247.5 (log ε 3.94); ν_{max}/cm^{-1} 3460infl, 3295, 3062, 2109, 1756, 1689, 1645, 1537, 1533, 1462, 1273, 1225, 1217, 1064, 816, 717 and 692.

1-(2-O-*Acetyl*-3-*azido*-5-*benzamido*-3,5-*dideoxy*-β-D-*arabinofuranosyl*)*uracil* **22**. From **21**: 71%; R_f 0.44; m.p. 86–88 °C from dichloromethane–diethyl ether–hexane) (Found: C, 52.4; H, 4.55; N, 20.25. $C_{18}H_{18}N_6O_6$ requires C, 52.15; H, 4.4; N, 20.3%); $[\alpha]_D^{22}$ +87.5 (*c* 0.8 in MeOH); λ_{max}/nm 220 and 256 (log ε 4.01 and 3.89); λ_{min}/nm 246 (log ε 3.88); ν_{max}/cm^{-1} 3344, 3203, 3061, 2932, 2111, 1753, 1713infl, 1693br, 1647infl, 1536, 1459, 1377, 1280, 1218, 1104, 810, 714 and 693.

2,5′-*Imino*-1-(2-O-*acetyl*-3-O-*methylsulfonyl*-β-D-*arabinofuranosyl*)*uracil* **33**. From **32**: 79.6%; R_f 0.22; m.p. 217–219 °C (from MeOH) (Found: C, 41.9; H, 4.65; N, 12.3. $C_{12}H_{15}N_3O_7S$ requires C, 41.75; H, 4.4; N, 12.15%); $[\alpha]_D^{23}$ −46 (*c* 0.75 in MeOH); λ_{max}/nm 218.5 (log ε 4.35); ν_{max}/cm^{-1} 3414, 3225, 3084, 2934, 1750, 1663, 1624, 1576, 1502, 1410, 1223, 1177, 1000 and 970. From methanolic mother liquor an additional amount of **33** was isolated by preparative TLC; overall yield 92%.

Intramolecular Rearrangements of the 2,5′-*Imino Compound* **32**.—To a solution of **32** (50 mg, 0.16 mmol) in pyridine (6 cm^3) benzoyl chloride (50 mg, 0.36 mmol) was added and the mixture stirred at room temperature for 1.5 h; it was then treated with methanol (8 cm^3). The solvent was coevaporated with toluene. The residue was recrystallized from methanol to give the crystalline 2,2′-anhydro compound **3** (48 mg, 74%), m.p. 186–188 °C; identical (mixed m.p., NMR and IR spectra) with an authentic specimen. From the mother liquor **12** was also isolated by preparative TLC [CH_2Cl_2–MeOH (10:0.6)] (16 mg, 23.5%), m.p. 173–176 °C; identical (mixed m.p., NMR and IR spectra) with that obtained from the 2,2′-anhydro compound **3**.

5′-N-*Acetyl*-2,5′-*imino*-1-(2-O-*acetyl*-3-O-*methylsulfonyl*-β-D-*arabinofuranosyl*)*uracil* **34**.—To a solution of the 2,5′-imino compound **32** (80 mg, 0.26 mmol) in pyridine (5 cm^3) acetyl chloride (98 mg, 1.25 mmol) was added and the mixture stirred at room temperature for 1 h. The solvent was coevaporated with toluene and the residue purified by preparative TLC [CH_2Cl_2–MeOH (10:0.6), two developments] and recrystallized from methanol–diethyl ether. It afforded the 5′-*N*-acetyl compound **34** (86 mg, 85%); R_f 0.42; m.p. 126–129 °C (Found: C, 43.2; H, 4.75; N, 10.75. $C_{14}H_{17}N_3O_8S$ requires C, 43.4; H, 4.4; N, 10.85%); $[\alpha]_D^{22}$ −131 (*c* 0.54 in MeOH); λ_{max}/nm 230 (log ε 4.33); ν_{max}/cm^{-1} 1750, 1689, 1668, 1657, 1651, 1645, 1520, 1361, 1220, 1175, 1069 and 968.

5′-N-*Benzoyl*-2,5′-*imino*-1-(2-O-*benzoyl*-3-O-*methylsulfonyl*-β-D-*arabinofuranosyl*)*uracil* **37**.—To a solution of the 2,5′-imino compound **35** (36 mg, 0.09 mmol) in pyridine (5 cm^3) benzoyl chloride (24.4 mg, 0.17 mmol) was added. The mixture was then stirred at room temperature for 15 min and treated with methanol (4 cm^3). The solvent was coevaporated with toluene and the residue purified by preparative TLC (CH_2Cl_2–MeOH 10:0.6). It afforded the 5′-*N*-benzoyl compound **37** (38 mg, 82.6%); R_f 0.42; m.p. 151–153 °C (from acetone) (Found: C, 56.15; H, 4.05; N, 8.35. $C_{24}H_{21}N_3O_8S$ requires C, 56.35; H, 4.15; N, 8.2%); $[\alpha]_D^{22}$ −171 (*c* 0.42 in MeOH); λ_{max}/nm 228.5 (log ε 4.34); ν_{max}/cm^{-1} 1736, 1652, 1512, 1451, 1358, 1269, 1175, 1119, 1071, 971, 878 and 830.

General Procedure for the Preparation of Diphenylphosphoramidates **38**–**40**.—To a suspension of the azide **5**, **10** or **22** (0.45 mmol) in dioxane (9 cm^3) triphenyl phosphite (3.05 mmol) was added and the mixture heated under reflux in the presence of equimolar amount of water (1.5 h in the case of **5** and 3 h in the case of **10** and **22**). The reaction mixture was evaporated to dryness and the residue subjected to preparative TLC [CH_2Cl_2–MeOH (10:0.7), two developments].

2,2′-*Anhydro*-1-(5-*deoxy*-5-*diphenylphosphoramido*-3-O-*methylsulfonyl*-β-D-*arabinofuranosyl*)*uracil* **38**. From **5**: 89.3%; R_f 0.18; m.p. 228–230 °C (from MeOH) (Found: C, 49.15; H, 4.4; N, 8.1. $C_{22}H_{22}N_3O_9PS$ requires C, 49.35; H, 4.15; N, 7.85%); $[\alpha]_D^{24}$ −40 (*c* 0.2 in DMF); λ_{max}/nm 221 and 245 (log ε 3.79 and 3.72); λ_{min}/nm 234 (log ε 3.70); ν_{max}/cm^{-1} 3152, 3092, 2932, 1660, 1634infl, 1638infl, 1622, 1534, 1477, 1337, 1254, 1196, 1173, 1023, 951, 940, 915, 902, 841 and 823; δ_H([$^2H_6$]-DMSO) 7.75 (1 H, d, *J* 7.6, 6-H), 7.45–7.11 (10 H, m, ArH), 6.40 (1 H, d, *J* 5.6, 1′-H), 6.05 (1 H, m, 5′-NH), 5.85 (1 H, d, *J* 7.6, 5-H), 5.62 (1 H, d, *J* 5.6, 2′-H), 5.46 (1 H, d, *J* 2.4, 3′-H), 4.33 (1 H, sext, *J* 2.4 and 7.1, 4′-H), 3.28 (3 H, s, MsMe) and 3.02–2.91 (2 H, m, 5′-H_2); *m*/*z* 535 (M^+).

1-(5-*Deoxy*-5-*diphenylphosphoramido*-2,3-*epoxy*-β-D-*lyxofuranosyl*)*uracil* **39**. From **10**: 78%; R_f 0.36; m.p. 128–130 °C (from dichloromethane–diethyl ether–hexane) (Found: C, 54.95; H, 4.65; N, 9.05. $C_{21}H_{20}N_3O_7PS$ requires C, 55.15; H, 4.4; N, 9.2%); $[\alpha]_D^{32}$ +21 (*c* 1 in MeOH); λ_{max}/nm 256 (log ε 3.94); ν_{max}/cm^{-1} 3419, 3168, 3067, 2922, 1758, 1717, 1696, 1673, 1648, 1634, 1519, 1488, 1459, 1385, 1255, 1218, 1196, 1103, 957, 907, 888 and 811; δ_H([$^2H_6$]-DMSO) 11.06 (1 H, br s, 3-NH), 7.59 (1 H, d, *J* 8.2, 6-H), 7.46–7.06 (10 H, m, ArH), 5.99 (1 H, s, 1′-H), 5.91–5.72 (1 H, m, 5′-NH), 5.57 (1 H, d, *J* 8.2, 5-H), 4.07–3.87 (3 H, m, 2′-, 3′- and 4′-H), 3.30 (1 H, dd, *J* 12.6 and 1.8, 5′-H_A), 3.22 (1 H, dd, *J* 12.6 and 2.1, 5′-H_B); *m*/*z* 457 (M^+).

1-(2-O-*Acetyl*-5-*benzamido*-3,5-*dideoxy*-3-*diphenylphosphoramido*-β-D-*arabinofuranosyl*)*uracil* **40**. From **22**: 83%; R_f 0.42;

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m.p. 197–200 °C (from MeOH) (Found: C, 57.9; H, 4.95; N, 9.0. $C_{30}H_{29}N_4O_9P$ requires C, 58.05; H, 4.7; N, 9.05%); $[\alpha]_D^{23}$ +66 (*c* 0.7 in MeOH); λ_{max}/nm 253 (log ε 4.07); λ_{infl}/nm 228 (log ε 4.09); λ_{min}/nm 240 (log ε 4.05); ν_{max}/cm^{-1} 3369, 3168, 3067, 2922, 1758, 1717, 1696, 1673, 1648, 1634, 1519, 1488, 1459, 1385, 1255, 1218, 1196, 1103, 957, 907 and 811; *m*/*z* 621 (M^+).

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