A Novel Synthesis of Benzyl 1,5-Dithio-α- and β-L-arabinopyranosides from 5-*O*-Toluene-*p*-sulphonyl-L-arabinose Dibenzyl Dithioacetal

By J. HARNESS and N. A. HUGHES*

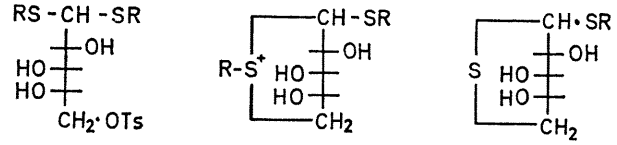
(*School of Chemistry, The University, Newcastle upon Tyne* NE1 7RU)

Summary Benzyl 1,5-dithio-α- and -β-L-arabinopyranosides are formed when 5-*O*-toluene-*p*-sulphonyl-L-arabinose dibenzyl dithioacetal is heated in acetone containing sodium iodide.

MONOSACCHARIDES having a sulphur atom in place of the ring oxygen atom are currently of interest.[1] Recently we reported[2] the formation of ethyl 5-*S*-ethyl-1,5-dithio-α- and -β-L-arabinofuranosides (**4**) on heating 5-*O*-toluene-*p*-sulphonyl-L-arabinose diethyl dithioacetal (**1**) in aqueous acetone. The reaction pathway suggested [(**1**) → (**2**) → (**3**) → (**4**)] involved a cyclic sulphonium ion (**2**) which opened up to give an isomeric acyclic ion (**3**). No evidence was obtained for the cyclic ion (**2**) undergoing dealkylation to give a 1,5-dithiopyranoside (**5**). From a study of results obtained[3] on simpler cyclic oxonium ions it seemed that such a dealkylation would occur more readily with a benzyl group rather than an ethyl group.

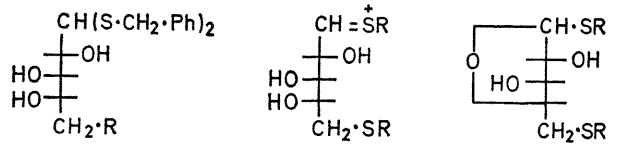
Heating 5-*O*-toluene-*p*-sulphonyl-L-arabinose dibenzyl dithioacetal (**6**) in aqueous acetone gave benzyl 5-*S*-benzyl-1,5-dithio-β-L-arabinofuranoside (**9b**) but no 1,5-dithiopyranosides (**10**). Reasoning that under these S_N1 conditions the debenzylation of the cyclic sulphonium ion (**7**) was not able to compete with the isomerisation to the acyclic ion (**8**), the use of S_N2 conditions was examined. Iodide ion was chosen as the nucleophile since, even if it displaced the sulphonate group directly, the resultant iodo-compound (**11**) would still undergo the intramolecular displacement leading to the ion (**7**); dry acetone was used instead of aqueous acetone. Under these conditions the furanoside (**9b**) was still formed in small yield but the required pyranosides (**10**) were the major products. Reaction of the ethyl compound (**1**) under these conditions gave only the furanoside (**4b**) suggesting that both the benzyl group and the S_N2 conditions are necessary for the dealkylation of the cyclic sulphonium ion.

The furanoside (**9b**) was readily hydrolysed by acid to give toluene-α-thiol and a sulphur-containing reducing sugar. Its structure was confirmed by independent synthesis. Treatment of the sulphonate (**6**) with sodium toluene-α-thiolate gave the benzyl thio-ether (**12**) which when treated with one equivalent of mercuric chloride gave the furanoside (**9b**).



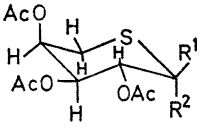
(1) R = Et; (6) R = Ph·CH$_2$ — (2) R = Et; (7) R = Ph·CH$_2$ — (5) R = Et; (10) R = Ph·CH$_2$

(α,α-anomer; b,β-anomer)



(11) R = I; (12) R = Ph·CH$_2$·S — (3) R = Et; (8) R = Ph·CH$_2$ — (4) R = Et; (9) R = Ph·CH$_2$

(a,α-anomer; b,β-anomer)



(13a) R^1 = Ph·CH$_2$·S; R^2 = H

(13b) R^1 = H; R^2 = Ph·CH$_2$·S

Reductive desulphurisation of the pyranosides (**10**) gave material chromatographically indistinguishable from that similarly obtained from 5-*S*-ethyl-5-thio-L-arabinose diethyl dithioacetal.[4] The mass spectra of the pyranosides (**10**) were very similar with prominent molecular ions at *m/e* 272 and large peaks at *m/e* 181 ($M^+ - PhCH_2$). Both pyranosides (**10**) gave triacetates (**13**) whose n.m.r. spectra confirmed their structures and showed the triacetates (**13**) to have the *C*1 conformation.

(*Received, May 13th*, 1971; *Com.* 764.)

[1] H. Paulsen and K. Todt, *Adv. Carbohydrate Chem.*, 1968, **23**, 114.
[2] N. A. Hughes and R. Robson, *J. Chem. Soc.* (*C*), 1966, 2366.
[3] E. V. Alldred and S. Winstein, *J. Amer. Chem. Soc.*, 1967, **89**, 3991; G. R. Gray, F. C. Hartmann, and R. Barker, *J. Org. Chem.*, 1965, **30**, 2020.
[4] M. L. Wolfrom and T. E. Whiteley, *J. Org. Chem.*, 1962, **27**, 2109.