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Preliminary communication

Transformation of nucleosides containing β-D-xylofuranuronic acid into the D-*ribo* analogues

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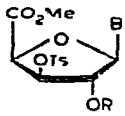
Nucleosides containing 3-*O*-toluene-*p*-sulphonyl-β-D-xylofuranuronic acid (*e g* , **1**–**3**) are convenient precursors of unsaturated purine and pyrimidine nucleosides, and also of O^2,2-cyclonucleosides and pyrimidine nucleosides having the D-*arabino* configuration[1,2] We now report on a simple route for the transformation of **1** and **3** into the D-ribofuranuronic acid derivatives **6** and **7**, respectively

Treatment of 1-(methyl 2-*O*-acetyl-3-*O*-toluene-*p*-sulphonyl-β-D-xylofuranosyluronate)uracil[1,2] (**1**) with excess of phthalimide in anhydrous *N*,*N*-dimethylformamide at 130° for 10 h afforded a mixture of the isomeric acetates **4** and **5** (84% after chromatography on silica gel) P m r data ($CDCl_3$) δ 10 24 and 9 96 (2 s, NH), 8 20 and 8 16 (2 d, $J_{5,6}$ 8 0 Hz, H-6), 6 34 and 6 18 (2 d $J_{1',2'}$ 6 0 Hz, H-1'), 5 88 (d, $J_{5\ 6}$ 8 0 Hz, H-5), 3 84 (s, COOMe), 2 20 and 2 12 (2 s, OAc)

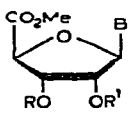
Treatment of **4**/**5** with 3% methanolic hydrogen chloride gave 1-(methyl β-D-ribofuranosyluronate)uracil (**6**, 80%), m p 229–231° (from methanol), $[\alpha]_D^{20}$ –32° (*c* 1 3, methyl sulphoxide), lit [3] m p 236° P m r data (Me_2SO-d_6 with a few drops of CF_3COOH to remove the signal of the rapidly exchanging protons) δ 8 12 (d, 1 H, $J_{5,6}$ 8 0 Hz, H-6), 6 12 (d, 1 H, $J_{1',2'}$ 6 0 Hz, H-1'), 5 90 (d, 1 H, H-5), 4 52 (d, 1 H $J_{3',4'}$ 2 0 Hz, H-4'), 4 30 (dd, 1 H, $J_{2',3'}$ 4 0 Hz, H-3'), 4 16 (dd, 1 H, H-2')

Under analogous reaction conditions, **3** gave 6-benzamidopurine (71%) and a mixture of acetates (24%) which, on deacetylation with methanolic trimethylamine, yielded 6-benzamido-9-(methyl β-D-ribofuranosyluronate)purine (**7**) as an oil, $[\alpha]_D^{20}$ –7° (*c* 1 8, methyl sulphoxide) P m r data (Me_2SO-d_6) δ 8 56 and 8 52 (2 s, H-2,8), 7 88–7 32 (Bz), 6 08 (d, 1 H, $J_{1',2'}$ 6 0 Hz, H-1'), 4 64 (dd, 1 H, $J_{2',3'}$ 3 0 Hz, H-2'), 4 46 (d, 1 H, $J_{3',4'}$ 3 0 Hz, H-4'), 4 32 (dd, 1 H, H-3'), 3 08 (s, COOMe)

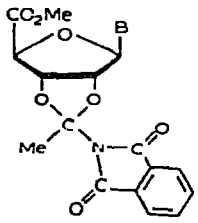
The transformation **1**→**4**/**5** probably involves the intermediate **8** or a related, solvated ion-pair (acyloxonium cation–phthalimide anion) which undergoes a decomposition of the Woodward type[4] The presence of acidic agents (phthalimide and toluene-*p*-sulphonic acid) in the reaction mixture should reduce the possibility of intramolecular at-



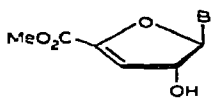
1 R = Ac, B = uracil 1-yl
2 R = H, B = uracil 1-yl
3 R = Ac, B = 6-benzamidopurine 9-yl



4 R = H, R' = Ac B = uracil 1 yl
5 R = Ac, R' = H B = uracil 1 yl
6 R = R' = H, B = uracil 1-yl
7 R = R' = H B = 6-benzamidopurine 9 yl



8



9 B = uracil 1 yl

tack by O-2 on C-2′ in **8**

1-(*O*^{2},2′-Cyclo-β-D-arabinofuranosyluronamide)uracil[2] is not affected by prolonged heating of its solution in *N*,*N*-dimethylformamide at 130° in the presence of phthalimide Under similar conditions, **2** is converted[2] into the nucleoside **9**

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