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Synthesis of Phenyl α-Tyvelopyranoside

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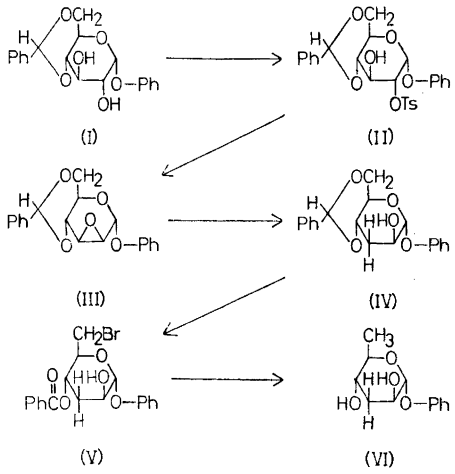
Phenyl α-tyvelopyranoside (phenyl 3,6-dideoxy-α-D-*arabino*-hexopyranoside, VI) was needed in connection with other studies and the present paper reports the synthesis of this substance. In a recent paper Stirm *et al.*[1] describe the synthesis of *p*-nitrophenyl α-tyvelopyranoside from tyvelose triacetate, *p*-nitrophenol, and mercuric chloride. The resulting mixture of α- and β-anomers was separated by chromatography but the yield of the α-glycoside was low and another route was therefore attempted.

Phenyl α-D-glucopyranoside was transformed into the 4,6-*O*-benzylidene derivative (I) and reacted with one equivalent of tosyl chloride in pyridine. A good yield of a monotosylate was obtained and shown by methylation analysis to be the 2-*O*-tosylate (II). On treatment with sodium methoxide in methanol it yielded phenyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannoside (III), which was reduced with lithium aluminium hydride into phenyl 4,6-benzylidene-3-deoxy-α-D-*arabino*-hexoside (IV). This intermediate, which gave a single spot on TLC, was obviously not pure as it showed a broad m.p. interval and gave a poor elemental analysis. Attempted purification by crystallisation was not successful. It was reacted with *N*-bromo-succinimide in carbon tetrachloride to yield amorphous phenyl 4-*O*-benzoyl-6-bromo-3,6-dideoxy-α-D-*arabino*-hexoside (V), which was purified by chromatography. The latter reaction generally gave good yields of V, but in some experiments the oxidation was slow and a complex mixture of products, containing only a low percentage of V, was obtained. The reason for this is not known, but as IV was not pure, it may be due to a contaminant, present in some samples but not in others. V was finally reduced with lithium aluminium hydride yielding phenyl α-tyvelopyranoside (VI). The overall yield of VI from phenyl α-D-glucopyranoside was 34 %.

The structure of VI is evident from its mode of synthesis and was further corroborated by converting it into tyvelitol tetraacetate; the product was indistinguishable by GLC and mass spectrometry from an authentic sample.



Experimental. Melting points are corrected. Concentrations were performed 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, v/v) (A) or ethyl acetate (B). Compounds were detected with 8% sulphuric acid at 100°. GLC was carried out on a column (200 × 0.3 cm), containing 3 % (w/w) of ECNSS-M on Chromosorb G (80–100 mesh), at 200°. A Perkin-Elmer 881 Gas Chromatograph with flame ionisation detector was used.

For mass spectrometry the alditol acetates, dissolved in chloroform, were injected into an ECNSS-M column, mounted in an LKB 9000 combined gas chromatograph-mass spectrometer. The mass spectra were recorded at an inlet temperature of 250°, ionisation potential of 70 eV, ionisation current of 60 μA and a temperature of the ion source of 290°.

Phenyl 4,6-O-benzylidene-α-D-glucoside (I) was prepared from phenyl α-D-glucopyranoside,

following the direction for the analogous preparation of methyl 4,6-*O*-benzylidene-α-D-glucoside.[3] The product, m.p. 213–215°, $[\alpha]_{578}^{20}$ +189° (*c* 1.0, chloroform) was obtained in 82 % yield after crystallisation from aqueous ethanol. (Found: C 66.20; H 5.81. $C_{19}H_{20}O_6$ requires: C 66.27; H 5.85).

Phenyl 4,6-O-benzylidene-2-O-p-toluenesulphonyl-α-D-glucoside (II) was prepared from I, following the directions for the analogous preparation of the corresponding methyl glucoside derivative.[4] The product, m.p. 184–189°, $[\alpha]_{578}^{20}$ +129° (*c*. 1.2, chloroform) was obtained in 85 % yield after crystallisation from aqueous ethanol. (Found: C 62.76; H 5.29; S 6.39. $C_{26}H_{26}O_8S$ requires: C 62.63; H 5.26; S 6.43).

A sample of II (20 mg) and silver oxide (1 g) in methyl iodide (10 g) was refluxed overnight. The methylated product and lithium aluminium hydride (500 mg) in ethyl ether (20 ml) were refluxed for 8 h, the reduced product hydrolysed, reduced with borohydride and acetylated. The product was analysed by GLC [5]-mass spectrometry,[6] revealing the presence of 1,2,4,5,6-penta-*O*-acetyl-3-*O*-methyl-D-glucitol and traces of 1,3,4,5,6-penta-*O*-acetyl-2-*O*-methyl-D-glucitol. II is consequently the 2-*O*-tosylate, slightly contaminated with the 3-*O*-tosylate.

Phenyl 2,3-anhydro-4,6-O-benzylidene-α-D-mannoside (III) was prepared from II, following the directions for the analogous preparation of the methyl α-D-mannoside derivative.[4] The product, m.p. 182–184°, $[\alpha]_{578}^{20}$ +200° (*c* 1.0, chloroform), was obtained in 84 % yield after two crystallisations from ethanol. (Found: C 69.86; H 5.46. $C_{19}H_{18}O_5$ requires: C 69.93; H 5.56).

Phenyl 4,6-O-benzylidene-3-deoxy-α-D-arabino-hexoside (IV) Lithium aluminium hydride (10 g) was added during 30 min to a solution of III (10 g) in the minimum amount of dry ether (4 l). The reaction mixture was then refluxed and the reaction followed by TLC (solvent A). After 2 h, when no starting material remained, the mixture was allowed to cool and water was added dropwise to decompose the excess of hydride. The solution was filtered, dried over anhydrous sodium sulphate and concentrated to dryness. The crystalline residue (8.2 g), m.p. 135–145° $[\alpha]_{578}^{20}$ +159° (*c* 1.3, chloroform) gave a single spot on TLC (solvent A). Crystallisation of the product from aqueous ethanol did not improve its m.p., and the crude product was used in the next step. (Found: C 67.58; H 5.95. $C_{19}H_{20}O_5$ requires: C 69.50; H 6.14).

Phenyl 4-O-benzoyl-6-bromo-3-deoxy-α-D-arabino-hexoside (V). To a solution of crude IV (5 g) in carbon tetrachloride (150 ml) was added *N*-bromo-succinimide (3 g) and barium carbonate (10 g). The mixture was refluxed and the reaction followed by TLC (solvent A). The formation of a major, fast moving, and a minor, slow moving component was observed, and after 5 h, when no starting material remained, the mixture was filtered and concentrated to a brown syrup (7 g). This syrup was added to the top of a silica gel column (4×30 cm) which was then irrigated with solvent A. The separation was followed polarimetrically and the fast moving component (V) obtained as a light brown syrup (5 g).

Phenyl α-tyvelopyranoside (VI) Amorphous V (5 g) was dissolved in dry ethyl ether (100 ml) and lithium aluminium hydride (5 g) was added in portions during 30 min. The reaction mixture was then refluxed and the reaction followed by TLC (solvents A and B). After 4 h, when no starting material remained, ethyl acetate was added dropwise to decompose the excess of hydride, the solution was filtered and concentrated to dryness. The crystalline residue (2.1 g) was recrystallised from acetone-light petroleum to yield colourless plates, m.p. 121–122°, $[\alpha]_{578}^{20}$ +140° (*c* 1.0, acetone). (Found: C 64.24; H 7.19. $C_{12}H_{16}O_4$ requires: C 64.27; H 7.19).

A sample of VI (5 mg) was hydrolysed with 0.25 M sulphuric acid (5 ml) at 100° for 4 h. After neutralisation with barium carbonate the product was reduced with sodium borohydride and acetylated with acetic anhydride-pyridine. The resulting alditol acetate was indistinguishable from an authentic sample of tyvelitol tetraacetate by GLC and mass spectrometry.

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