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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 ^{1}H 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′-Epithiopyrimidine 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.