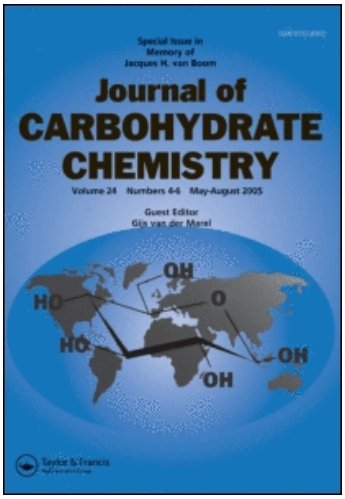

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Novel Synthesis of HEX-2-Enopyranosides

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Communication

NOVEL SYNTHESIS OF HEX-2-ENOPYRANOSIDES

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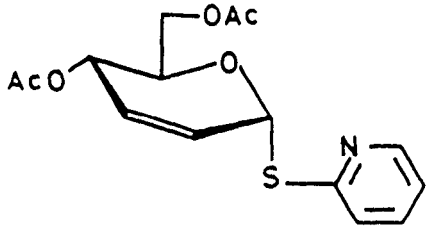
The usefulness of thioglycosides,[1] particularly 2-thiopyridyl glycosides[2] having a suitable activating group at the anomeric center for glycosylation, has been well documented. Glycosylations of 2-thiopyridyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**1**) with aglycones to furnish the corresponding 2,3-unsaturated-O-glycosides have been studied. The latter compounds are suitable for the preparation of 2,3-dideoxy-sugar glycosides.[3]

It has been observed[4] that 3,4,6-tri-O-acetyl-D-glucal (**2**) undergoes a 1,2-addition reaction with 2-thiopyridine in the presence of p-toluenesulphonic acid to afford compound **3**. However, when the reaction was conducted in the presence of boron trifluoride-etherate, in accordance with the Ferrier conditions,[5] migration of the double bond occurred with concomitant attack of the 2-thiopyridine group at C-1 to yield **1**. The structure of compound **1** was suggested from its ^{1}H-NMR spectrum in which the anomeric proton was observed as a broad singlet at 6.60 ppm, and the thiopyridyl protons as a multiplet between 6.8-8.1 ppm.

Treatment of **1** with CH_3OH, C_2H_5OH, $(CH_3)_2CHOH$ and compound **4** in methylene chloride containing 1.2 equivalents of N-bromosuccinimide at room temperature afforded the corresponding glycosides[5] (**5** to **8**) in above 90% yield. In accordance with the literature, hydrogenations of compounds **5** and **6** were carried out with freshly prepared Raney nickel at



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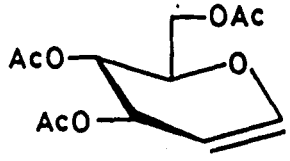

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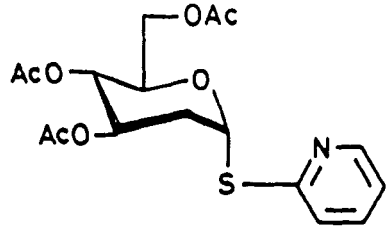

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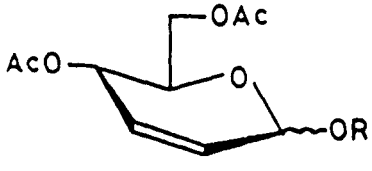
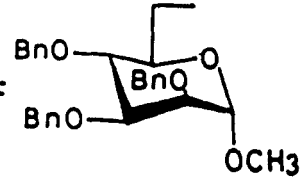


(α : β - ratio)

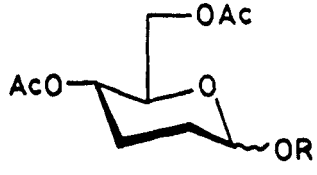
5 R = CH_3 (08·5 : 01·5)

6 R = C_2H_5 (09·0 : 01·0)

7 R = $CH(CH_3)_2$ (08·4 : 01·6)

8 R = 

(10·0 : 00·0)



9 R = CH_3

10 R = C_2H_5

45 p.s.i. for 6h to give the 2,3-dideoxy-glycosides **9**[6] and **10**[7] in almost quantitative yields.

EXPERIMENTAL

General. Solvents were removed on rotatory evaporator under diminished pressure and below 40 °C. ^{1}H-NMR spectra were run on Jeol-FX-90 Q in $CDCl_3$ with TMS as an internal standard. Light petroleum refers to the fraction with bp 60-80 °C.

2-Thiopyridyl 4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (1). To compound **2** (1.3 g, 4.78 mmol) and 2-thiopyridine (0.53 g, 4.78 mmol) in dichloromethane (10 mL) was added boron trifluoride-etherate (0.1 mL). After 1h at room temperature, the reaction mixture was diluted with dichloromethane, washed with aqueous sodium bicarbonate, water, dried (Na_2SO_4) and concentrated to give **1** (1.4 g, 92%), mp 118 °C, $[\alpha]_D$ + 328° (c 0.5, chloroform); ^{1}H-NMR ($CDCl_3$) δ 1.97, 2.10 (2s, 6H, 2xAc), 3.8-4.2 (m, 3H, H-5,6,6'), 5.10 (bd, 1H, J=7.5 Hz, H-4), 5.3-6.0 (m, 2H, H-2,3), 6.60 (bs, 1H, H-1), 6.8-8.1 (m, 4H, aromatic).

Anal. Calcd for $C_{15}H_{17}NO_5S$: C, 55.7; H, 5.2; S, 9.9. Found: C, 55.4; H, 5.2; S, 9.4.

General procedure of O-glycosylation. To compound **1** (0.4 mmol) in dichloromethane (5 mL) was added 1 mL of an alcohol (MeOH, C_2H_5OH or $(CH_3)_2CHOH$) followed by N-bromosuccinimide (0.213 g). The reaction mixture was stirred for 15 min during which time reaction colour changed from brown to pale yellow. The solution was diluted with dichloromethane and washed successively with aqueous sodium thiosulfate, aqueous sodium bicarbonate, water dried, and concentrated. The residue was chromatographed on silica gel to afford the products **5-7** (90, 93, 91% yields respectively). The spectral data from these compounds were identical with the reported[5] values. The ratio of α and β-isomers was determined by GLC analysis (OV 17, column temperature 200 °C, nitrogen flow).

Methyl 6-O-(4,6-di-Acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-2,3,4-tri-O-benzyl-α-D-mannopyranoside (8). A mixture of **1** (0.25 g, 0.77 mmol), compound **4**[8] (0.36 g, 0.77 mmol) and powdered 4°A molecular sieves (0.15 g) in dichloromethane was treated with N-bromo-

succinimide (0.15 g, 0.84 mmol) under nitrogen. After 15 min the reaction was worked up and the residue was purified on a silica gel column by eluting with ethyl acetate-light petroleum (3:7) to give **8** (0.45 g, 92%) $[\alpha]_D$ + 62° (c 0.5, chloroform); ^{1}H-NMR ($CDCl_3$) δ 1.90, 1.96 (2s, 6H, 2xAc), 3.13 (s, 3H, OCH_3), 3.2-5.2 (m, 18 H), 5.53 (s, 2H, H-1', 2'), 7.46 (s, 15 H, 3 Ph); ^{13}C-NMR ($CDCl_3$) δ 93.3 (C-1), 97.5 (C-1').

Anal. Calcd for $C_{38}H_{44}O_{11}$: C, 72.1; H, 7.0. Found: C, 72.0; H, 6.95.

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