Note

Synthesis of 2,3-epoxypropyl β-D-xylopyranoside and 1,5-anhydroxylitol

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The title compounds were synthesized as potential inhibitors of β-D-xylosidases, and are being used to study[1] the structure of the active site Epoxypropyl derivatives have been used[1–5] as affinity-labelling agents for various enzymes

Syntheses of epoxypropyl glycosides have been described by Thomas *et al*[2] and by Barnett and Ralph[6]. The synthesis of 2,3,4-tri-*O*-acetyl-1,5-anhydroxylitol by two different methods has been described[7] The compound can be obtained either by catalytic hydrogenation of 2,3,4-tri-*O*-acetyl-D-xylal, or by desulphurisation of phenyl 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranoside However, we found that the unpleasant synthesis of the latter compound can be avoided by using 2,3,4-tri *O*-acetyl-1-thio-β-D-xylopyranose[8] The final yield is not lowered, since the synthesis of the intermediate mercaptan results in high yields

EXPERIMENTAL

General methods — Melting points were determined with a Mettler FP2 instrument and are uncorrected The optical rotations were measured with a Perkin–Elmer Model 141 polarimeter The purity of products was tested by using t l c on Silica Gel G (Merck) with acetic acid–water–ethyl acetate (1.1 3), or in ethyl acetate–benzene (3 7) for the acetates Detection was effected with 5% sulphuric acid in ethanol (10 min at 120°) The structure of the products was proved by elemental analysis, quantitative determination of the epoxide content[9], or by periodate oxidation[10]

Allyl 2,3,4-tri-O-*acetyl-β-D-xylopyranoside* — Yellow mercuric oxide (21 6 g), mercuric bromide (1 5 g), allyl alcohol (50 ml), and Sikkon (calcium sulphate, Fluka) were mixed in benzene (100 ml) and shaken overnight at room temperature 2,3,4-Tri-*O*-acetyl-α-D-xylopyranosyl bromide[11] (34 g) was added, and the mixture was further agitated (4 h) After filtration and evaporation *in vacuo*, the resulting syrup was crystallised from ethanol Yield, 18 5 g (58%), m p 101–102°, $[\alpha]_D^{22}-61°$ (*c* 0 5, chloroform) (Found C, 52 9, H, 6 34 $C_{14}H_{20}O_8$ calc C, 53 1; H, 6 2%)

(R,S)-*2,3-Epoxypropyl 2,3,4-tri*-O-*acetyl-β-D-xylopyranoside* — Allyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (3 16 g) was dissolved in chloroform (10 ml), and a solution of monoperphthalic acid[12] (3 6 g) in chloroform (10 ml) was added The

mixture was gently refluxed for 2 h, during which time a white precipitate of phthalic acid was formed T l c indicated an approximately 50% yield of epoxide (R_F 0 14) Further portions of the peracid were then added until t l c showed complete conversion into the epoxide The chloroform solution was filtered, washed with 0 5M potassium hydrogen carbonate, and evaporated *in vacuo* After trituration with methanol, the epoxide crystallised on standing at −18° Yield, 0 8 g (28%), m p 83–84°, $[\alpha]_D^{22}$ −58° (*c* 0 5, chloroform) (Found C, 50 6; H, 6 1 $C_{14}H_{20}O_9$ calc · C, 50 6; H, 6 0) No attempt was made to determine the stereochemistry at C-2 of the epoxypropyl group

(R,S)-*2,3-Epoxypropyl β-*D*-xylopyranoside* — Deacetylation[13] of (*R,S*)-2,3-epoxypropyl 2,3,4-tri-*O*-acetyl-*β*-D-xylopyranoside (2 1 g), using methanolic barium methoxide, yielded the title compound Crystallisation from methanol occurred after several days at −18° Yield, 0 5 g (38%), m p 93–97° (dec), $[\alpha]_D^{22}$ −52° (*c* 0.2, water) (Found· C, 46 4; H, 6 9 $C_8H_{14}O_6$ calc C, 46 6, H, 6 8%) The product was homogeneous by t l c , and epoxide estimation indicated greater than 98% purity.

1,5-Anhydroxylitol — A solution of 2,3,4-Tri-*O*-acetyl-1-thio-*β*-D-xylopyranose[8] (12 g) in ethanol (150 ml) was refluxed for 90 min with Raney nickel (*ca* 70 g) The syrup obtained upon filtration and evaporation crystallised spontaneously, yielding 2,3,4-tri-*O*-acetyl-1,5-anhydroxylitol Yield, 4 5 g (45%), m p 110–115° (Found C, 50 7, H, 6 4. $C_{11}H_{16}O_7$ calc C, 50 8, H, 6 2) Deacetylation yielded 1,5-anhydroxylitol (75%), m p 114° (from ethanol) (Found C, 44 6, H, 7 7 $C_5H_{10}O_4$ calc . C, 44 8; H, 7.5). The compound consumed 2 mol of periodate, with formation of 1 mol of formic acid

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