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Preliminary communication

New route for preparation of 5,6-dideoxy-5-*C*-phosphinyl-D-*xylo*-hexose derivatives

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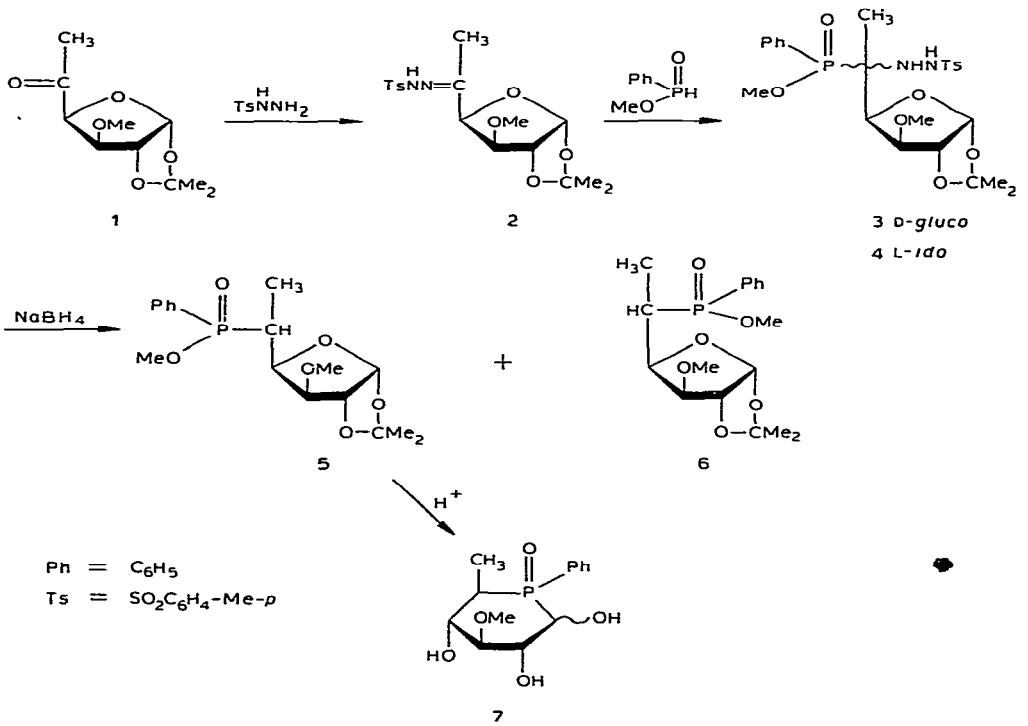
In a previous paper[1] was described the synthesis of 5,6-dideoxy-1,2-*O*-isopropylidene-5-*C*-[(methoxy)phenylphosphinyl]-3-*O*-methyl-α-D-glucofuranose (**5**) as the pre-



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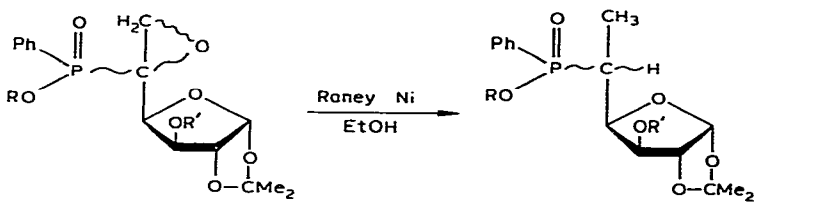

8 R = R′ = Me
9 R = Et, R′ = Bn
Bn = $PhCH_2$

5 R = R′ = Me D-*gluco*
6 R = R′ = Me L-*ido*
10 R = Et, R′ = Bn

cursor of 5,6-dideoxy-3-*O*-methyl-5-*C*-(phenylphosphinyl)-D-glucopyranose (**7**) by the sequence **1** → **3** → **5** → **7**.

We now report a new, convenient, and higher yielding route for preparation of **5** (+ **6**). We have found that 5,6-anhydro-1,2-*O*-isopropylidene-5-*C*-[(methoxy)phenylphosphinyl]-3-*O*-methyl-α-D-glucofuranose (**8**, D-*gluco*) can be synthesized in good yield by the reaction of 1,2-*O*-isopropylidene-3-*O*-methyl-6-*O*-*p*-tolylsulfonyl-α-D-*xylo*-hexofuranos-5-ulose with methyl phenylphosphinite in the presence[2] of 1,8-diazabicyclo[5.4.0]undec-7-ene. Very interestingly, hydrogenation of **8** in ethanol with hydrogen in the presence of Raney Ni (W-4) for 2 days at room temperature gave a mixture of **5** and **6** (3:2 molar ratio; n.m.r. evidence) in 85% yield. The mixture was separated by using a column of silica gel, with 2:1 ethyl acetate–benzene as the eluent, into **5** and **6** in 45 and 25% yield, respectively. Their configurations were confirmed by comparison of their n.m.r. spectra with those of authentic specimens.

Similarly, (5*RS*)-3-*O*-benzyl-5,6-dideoxy-5-*C*-[(ethoxy)phenylphosphinyl]-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**10**) {$[\alpha]_D^{23}$ −42.0° (*c* 5.43, $CHCl_3$); *m/z* 446 (M^+)} was prepared in 90% yield from **9**. Two isomers (5*R* and 5*S*) of **10** were separated by preparative t.l.c. (eluent: 1:1 ethyl acetate–benzene); the isomers had different n.m.r. spectra, as follows:

the upper band, δ ($CDCl_3$): 0.99 (q, 3 H, $J_{5,6}$ 7.5, $J_{P,CCH}$ 16.5 Hz, H-6,6′,6″), and 5.80 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1);

the lower band, δ ($CDCl_3$): 0.91 (q, 3 H, $J_{5,6}$ 7.5, $J_{P,CCH}$ 17.3 Hz, H-6,6′,6″), and 5.89 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1).

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