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Nucleosides. IV. Synthesis and Reactions of 2',3',5'-Trichloro-2',3',5'-trideoxy-2',3'-secouridines.

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Recently, acyclonucleoside analogues in which the ribosyl moiety is replaced by an acyclic side chain, *e.g.* acyclovir and DHPG, have received much attention due to their antiviral activity. 2',3',5'-Trichloro-2',3',5'-trideoxy-2',3'-secouridines (**1a, b**), a kind of acyclonucleosides, were synthesized from uridine or 5-fluorouridine by a combination of sodium metaperiodate oxidation, sodium borohydride reduction, and chlorination with Vilsmeier-Haack reagent. Reaction of **1a, b** with base gave some new pyrimidine acyclonucleosides and (uracil-1-yl)-1,4-dioxanes. The preparation of 5'-chloro-5'-deoxy-2',3'-secouridine from 5'-chloro-5'-deoxyuridine and its conversion into (uracil-1-yl)-1,4-dioxane and 5'-deoxy-2',3'-secouridine are also described.

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Nucleosides. Part 5. Isolation and Characterization of the Stable Cyclic Adducts, (5*R*,6*S*)-and (5*S*,6*S*)-Bromo-*O*⁶,5'-cyclo-5,6-dihydrouridines in the Bromination of 2',3'-*O*-Isopropylideneuridine with *N*-Bromosuccinimide.

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Bromination of 2',3'-*O*-isopropylideneuridine with *N*-bromosuccinimide in chloroform containing acetic acid gave two diastereoisomeric cyclic adducts, (5*R*,6*S*)-and (5*S*,6*S*)-bromo-*O*⁶,5'-cyclo-5,6-dihydro-2',3'-*O*-isopropylideneuridines (**1** and **2**), whose structures were determined on the basis of their chemical reactivities and ¹H n.m.r. spectral results. The two cyclic adducts formed an equilibrium mixture under acidic conditions (1/2=9:11), while under neutral and basic conditions both adducts were converted into 5-bromo-2',3'-*O*-isopropylideneuridine.

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Nucleosides. Part 6. New Chemical Modification of the Ribosyl Moiety in Uridines; Synthesis of 2,2'-Anhydro-1-[5-deoxy-5-(substituted thio)-β-D-arabinofuranosyl] uracil Derivatives and Their Conversion into 3',5'-Epithioprimidine Nucleosides.

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Treatment of 5-substituted 2',5'-dichloro-2',5'-dideoxyuridines (**1**) with thiols such as thiophenol, thioacetic *S*-acid, thiobenzoic *S*-acid, toluene-*α*-thiol, and ethanethiol in the presence of base in DMF gave the corresponding 2,2'-anhydro-1-[5-deoxy-5-(substituted thio)-β-D-arabinofuranosyl] uracils (**2a-f**) in good yield. Treatment of 5-substituted 2,2'-anhydro-1-(5-acetylthio-5-deoxy-β-D-arabinofuranosyl)uracils (**2**), prepared with ease by the reaction of (**1**) with thioacetic *S*-acid, with methanolic sodium methoxide gave the corresponding 1-(3,5-dideoxy-3,5-epithio-β-D-xylofuranosyl) uracils fused with a thietane ring in the sugar moiety.