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Preliminary communication

Synthesis of 5-deoxy-5-*C*-(diphenylphosphinyl)-1,2-*O*-isopropylidene-3-*O*-methyl-β-L-idofuranose

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Syntheses of sugar analogs having a phosphorus atom in the hemiacetal ring are interesting, not only from the point of view of their chemistry, but also from that of the possible utility of their biological activities. A few reports[1–4] have been published concerning the synthesis of phosphorus sugars of the pentopyranose type, compounds prepared from 5-deoxy-5-halo sugars by employing the Michaelis–Arbuzov reaction followed by reduction of the phosphorus ester and hydrolysis. 6-*C*-Nitro-L-idopyranose derivatives[5] having phosphorus in the hemiacetal ring have been synthesized; however, attempts to convert the nitro group into a hydroxyl group were unsuccessful.

We now report the synthesis of compound **2** by addition of diphenylphosphine oxide to a reactive, alkenic sugar, *i.e.*, 5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose[6] (**1**), and conversion of the 6-*C*-nitro group into a hydroxyl group.

Addition of diphenylphosphine oxide to **1** in oxolane (THF) for 24 h under reflux afforded a mixture of the L-idofuranose compound **2** and the D-glucofuranose compound **3**. A syrup containing **2** and **3** (the ratio of **2** to **3**, determined by ^{1}H-n.m.r. spectroscopy, was 11:1) was separated from the reaction mixture in 53% yield by chromatography on a column of silica gel. Crystalline 5,6-dideoxy-5-*C*-(diphenylphosphinyl)-1,2-*O*-isopropylidene-3-*O*-methyl-6-*C*-nitro-β-L-idofuranose (**2**) was isolated in 40% yield, m.p. 149–150°, $[\alpha]_D^{26}$ −49.8° (*c* 1.02, MeOH). ^{1}H-n.m.r. ($CDCl_3$): δ 1.20 (s, 6 H, Me_2C), 3.38 (s, 3 H, OMe), 3.7–5.1 (m, 6 H, H-2, -3, -4, -5, -6), 5.75 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), and 7.3–8.2 (m, 10 H, 2 Ph); *m/z* 447 (M^+).

Anal. Calc. for $C_{22}H_{26}NO_7P$: C, 59.06; H, 5.86; N, 3.13. Found: C, 58.92; H, 5.82; N, 3.03.

3-Nitrophosphinyl compound **2** was transformed into aldehyde **4** on treatment

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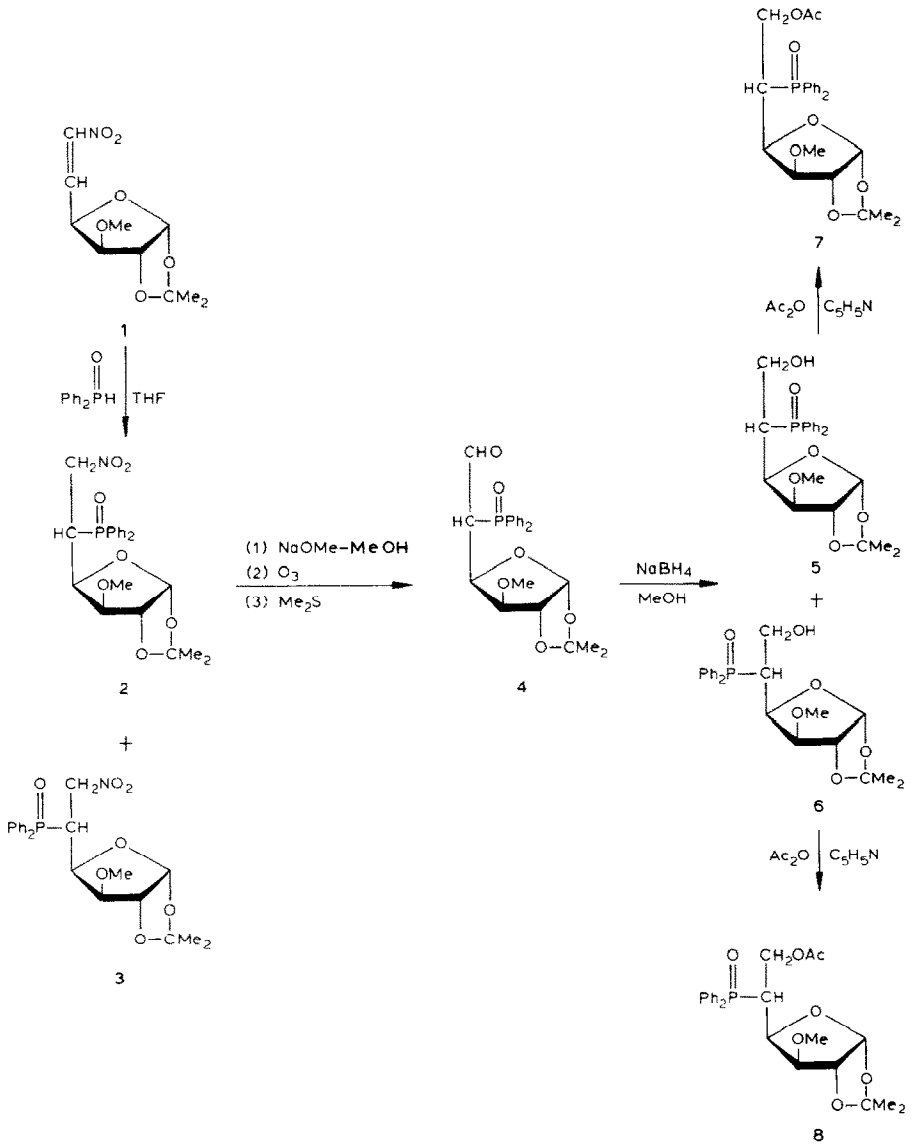
with ozone–sodium methoxide[7] at −78°. The ^{1}H-n.m.r. spectrum ($CDCl_3$) of **4** showed a signal due to the aldehyde proton at δ 9.90, and the i.r. spectrum showed absorption due to the carbonyl group, at 1770 cm^{-1}.

Reduction of **4** with[8] sodium borohydride ($NaBH_4$) gave a mixture of the L-ido-furanose compound **5** and the D-glucofuranose compound **6**. A syrup containing compounds **5** and **6** (in the molar ratio of 11 : 1, determined by ^{1}H-n.m.r. spectroscopy) was separated from the mixture in 65% yield by chromatography on a column of silica gel.



Crystalline 5-deoxy-5-*C*-(diphenylphosphinyl)-1,2-*O*-isopropylidene-3-*O*-methyl-β-L-idofuranose (**5**) was isolated in 34% yield; m.p. 175–176°, $[\alpha]_D^{25}$ [illegible] (*c* 1, MeOH); ¹H-n.m.r. ($CDCl_3$): δ 1.15, 1.20 (2 s, 6 H, CMe_2), 3.40 (s, 3 H, OMe), 3.7–4.2 (m, 7 H, H-2–6', OH), 5.70 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), and 7.2–8.1 (m, 10 H, 2 Ph); ν_{max}^{KBr} 3250 cm^{-1} (OH), *m/z* 418 (M^+).

Anal. Calc. for $C_{22}H_{27}O_6P$: 418.15572. Found: [illegible].

Acetylation of compounds **5** and **6** with acetic anhydride–pyridine[9] at room temperature gave compounds **7** and **8**, respectively; the ¹H-n.m.r. spectra ($CDCl_3$) of the acetates showed the acetyl signal at δ 1.68 (L-idofuranose deriv. **7**) and [illegible] (D-glucofuranose deriv. **8**).

The present synthetic method is the first, and a convenient one, for preparing 5-(phosphinyl)-β-L-idofuranose and -α-D-glucofuranose derivatives [illegible] of the 5-nitro group; it may be expected to provide sugar derivatives [illegible] acetal ring.

REFERENCES

1 R. L. Whistler and C.-C. Wang, *J. Org. Chem.*, 33 (1968) 4455–4458.
2 S. Inokawa, Y. Tsuchiya, K. Seo, H. Yoshida, and T. Ogata, *Bull. Chem. Soc. Jpn.*, 44 (1971) 2279.
3 S. Inokawa, H. Kitagawa, K. Seo, H. Yoshida, and T. Ogata, *Carbohydr. Res.*, 30 (1973) 127–132.
4 K. Seo and S. Inokawa, *Bull. Chem. Soc. Jpn.*, 46 (1973) 3301–3302; 48 (1975) 1237–1239.
5 H. Takayanagi, M. Yamashita, K. Seo, H. Yoshida, T. Ogata, and S. Inokawa, *Carbohydr. Res.*, 38 (1974) C19–C21; 63 (1978) 105–113.
6 R. L. Whistler and R. F. Pyler, *Carbohydr. Res.*, 12 (1970) 201–221.
7 M. Yamada, M. Yamashita, and S. Inokawa, *Synthesis*, in press.
8 M. Yamada, M. Yamashita, and S. Inokawa, unpublished results.
9 M. L. Wolfrom and A. Thompson, *Methods Carbohydr. Chem.*, 2 (1963) 211–215, see p. 212.