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Preliminary communication

Synthesis of 5-deoxy-3-*O*-methyl-5-*C*-(phenylphosphinyl)-L-idopyranose

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As a chemical modification of sugars, some "phosphorus sugars", which have a phosphorus atom in the hemiacetal ring instead of the oxygen atom, have been synthesized[1–3]. Synthesis of a phosphorus sugar that was a 6-*C*-nitro-L-idopyranose derivative was reported previously; however, attempts to convert the nitro group into a hydroxyl group were unsuccessful[4]. We now report the synthesis of 5-deoxy-3-*O*-methyl-5-*C*-(phenylphosphinyl)-L-idopyranose *via* a key conversion of a nitro group, by the ozone–methoxide method[5], into an aldehyde derivative.

Addition of an excess of phenylphosphine to 5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose (**1**) in benzene during 1 h at 40–50° under a nitrogen atmosphere, followed by removal of unreacted phenylphosphine and the solvent, and by separation of the products by chromatography on a column of silica gel, afforded the 1:1 adducts **2a** and **2b** in a yield of 51%, as well as the 1:2 adduct **3**. The ratio of 5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-6-*C*-nitro-5-*C*-(phenylphosphino)-β-L-idofuranose (**2a**) to 5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-6-*C*-nitro-5-*C*-(phenylphosphino)-α-D-glucofuranose (**2b**) was determined to be 3.8:1 by means of their ^{1}H-n.m.r. spectra. These two compounds showed the characteristic P–H absorption at 2300 cm^{-1} in their i.r. spectra.

Treatment of an oxolane solution of the 1:1 adduct **2a** with boiling 0.7M aqueous hydrochloric acid for 3 h under reflux, followed by processing with Amberlite IRA-410 ion-exchange resin gave crude product **4a** (82% yield), whose i.r. spectrum showed no P–H absorption, indicating that the phosphorus atom had been introduced into the hemiacetal ring. Conversion of the nitro group in compound **4a** into aldehyde **5a** (100% yield) was performed by oxidation with ozone in the presence of sodium methoxide in methanol at −78°; the i.r. spectrum of compound **5a** showed C=O absorption at 1730 cm^{-1}. Reduction of aldehyde **5a** with a boiling solution of sodium borotetrahydride in methanol for 16 h under reflux afforded syrupy 5-deoxy-3-*O*-methyl-5-*C*-(phenylphosphinyl)-L-idopyranose (**6a**),

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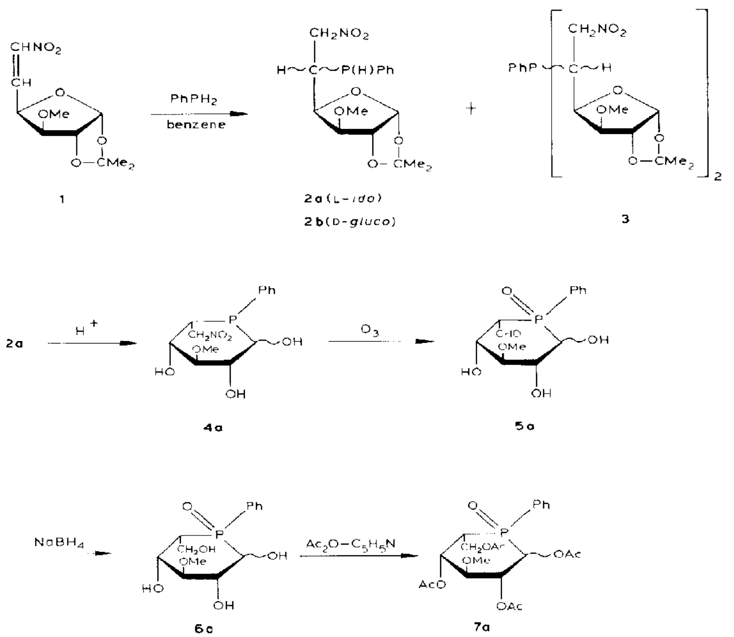

which was acetylated with acetic anhydride in pyridine for 3 days at room temperature, to give, on isolation by column chromatography on silica gel, 1,2,4,6-tetra-*O*-acetyl-5-deoxy-3-*O*-methyl-5-*C*-(phenylphosphinyl)-α,β-L-idopyranose (**7a**) in 3.2% yield from compound **2**; for **7a**, $[\alpha]_D^{17}$ +1.05° (*c* 0.86, $CHCl_3$); ν_{max}^{neat} 1750 (C=O), 1440 (P–Ph), 1180 (P=O), and 720 cm^{-1} (C–P); ^1H-n.m.r. ($CDCl_3$): δ 2.03, 2.18 (2 s, 12 H, 4 OAc), 3.64 (s, 1.8 H, OMe), 3.83 (s, 1.2 H, OMe), 3.9–4.5 (m, 3 H, H-5,6,6′), 4.9–5.3 (m, 2 H, H-3,4), 5.48 (d, 0.6 H, *J* 2.0 Hz, H-1), 5.95 (d, 0.4 H, *J* 2.5 Hz, H-2), 6.00 (d, 0.6 H, *J* 2.0 Hz, H-2), 6.13 (d, 0.4 H, *J* 2.5 Hz, H-1), and 7.1–8.5 (m, 5 H, Ph); *m/z* 470 (M^+).

The present synthetic method is the first in which a phosphorus sugar, a derivative of 5-deoxy-L-idopyranose, has been prepared *via* conversion of the 6-*C*-nitro group.

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