

glycerol. Yield: 4.6 g (48 %). (Found: C 47.6; H 6.82. Calc. C 47.7; H 6.88).

Thin layer chromatography. Mono-*O*-acetyl-glycerol, di-*O*-acetyl-glycerol, and tri-*O*-acetyl-glycerol were separated on glass plates coated with SiO₂ (Merck HF₂₅₄ nach Stahl) activated by heating 30 min at 120°C. Dry ethyl ether was used as solvent. The esters were detected by spraying the chromatogram with iodine in chloroform. Time for separation was 15 min.

Substance	RF-value
Mono- <i>O</i> -acetyl-glycerol	0.15
Di- <i>O</i> -acetyl-glycerol	0.42
Tri- <i>O</i> -acetyl-glycerol	0.62

NMR analysis. The glycerol esters were dissolved in deuteriochloroform and run with TMS as internal reference in a Varian A-60A Analytical NMR Spectrometer.

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Methyl 6-Deoxy-6-nitro- β -D-glucopyranosides

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During structural studies on branched dextrans a method was sought which would selectively remove the terminal non-reducing glucose residues. These are the only residues which contain primary hydroxyl groups. Replacement of the primary hydroxyls with a sequence of tosyl groups, iodide groups, and finally strong electron

attracting groups would render the modified sugar residues alkali labile.^{1,2} In a previous communication¹ the synthesis and alkaline degradation of methyl 6-deoxy-6-*p*-tolylsulphonyl- α - and - β -D-glucopyranoside was reported. The present paper reports the synthesis of the analogous 6-deoxy-6-nitro-derivatives. The synthesis of methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-nitro- α -D-glucoside by reaction of the corresponding 6-deoxy-6-iodo-derivative with sodium nitrite in an aprotic solvent has previously been reported by Sugihara *et al.*³ During the course of this work, Baer and Rank² have reported the synthesis of methyl 6-deoxy-6-nitroglycosides from 6-deoxy-6-nitrosugars by Fischer synthesis and have studied the alkaline degradation of these substances.

Methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-nitro- α - and - β -D-glucosides were formed in about 50 % yield by treatment of the corresponding 6-deoxy-6-iodo-derivatives with sodium nitrite in dimethylsulphoxide⁴ at 60°. Phloroglucinol was added to decompose the nitrite ester formed simultaneously, as devised by Kornblum *et al.*⁵ The nitro derivatives could also be prepared from the corresponding 6-*O*-tosylates but this reaction was less satisfactory. When 6-deoxy-6-iodo-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose was treated under the same conditions, no reaction was observed and under more drastic conditions severe decomposition of the product occurred. The low reactivity of primary tosylates and iodides in the galactose series is well known and has been assigned to steric hindrance by the axial substituent in the 4-position.^{3,6}

The acetates of the methyl 6-deoxy-6-nitro-glucosides cannot be deacetylated because of the alkaline lability of the free glucosides. Reaction of the methyl 6-deoxy-6-iodo-glucosides with sodium nitrite gave mixtures which made the isolation of the desired product difficult; however, the methyl 6-deoxy-6-nitro-glucosides could be prepared when the free hydroxyls were protected by reaction with 2,3-dihydro-4-H-pyran. This protecting group was later removed by mild acid treatment.

The inductive and steric effects of the nitro group should render the 6-deoxy-6-nitro-hexosides more stable to acid hydrolysis than the corresponding hexosides. In this connection, methyl β -D-glucopyranoside was hydrolysed about 5 times faster than methyl 6-deoxy-6-nitro- β -D-glucopyranoside in 4 M sulphuric acid at 80°.

Experimental. Melting points are corrected. Concentrating was done under reduced pressure, at a bath temperature not exceeding 40°. TLC was performed on Silica Gel (E. Merck AG, Darmstadt) using as irrigant ethyl ether-toluene (2:1) (A) or ethyl acetate (B). Compounds were detected with 8 % sulphuric acid at 100°.

Methyl 2,3,4-tri-O-acetyl-6-deoxy-6-nitro- α -D-glucoside. A mixture of methyl 2,3,4-tri-O-acetyl-6-deoxy-6-iodo- α -D-glucoside (200 mg), phloroglucinol dihydrate (60 mg) and sodium nitrite (50 mg) in dimethylsulphoxide (2 ml) was kept at 60°. The reaction was followed by TLC (solvent A). After 7 h, no starting material remained; the mixture was cooled and poured into ice-water (50 ml). The precipitate (90 mg), m.p. 178–180°, was collected and recrystallised from ethanol. The product was obtained as colourless needles, m.p. 181–182°, $[\alpha]_D^{20} + 143^\circ$ (c 1.6, chloroform), in good agreement with previously reported values.^{2,3}

Methyl 2,3,4-tri-O-acetyl-6-deoxy-6-nitro- β -D-glucoside was prepared analogously from methyl 2,3,4-tri-O-acetyl-6-deoxy-6-iodo- β -D-glucoside (200 mg). When the reaction mixture was poured into ice-water, no precipitate was formed. Therefore, the aqueous solution was extracted with chloroform (3 \times 50 ml). The combined chloroform extracts were dried over calcium chloride and concentrated to dryness. The crystalline product (80 mg, m.p. 150–154°) was recrystallised from aqueous ethanol to yield the pure substance as colourless needles, m.p. 154–155°, $[\alpha]_D^{20} - 47^\circ$ (c 1.2, chloroform). (Found: C 44.7; H 5.53. C₁₃H₁₉NO₁₀ requires: C 44.7; H 5.48).

Methyl 6-deoxy-6-nitro- α -D-glucopyranoside. Methyl 6-deoxy-6-iodo- α -D-glucopyranoside (1.0 g) was suspended in a mixture of acetone (10 ml), 2,3-dihydro-4-H-pyran (10 ml) and 37 % hydrochloric acid (4 drops). After a few minutes of gentle shaking, a clear solution was obtained which was kept at room temperature for 12 h. It was neutralised by shaking with potassium carbonate and poured into 5 % aqueous potassium carbonate (200 ml). The mixture was extracted with chloroform (3 \times 50 ml); the chloroform extracts were dried over calcium chloride and concentrated to a slightly yellow syrup (2.2 g).

This syrup, phloroglucinol dihydrate (0.30 g), and sodium nitrite (0.25 g) in dimethylsulphoxide (10 ml) was kept at 60° for 8 h. The solution was cooled and poured into ice-water (200 ml). The mixture was extracted with light petroleum (40–60°, 3 \times 50 ml); the light petroleum solution was dried over sodium sulphate and concentrated to a syrup (1.8 g).

This syrup, in 50 % aqueous acetic acid (50 ml) was heated on a steam bath for 4 h, concentrated to dryness and the last traces of acetic acid removed by repeated addition of water followed by concentration. The remaining product, consisting essentially of methyl 6-deoxy-6-nitro- α -D-glucopyranoside and methyl α -D-glucopyranoside, was fractionated by preparative TLC (solvent B). The 6-nitro-glucoside was obtained as a colourless syrup (0.25 g) that did not crystallise. Part of the syrup (35 mg) was acetylated with acetic anhydride-sodium acetate. The acetate obtained (47 mg) melted at 180–181°, undepressed on admixture with authentic methyl 2,3,4-tri-O-acetyl-6-deoxy-6-nitro- α -D-glucoside.

Methyl 6-deoxy-6-nitro- β -D-glucopyranoside was prepared analogously to the α -anomer, starting from methyl 6-deoxy-6-iodo- β -D-glucopyranoside (1.0 g). The product after preparative TLC (0.27 g, m.p. 152–153°) was crystallised from acetone-light petroleum to give colourless plates, m.p. 153–155°, $[\alpha]_D^{20} - 39^\circ$ (c 0.5, water). (Found: C 36.9; H 5.99. C₇H₁₃O₇N requires: C 37.6; H 5.83).

Hydrolyses of methyl 6-deoxy-6-nitro- β -D-glucopyranoside and methyl β -D-glucopyranoside by 4 M sulphuric acid were followed polarimetrically. The former substance yielded coloured products; consequently, the reaction could not be followed to completion. The rate constant was determined from the first part of the hydrolysis curve. A value of the end rotation was calculated assuming that the final product consisted essentially of 6-deoxy-6-nitro-D-glucose.

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