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Preliminary communication

A convenient synthesis of *p*-nitrophenyl 1-thio-β-D-glycopyranosides by using resin-bound *p*-nitrobenzenethioxide*

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Recently, a growing interest in the synthesis of 1-thioglycosides has developed, largely due to their proved versatility as investigational tools in studies on glycosidases[2–4], in which they may serve as inducers, as competitive inhibitors, or as ligands for affinity chromatography.

The synthesis of the fully acetylated *p*-nitrophenyl 1-thioglycopyranosides has generally been achieved by the reaction of the corresponding per-*O*-acetylglycosyl halide with *p*-nitrobenzenethiol in alkaline media[5–7], or with sodium *p*-nitrobenzenethioxide in anhydrous *N,N*-dimethylformamide[4] or hexamethylphosphoric triamide[2]. In the first method, the yields are generally low, and some deacetylation has been reported[6]. The second method gives reasonably good yields, and has found some application[2,8]. However, in addition to its simplicity, the procedure we now describe obviates the hazard associated with the preparation of the thiophenoxide salt.

In a typical experiment, a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (1 g) in 2-propanol (15 mL) and dichloromethane (5 mL) was stirred with Amberlyst A-26–*p*-nitrobenzenethioxide† (3 g) for 16 h at room temperature, by when, the original, brick-red color of the resin had disappeared. After dilution with dichloromethane (30 mL), the mixture was filtered, and the solids thoroughly washed with dichloromethane. The filtrate and washings were combined and evaporated, and the residue was recrystallized twice from methanol to afford *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (87.7%), m.p. 153–155°, $[\alpha]_D$ –6.8° (chloroform);

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†Amberlyst A-26–*p*-nitrobenzenethioxide was prepared similarly to its oxygen analog[10]. *p*-Nitrobenzenethiol (9.3 g) was dissolved in 0.4M aqueous sodium hydroxide (100 mL). Amberlyst A-26 (Cl^-) resin (26 g) was then added, and the mixture was shaken for 16 h. The resin complex was filtered off, washed successively with water, acetone, and dry ether, and dried over phosphorus pentaoxide *in vacuo* for 8 h at 56°.

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lit.[4] m.p. 154–155°, $[\alpha]_D$ −8.2° (chloroform); lit.[6] m.p. 158–159°, $[\alpha]_D$ −7.0° (chloroform). 2,3,4-Tri-*O*-acetyl-α-L-fucopyranosyl bromide reacted similarly with the thiophenoxide–resin, to give the corresponding 1-thio-β-L-glycoside (69%), m.p. 137–139°, $[\alpha]_D$ +4.1° (chloroform); lit.[4] m.p. 136–138°, $[\alpha]_D$ +4.5° (chloroform).

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride likewise afforded the corresponding 1-thioglycoside (67.8%), m.p. 280–282°, $[\alpha]_D$ −24.8° (*N*,*N*-dimethylformamide); lit.[4] m.p. 282–284°, $[\alpha]_D$ −26.8° (*N*,*N*-dimethylformamide).

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