Heterocyclization of 3-deoxy-D-erythro-hexos-2-ulose-1,2-bis(thiosemicarbazone). Crystal structure of the major diastereomer

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Both thiosemicarbazone groups of the derivative 1 of 3-deoxy-D-erythro-hexos-2-ulose underwent, on acetylation, a heterocyclization process to give (5R,5?R)-2,2?-diacetamido-4,4?-di-N-acetyl-5?-(1-deoxy-2,3,4-tri-O-acetyl-D-erythritol-1-yl)-5,5?-bis(1,3,4- thiadiazoline) (2) as a major product. The X-ray diffraction data of a single crystal of 2 indicated the R,R configuration for the stereocenters of the thiadiazoline rings (C-5 and C-5?). In the solid state, 2 adopts a sickle conformation (by clockwise rotation of the C-2-C-3 axis of the sugar chain) which has a S//O 1,3-parallel interaction. In solution, as determined by 1H NMR spectroscopy which included NOE experiments, a similar sickle conformation was observed. From the reaction mixture of acetylation of 1 was isolated the bis(thiadiazoline) 3 as a by-product . The configuration of the C-5 and C-5? stereocenters of 3 were respectively assigned as S,R by comparison of the physical and spectroscopic data of this compound with tho