The Reaction of L-Arabinose Dithioacetals with Thiols; Migration of a Methylthio-group

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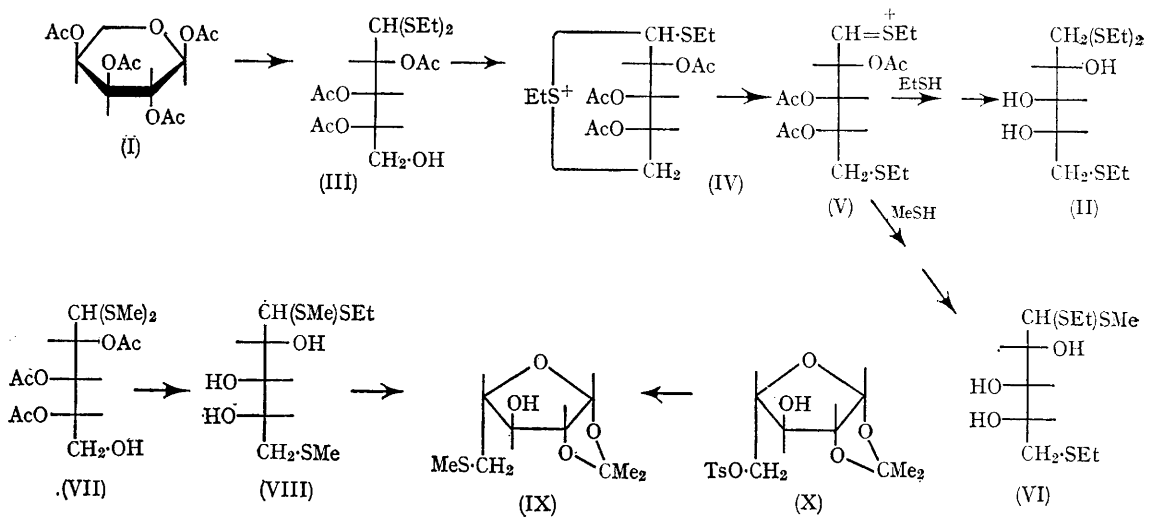
IN 1962 Wolfrom and Whiteley[1] reported that treatment of 1,2,3,4-tetra-*O*-acetyl-α-L-arabinopyranoside (I) with ethanethiol in the presence of zinc chloride or boron trifluoride gave, after deacetylation of the products, 5-*S*-ethyl-5-thio-L-arabinose diethyl dithioacetal (II). They suggested that the tetra-acetate (I) underwent ring opening to give the dithioacetal (III) the C-5 hydroxy-group of which was then replaced by the ethylthio-function.



In view of our findings reported in the preceding Communication and in an earlier paper[2] it seemed likely that while the dithioacetal (III) was a probable intermediate, the C-5 ethylthio-group of (II) arose from the dithioacetal function of the intermediate (III) *via* the ions (IV) and (V). A 1,2-episulphonium ion has been suggested[3] as an intermediate in the formation of 2-*S*-ethyl-2-thio-D-glucose by the action of nitrous acid on 2-amino-2-deoxy-D-glucose diethyl dithioacetal.

Some supporting evidence for this proposal has now been obtained. 2,3,4-Tri-*O*-acetyl-L-arabinose diethyl dithioacetal (III) was synthesised in the manner described[4] for the D-enantiomorph. When treated with ethanethiol in the presence of zinc chloride, and subsequent deacetylation, it gave the ethyl thioether (II). If the proposed ions (IV) and (V) were intermediates then treatment of the diethyl dithioacetal (III) with methanethiol was expected to give 5-*S*-ethyl-5-thio-L-arabinose ethyl methyl dithioacetal (VI). Unfortunately, this reaction gave a complex mixture of products which was not readily resolved. The alternative approach was adopted and 2,3,4-tri-*O*-acetyl-L-arabinose dimethyl dithioacetal (VII) was synthesised and treated with ethanethiol in the presence of zinc chloride. Deacetylation of the reaction product now gave the expected ethyl methyl dithioacetal (VIII) whose structure (apart from the stereochemistry at C-1) was confirmed by mass spectrometry[5] [base peak: *m/e* 121 $(\text{EtS}-\overset{+}{\text{C}}\text{H}-\text{SMe})$]. Further proof of the presence of the methylthio-group at C-5 was obtained by treating the ethyl methyl dithioacetal (VIII) with mercuric chloride in acetone which gave 1,2-*O*-isopropylidene-5-*S*-methyl-5-thio-α-L-arabinofuranose (IX). Compound (IX) was synthesised by the action of sodium methanethiolate on the known[6] toluene-*p*-sulphonate (X).

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