

Synthesis of 5-Thio-D-allose and 5-Thio-D-altrose

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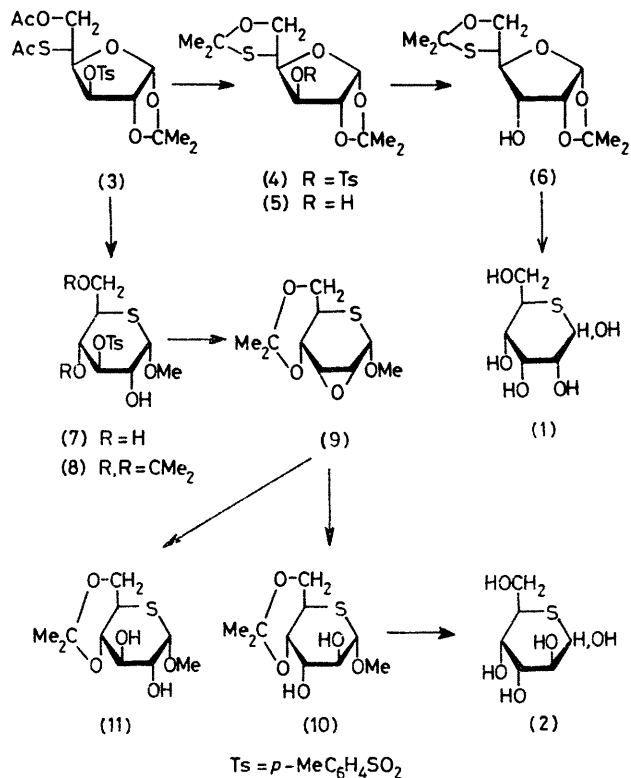
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Summary Syntheses of 5-thio-D-allose and 5-thio-D-altrose from 6-O-acetyl-5-S-acetyl-5-thio-3-O-*p*-tolylsulphonyl- α -D-glucofuranose are described.

For some years now there has been a continuing interest in monosaccharides containing ring heteroatoms other than oxygen.¹ We now report the synthesis of 5-thio-D-allose (1) and 5-thio-D-altrose (2).

Treatment of the diacetate (3)² with methanol and 2,2-dimethoxypropane in the presence of toluene-*p*-sulphonic acid resulted in deacetylation and subsequent acetalation of the thio-glycol system to give the diacetal (4). The sulphonate ester group in (4) was cleanly cleaved by alkaline methanolysis to give the alcohol (5) ($J_{1,2}$ 4.0; $J_{2,3}$ < 0.5 Hz) which could be hydrolysed by acid to the known³ 5-thio-D-glucose. Epimerisation of the alcohol (5) was brought about by oxidation with dimethyl sulphoxide-acetic anhydride to the corresponding ketone which was reduced with sodium borohydride to give the *allo*-diacetal (6) ($J_{1,2}$ 4.0; $J_{2,3}$ 4.5 Hz). Hydrolysis of (6) with dilute sulphuric acid gave 5-thio-D-allose (1).

When the diacetate (3) was refluxed with methanol containing hydrochloric acid the α -glycoside (7) was the main product. An appreciable quantity of 5-thio-3-O-*p*-tolylsulphonyl-D-glucose was detected during the early stages of this reaction. The 4- and 6-hydroxy groups of (7) were most conveniently protected by isopropylideneation giving the highly crystalline acetal (8) from which the syrupy epoxide (9) was obtained on treatment with base. Opening of the epoxide ring in (9) by reaction with aqueous sodium hydroxide proceeded mainly in a diaxial fashion to



give the *altro* and *gluco* products (10) and (11) in the ratio 4:1. Mild acid hydrolysis of these products gave methyl 5-thio- α -D-altropyranoside and the known⁴ methyl 5-thio-D-glucopyranoside, respectively. More vigorous hydrolysis of the *altro*-acetal (10) gave 5-thio-D-altrose (2). Interestingly, and in contrast to D-altrose itself, no 1,5-anhydro

derivative was detected in this last hydrolysis. Presumably this is because substitution of sulphur for oxygen in the ¹C₄ pyranose ring places C-1 and C-6 too far apart.

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³ R. M. Rowell and R. L. Whistler, *J. Org. Chem.*, 1966, **31**, 1514.

⁴ M. S. Feather and R. L. Whistler, *Tetrahedron Letters*, 1962, 667.