

A Synthesis of Paratose (3,6-Dideoxy-D-ribo-hexose)

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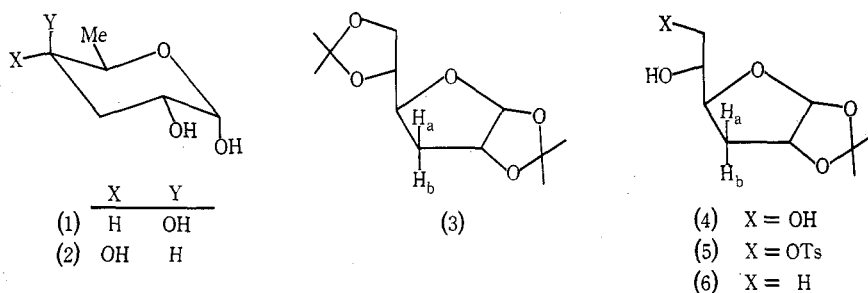
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Abstract

Deoxygenation at C 6 of 3-deoxy-1,2-*O*-isopropylidene- α -D-ribo-hexofuranose, followed by hydrolysis, gave paratose.

Recently we reported¹ a synthesis of abequose (1) (3,6-dideoxy-D-xylo-hexose), and now describe a parallel synthesis of paratose (2) (3,6-dideoxy-D-ribo-hexose). Paratose, found with abequose as a constituent of the polysaccharide of *Salmonella*,² has been synthesized previously.³⁻⁶ Our synthesis again profits from the Barton-McCombie deoxygenation procedure⁷ in readily providing 3-deoxy-1,2:5,6-di-*O*-isopropylidene- α -D-ribo-hexofuranose (3).



Compound (3) was treated with aqueous acetic acid to form 3-deoxy-1,2-*O*-isopropylidene- α -D-ribo-hexofuranose (4). Treatment of this diol (4) with 1 equiv. of *p*-toluenesulfonyl chloride in pyridine yielded the tosylate (5) which, when reduced with lithium aluminium hydride, formed 3,6-dideoxy-1,2-*O*-isopropylidene- α -D-ribo-hexofuranose (6). Acid hydrolysis then yielded paratose (2). Reduction of compound (2) with sodium borohydride³ gave crystalline 3,6-dideoxy-D-ribo-hexitol.

¹ Copeland, C., and Stick, R. V., *Aust. J. Chem.*, 1977, **30**, 1269.

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⁴ Barnett, J. E. G., Ralph, A., and Munday, K. A., *Biochem. J.*, 1969, **114**, 569.

⁵ Williams, E. H., Szarek, W. A., and Jones, J. K. N., *Can. J. Chem.*, 1971, **49**, 796.

⁶ Ekborg, G., and Svensson, S., *Acta Chem. Scand.*, 1973, **27**, 1437.

⁷ Barton, D. H. R., and McCombie, S. W., *J. Chem. Soc., Perkin Trans. 1*, 1975, 1574.

Experimental

General experimental details have been given elsewhere.¹

3-Deoxy-1,2-O-isopropylidene- α -D-ribo-hexofuranose (4)

The 3-deoxy sugar (3) (2.4 g, 10 mmol) was stirred (6 h) in aqueous acetic acid (50 ml of 15%). The reaction mixture was then concentrated and the residue dissolved in water (10 ml) and neutralized with resin (Amberlite 45, OH⁻ form). The mixture was then filtered and evaporated to leave an oily residue which crystallized on seeding to give the diol (4) as colourless needles (1.7 g, 85%), m.p. 82–83° (lit.⁸ 84°).

3-Deoxy-1,2-O-isopropylidene-6-O-p-toluenesulfonyl- α -D-ribo-hexofuranose (5)

The diol (4) (350 mg, 1.7 mmol) was stirred in dry pyridine (5 ml) with *p*-toluenesulfonyl chloride (330 mg, 1.7 mmol; 4 h, 0°) under nitrogen. The reaction mixture was then concentrated and subjected to normal workup with chloroform to give an oily residue which, upon chromatography, yielded the *tosylate* (5) as a syrup (550 mg, 90%), $[\alpha]_D^{22} -3^\circ$. P.m.r. 1.30, 1.47, 2 s, isopropylidene; 1.78, ddd, $J_{2,3a}$ 4.5 Hz, $J_{3a,4}$ 9.5 Hz, $J_{3,3}$ 14.0 Hz, H 3a; 2.09, dd, $J_{2,3b}$ 0.0 Hz, $J_{3b,4}$ 5.0 Hz, H 3b; 2.45, s, CH₃; 2.4–2.7, s (b), OH; 3.9–4.3, m, H 4,5,6,6'; 4.71, t, $J_{1,2}$ 4.0 Hz, H 2; 5.76, d, H 1; 7.34, 7.80, AA'BB', 4H, Ar. *m/e* 343.0851 (M–15 for C₁₅H₁₉O₇S requires 343.0851).

3,6-Dideoxy-1,2-O-isopropylidene- α -D-ribo-hexofuranose (6)

The *tosylate* (5) (200 mg, 0.6 mmol) in dry ether (10 ml) was added dropwise to lithium aluminium hydride (43 mg, 1.1 mmol) and ether (20 ml) and the mixture stirred under nitrogen overnight. Water (0.2 ml) was added and the mixture filtered and concentrated to leave an oily residue. Vacuum sublimation (10⁻⁴ mmHg, 40°) gave the pure *alcohol* (6) as colourless, very hygroscopic needles (95 mg, 90%), m.p. 35.5–37°, $[\alpha]_D^{22} -28^\circ$. P.m.r. 1.13, d, J 6.5 Hz, CH₃; 1.32, 1.50, 2s, isopropylidene; 1.8–2.0, m, H 3a,b; 2.4, s, OH; 3.9–4.3, m, H 4,5; 4.7–4.8, m, H 2; 5.80, d, $J_{1,2}$ 4.0 Hz, H 1. *m/e* 173.0813 (M–15 for C₉H₁₆O₄ requires 173.0813).

3,6-Dideoxy-D-ribo-hexose, Paratose (2)

Compound (6) (180 mg, 1.0 mmol) was dissolved in water (5 ml) and stirred (7 h) with resin (1 ml of Amberlite 120 R, H⁺ form). Filtration, evaporation and chromatography (10% MeOH in EtOAc) yielded paratose (2) as an oil (80 mg, 56%), $[\alpha]_D^{22} 8.0^\circ$ (c, 1.1 in H₂O) (lit.⁵ 7°). T.l.c., single spot, R_F 0.4.

3,6-Dideoxy-D-ribo-hexitol

Paratose (2) (45 mg, 0.30 mmol) in water (5 ml) was stirred overnight with sodium borohydride (100 mg), the solution neutralized with resin (Amberlite MB1), filtered and evaporated to leave an oil. Distillation (130°, 6 × 10⁻³ mmHg) then yielded crystalline 3,6-dideoxy-D-ribo-hexitol (22 mg, 50%), m.p. 67–69° (lit.³ 67–68.5°), $[\alpha]_D^{22} -23^\circ$ (c, 0.03 in H₂O) [lit.³ –17° (c, 0.94)].

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⁸ Hedgley, E. J., Overend, W. G., and Rennie, R. A. C., *J. Chem. Soc.*, 1963, 4701.