

**Synthesis and Stereochemical Correlation of Acyclic Sugar Nucleoside Analogues:  
X-Ray Crystal Structure of (1*R*)-2,3,4,5-Tetra-*O*-acetyl-1-*S*-ethyl-1-  
(1,6-dihydro-6-thioxopurin-9-yl)-1-thio-*D*-arabinitol**

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*Summary* A crystal structure determination has been used to establish the absolute stereochemistry of a mixed acetal derivative, a nucleoside analogue (**1**) having purine-6-thione ('6-mercaptapurine') attached to an acyclic *D*-arabinose derivative.

THE attachment of acyclic sugar chains to nucleic acid bases leads to nucleoside analogues that are of interest as potential antimetabolites, antitumor agents, and as biochemical probes.<sup>1,2</sup> By treating acylated aldose dialkyl dithioacetals,  $R^1-CH(SR^2)_2$ , with bromine and then condensing the resultant unstable bromide,  $R^1-CH(SR^2)Br$ , with an appropriate heterocyclic base derivative B, various stereochemical and structural series of the corresponding nucleoside analogues,  $R^1-CH(SR^2)B$ , have been prepared.<sup>1,3,4</sup> These compounds are formally derivatives of

unsymmetrical aldehydols and are frequently encountered as separable mixtures of the two diastereoisomers differing in configuration at the acetal carbon atom.<sup>4,5</sup> Their complete structural characterization requires (a) proof of the position of attachment of the sugar chain to the heterocycle, (b) determination of the absolute stereochemistry at the acetal carbon atom, (c) establishment of the particular tautomeric form of the heterocycle, and (d) evidence for the conformational disposition of the sugar chain. As the route of synthesis does not provide absolute proof of (a) the linkage position, and as optical methods do not provide secure assignment of (b) the stereochemistry at the acetal carbon atom in the absence of a suitable reference-standard, the crystal structure determination reported here was undertaken to provide a point of reference for further structural correlation of the entire series of related derivatives.

