Carbohydrate Research, 122 (1983) C1–C3
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Preliminary communication

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

MITSUJI YAMASHITA*, MANABU YAMADA, KENJI TSUNEKAWA, TATSUO OSHIKAWA,
Department of Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432 (Japan)
KUNIAKI SEO,
Department of Industrial Chemistry, Numazu College of Technology, Numazu-shi 410 (Japan)
and SABURO INOKAWA
Department of Chemistry, Faculty of Science, Okayama University, Okayama 700 (Japan)

(Received July 8th, 1983; accepted for publication, July 18th, 1983)

We have previously described[1] a synthesis of 5-deoxy-3-*O*-methyl-5-*C*-(phenylphosphinyl)-L-idopyranose wherein a process for converting the nitro group of 5,6-dideoxy-3-*O*-methyl-6-*C*-nitro-5-*C*-(phenylphosphinyl)-L-idopyranose into an aldehyde derivative by means of ozone–methoxide was employed.

Synthesis of 5-deoxy-5-*C*-(phenylphosphinyl)-L-idopyranose, having a phosphorus atom in its hemiacetal ring, is of interest, and this communication deals with a synthesis of the title compound from 5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose.

Addition to 3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose (**1**) of phenylphosphine (in large excess) for 1 h at 40–50° under a nitrogen atmosphere gave two kinds of corresponding 1:1 adducts (**2**) and the 2:1 adduct (**3**), in 65 and 35% yield, respectively. The ratio of 5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-5-*C*-(phenylphosphino)-β-L-idofuranose[2] (**2a**) to 5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-5-*C*-(phenylphosphino)-α-D-glucofuranose (**2b**) was determined by ^{1}H-n.m.r. spectroscopy to be 3.5:1. These two 1:1 adducts showed the characteristic, P–H absorption at 2325 cm^{-1} in their i.r. spectra. Compound **2a** was recrystallized from methanol, m.p. 104–106°; ^{1}H-n.m.r. ($CDCl_3$): δ 1.23, 1.35 (2 s, 6 H, 2 Me), 1.98, 2.06 (2 s, 3 H, OAc), 2.7–3.3 (m, 1 H, H-5), 3.9–4.6 (m, 4 H, H-2,4,6,6′), 4.17, 4.26 (2 dd, 1 H, J_{HP} 219, J_{HH} 6.0, J'_{HP} 215, J'_{HH} 3.5 Hz, PH), 5.03 (d, 1 H, J 2.5 Hz, H-3), 5.81, 5.83 (2 d, 1 H, J 4.0 Hz, H-1), and 7.1–7.7 (m, 5 H, Ph).

Compound **2a** was subjected to hydrolysis with 0.5 M hydrochloric acid under a nitrogen atmosphere for 2 h at 80°, and then the mixture was kept for 16 h at 40–50°. Removal of the chloride anion by means of the ion-exchange resin Amberlite IRA-410 gave the syrupy products **4a** in 88% yield. A mixture of compounds **4a** and one equivalent of

---

*To whom correspondence should be addressed.

0008-6215/83/$03.00 © 1983 Elsevier Science Publishers B.V.

[1] M. Yamashita, M. Yamada, K. Tsunekawa, T. Oshikawa, K. Seo, and S. Inokawa, *Carbohydr. Res.*, 121 (1983) C4–C5.

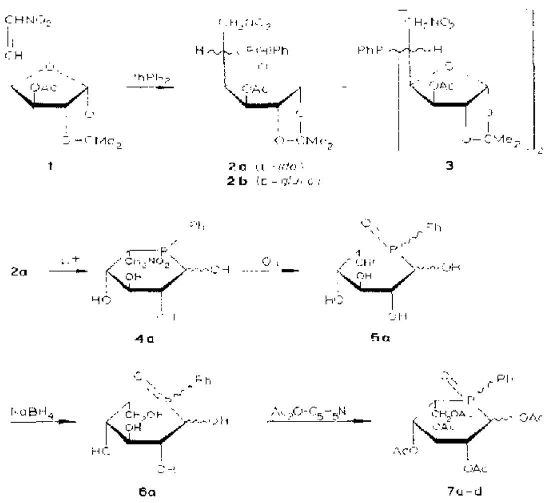
[2] P. Luger, M. Yamashita, and S. Inokawa, *Carbohydr. Res.*, 84 (1980) 25–33.

[3] M. Yamada, M. Yamashita, and S. Inokawa, *Synthesis*, (1982) 1026–1027.

[4] M. Yamada, M. Yamashita, and S. Inokawa, *Carbohydr. Res.*, 113 (1983) C10–C12.

sodium methoxide in absolute methanol was cooled to −78°, and then an ozone–oxygen flow was introduced until the color of the solution turned blue. Addition of methyl sulfide to the reaction mixture, followed by de-ionization by means of the ion-exchange resin Amberlite IR-120B, and evaporation of the solvent *in vacuo*, gave aldehydes **5a** in 100% yield; ν_{max}^{neat} 3250 (OH), 1720 (C=O), 1440 (P–Ph), 1160 (P=O), and 720 cm^{-1} (C–P); see refs. 1, 3, and 4).

Reduction of aldehyde **5a** with sodium borotetrahydride in methanol overnight at room temperature, followed by de-ionization with Amberlite IR-120B, and evaporation of the solvent *in vacuo*, gave syrupy 5-deoxy-5-*C*-(phenylphosphinyl)-L-idopyranoses (**6a**) in 100% yield: ν_{max}^{neat} 3300 (OH), 1440 (P–Ph), 1160 (P=O), and 720 cm^{-1} (C–P). Treatment of syrup **6a** in pyridine with acetic anhydride for 1 day at room temperature afforded acetates **7** (upon processing and purification by column chromatography); the overall yield of the compounds **7** was 8.6% (based on compound **2a**).



δ 1.50, 1.82, 1.95, 2.04 (4 s, 15 H, 5 OAc), 2.2–2.9 (m, 2 H, H-6,6′), 4.0–4.4 (m, 2 H, H-3,4), 4.9–5.4 (m, 1 H, H-5), 5.5–5.9 (m, 2 H, H-1,2), and 7.3–8.1 (m, 5 H, Ph); *m/z* 498 (M^+).

These four compounds, **7a–d**, are presumed to be 1,2,3,4,6-penta-*O*-acetyl-5-deoxy-5-*C*-[(*R* and *S*)-phenylphosphinyl]-α-L-idopyranose and 1,2,3,4,6-penta-*O*-acetyl-5-deoxy-5-*C*-[(*R* and *S*)-phenylphosphinyl]-β-L-idopyranose.

REFERENCES

1 M. Yamashita, M. Yamada, K. Tsunekawa, T. Oshikawa, K. Seo, and S. Inokawa, *Carbohydr. Res.*, 121 (1983) C4–C5.
2 P. Luger, M. Yamashita, and S. Inokawa, *Carbohydr. Res.*, 84 (1980) 25–33.
3 M. Yamada, M. Yamashita, and S. Inokawa, *Synthesis*, (1982) 1026–1027.
4 M. Yamada, M. Yamashita, and S. Inokawa, *Carbohydr. Res.*, 113 (1983) C10–C12.