scale as above) were: ethyl acetate, 0.9; carbon tetrachloride, 1.6.

Determination of $\phi_{r(sens)}$.—To determine the sensitized quantum yield of IIb formation ($\phi_{r(sens)}$), the Bausch and Lomb monochrometer apparatus was used. The grating was set at 366 mμ and the exit slit was opened to 3.4 mm. A 70-min irradiation of 60 ml of standard actinometry solution (done before and after the reaction) gave about 5% decomposition of oxalic acid. The initial intensity was 4.03×10^{16} $h\nu$/sec and the final intensity was 4.15×10^{16} $h\nu$/sec for an average of $4.09 \pm 0.06 \times 10^{16}$ $h\nu$/sec.

For the reaction, 2.656 g of coumarin (0.303 M), 1.110 g of benzophenone (0.101 M), and 60 ml of carbon tetrachloride were degassed for 1 hr with nitrogen and then irradiated (with stirring) for 8 hr. Benzophenone absorbs all of the incident energy at this wavelength and concentration (at 366 mμ $\epsilon\phi_{BCO}$ 50; ϵ_{cou} 0.11). The IIb isolated was 173 mg (0.593 mmol), thus giving $\phi_{r(sens)} = 0.30$

Determination of Relative $\phi_{r(sens)}$ Values.—This determination was made using the 450-W mercury arc lamp–turntable system. A corex filter was used and soft glass tubes were irradiated for 3 hr. Table X shows the initial contents of the tubes and the amounts of IIb isolated after the reaction.

TABLE X

RESULTS OF $\phi_{(sens)}$ (RELATIVE) EXPERIMENT

Solvent	Coumarin, g	Benzophenone, g	IIb, g
Toluene	2.215		(0.012)[a]
Toluene	2.215	0.0496	0.842
Ethyl acetate	2.250		(0.004)
Ethyl acetate	2.225	0.0489	0.272
Acetonitrile	2.225		(0.004)
Acetonitrile	2.237	0.0491	0.086
Carbon tetrachloride	2.219		0.028
Carbon tetrachloride	2.192	0.0497	1.090

[a] Parenthesized values are estimates based on the carbon tetrachloride value of 28.

From the amounts of IIb formed and the ϕ_r and $\phi_{r(sens)}$ values for carbon tetrachloride, it was calculated that benzophenone absorbed 0.012 einsteins and coumarin absorbed 0.27 einsteins of light during the irradiation.

Determination of $\phi'_{r(IIb)}$.—The apparatus for this experiment was the Rayonet reactor with 3500 Å lamps and the quartz well with $NiSO_4$ and Pyrex filters. Coumarin absorbs >99.88% of the incident light under the conditions of the reaction which were 13.16 g of coumarin (0.30 M), 0.337 g of benzophenone (0.006 M), and 300 ml of ethyl acetate.

The irradiation time was 62 hr, 25 min. The initial intensity was 2.31×10^{17} $h\nu$/sec and the final intensity was 2.49×10^{17} $h\nu$/sec, for an average of $2.40 \pm 0.9 \times 10^{17}$ $h\nu$/sec. The IIb isolated was 34 mg (1.16×10^{-4} mol), $\phi'_{r(IIb)} = 1.3 \times 10^{-3}$.

Comparable experiments were run with carbon tetrachloride and toluene as solvents. The data here were 9 mg of IIb ($\phi'_{r(IIb)} = 3.1 \times 10^{-3}$) and 13 ± 3 mg of IIb ($\phi'_{r(IIb)} = 2 \pm 1 \times 10^{-3}$), respectively.

Determination of ϕ_{ic} for Coumarin, Trace of Benzophenone Present.—The apparatus for this experiment was the Rayonet reactor (with 3500 Å lamps) and the quartz well. The reaction mixtue contained 13.184 g of coumarin (0.30 M), 2.049 g of *cis*-piperylene (0.10 M), 1.3 ml of *n*-hexane, 0.349 g of benzophenone (0.006 M), and 300 ml of ethyl acetate. Since the intensity of the lamps in this system was 2.4×10^{17} $h\nu$/sec in every previous determination, this value was assumed. The irradiation was carried out for 95 hr giving a total energy absorbed by coumarin of 0.136 einsteins.

Initially the ratio of standard to piperylene was 1.00:2.44. After irradiation, the ratio in two trials was 1.00:2.42, showing no loss of piperylene. The per cent of trans isomer found in two trials was 3.5 and 3.7% for an average of 3.6 ± 1% trans (1.08×10^{-3} mol) which implies quenching of 1.96×10^{-3} mol of coumarin triplets. Thus ϕ_{ic} was found to be 1.4×10^{-2}.

Registry No.—I, 91-64-5; IIa, 5248-11-3; IIb, 5248-12-4.

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4-Thio-D-arabinofuranosylpyrimidine Nucleosides[1]

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Reaction of 2,3,5-tri-*O*-benzoyl-4-thio-β-D-arabinofuranosyl bromide (II) with the appropriate trimethylsilylated pyrimidine has led to the preparation and isolation of the α-D and β-D forms of 1-(4-thio-D-arabinofuranosyl)uracils (Va and Vb) and the β-D forms of thymine VIIb and cytosine IXb. The synthesis of IXb has also been accomplished by ammonolysis of 1-(2,3,5-tri-*O*-benzoyl-4-thio-β-D-arabinofuranosyl)-4-thiouracil (X).

1-(β-D-Arabinofuranosyl)cytosine has been shown to possess significant carcinostatic activity,[2,3] as well as a broad spectrum antiviral activity[4-9] *in vitro* against DNA viruses. Here we describe the preparation of the nucleoside analog in which the ring oxygen of the sugar moiety is replaced by a sulfur atom. The syntheses of 1-(4-thio-β-D-arabinofuranosyl)thymine (VIIb) and both anomers of 1-(4-thio-D-arabinofuranosyl)uracil (Va and Vb) are also described.

The synthesis of methyl 4-thio-β-D-arabinofuranoside from D-glucose has been reported.[10] This compound is

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converted to 2,3,5-tri-*O*-benzoyl-4-thio-β-D-arabinofuranosyl bromide (II) according to a procedure given by Ness and Fletcher.[11] Assignment of the β-D configuration to the major product formed is based on its being more levorotatory than the minor product α-D-III. Also, the greater coupling constant *J* for the β-D anomer is consistent with the cis relationship of the hydrogen atoms on C-1 and C-2.

Displacement of bromide ion from II by trimethylsilyl derivatives[12] of uracil and thymine leads to the formation of anomeric mixtures of the benzoylated nucleosides, which are separated chromatographically. Nishimura and Shimizu[13] have used similar procedures in their synthesis of the anomeric pyrimidine nucleosides of D-arabinofuranose. Debenzoylation is achieved by treatment of the blocked nucleosides with sodium in methanol.

1-(4-Thio-β-D-arabinofuranosyl)cytosine (IXb) is prepared by two methods. Reaction of II with bis(trimethylsilyl)-*N*-acetylcytosine yields a mixture of the anomeric forms of the blocked nucleosides, from which the β-D anomer (VIIIb) crystallizes. The other method of producing this nucleoside involves thiation[14] of 1-(2,3,5-tri-*O*-benzoyl-4-thio-β-D-arabinofuranosyl)uracil (IVb) to its 4-thiouridine analog X. This derivative, upon treatment with methanolic ammonia, gives 1-(4-thio-β-D-arabinofuranosyl)cytosine (IXb).

It has been observed,[15] previously, that the optical rotatory relationship of the anomeric pyrimidine nucleosides do not obey Hudson's isorotation rules. These exceptions to Hudson's rules have been found to hold for the anomeric D-arabinofuranosyluracils[13] and is further supported by the optical rotatory dispersion (ORD) measurements on a large number of pyrimidine nucleosides.[16] The anomeric configuration of the nucleosides described here cannot be assigned from ORD measurements since both anomers show positive Cotton effects in blocked and unblocked forms. Tentative anomeric configurations are assigned on the basis that the β-D anomer is expected in greatest yield. Far less significant is the observation that benzoylated β-D anomers have had, in our hands, the slowest chromatographic mobilities on silica gel G in solvent C.

Experimental Section

Analytical Methods.—Purity of products was determined by thin layer chromatography (tlc) on silica gel G[17] coated glass plates (5 × 13 cm) irrigated with (a) benzene–ethyl acetate (6:1), (b) hexane–ethyl acetate (4:1), (c) benzene–ethyl acetate (10:1), (d) chloroform–acetone (15:1), (e) chloroform–acetone (30:1), and (f) chloroform–acetone (9:1). Solvent ratios are based on volumes. Components were located by spraying with 5% sulfuric acid in ethanol and heating until permanent char spots were visible. Melting points were determined on a Fisher–Johns apparatus and are corrected. Nuclear magnetic resonance (nmr) spectra were obtained with a Varian Associates A-60 instrument. Evaporations were done under diminished pressure with a bath temperature below 40°. Absorption chromatography was made on silica gel.[18] Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter.

Methyl 2,3,5-Tri-*O*-benzoyl-4-thio-β-D-arabinofuranoside (I).—To a stirred, ice-cooled solution of methyl 4-thio-β-D-arabinofuranoside (9 g, 0.05 mol) in 100 ml of dry pyridine was added benzoyl chloride (23.26 g, 0.165 mol) dropwise over a period of 30 min. Benzoylation was complete in 2 hr as monitored by tlc in solvent A. The reaction mixture was poured into 600 ml of ice and water under stirring and stirring continued for 2 hr at which time the mixture was extracted with 500 ml of chloroform. The chloroform extract was washed sequentially with water, 2 *N* hydrochloric acid until slightly acidic, 1 *N* sodium hydroxide solution until slightly alkaline, and water until neutral. The chloroform solution so washed was dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under diminished pressure to obtain 25 g of pure syrup methyl 2,3,5-tri-*O*-benzoyl-4-thio-β-D-arabinofuranoside (I): $[\alpha]^{25}D$ −174.3° (*c* 1.05, $CHCl_3$). Compound I was used directly for the preparation of the bromo sugar.

Anomeric 2,3,5-Tri-*O*-benzoyl-4-thio-D-arabinofuranosyl Bromides (II and III).—To a stirred solution of compound I (25 g) in 125 ml of glacial acetic acid was added 125 ml of 32% (w/w) hydrogen bromide in glacial acetic acid. The reaction mixture was stirred for 20 min at 25° during which time the entire mass solidified. This was diluted with 750 ml of dry methylene chloride. The solution was poured into 2.5 l. of ice and water and the organic layer was quickly washed sequentially with water, a 10% aqueous sodium bicarbonate solution, and water. The washed methylene chloride solution was dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under diminished pressure at a bath temperature of 30°. The residue solidified when concentrated and was recrystallized from methylene chloride–hexane (75 ml:300 ml). Needle-shaped crystals of 2,3,5-tri-*O*-benzoyl-4-thio-β-D-arabinofuranosyl bromide (II) separated: yield 22 g; mp 126°; $[\alpha]^{25}D$ −171° (*c* 1, CH_2Cl_2).

Anal. Calcd for $C_{26}H_{21}BrO_6S$: C, 57.67; H, 3.91; Br, 14.56; S, 6.05. Found: C, 57.80; H, 4.03; Br, 14.58; S, 6.05.

Further concentration of the mother liquors produced 5 g more of II to give a total yield of 27 g. Additional concentration produces a small amount of the α-D anomer III: $J_{1,2}$ = 4.5 cps for II and 0 cps for III.

Anomeric 1-(2,3,5-Tri-*O*-benzoyl-4-thio-D-arabinofuranosyl)-uracils (IVa and IVb).—A stirred mixture of 5.41 g (0.01 mol) of compound II and 3.84 g (0.015 mol of bis(trimethylsilyl)uracil was heated on an oil bath at 130–135° for 3 hr in a current of dry nitrogen. During this time the bromo sugar II disappeared as indicated by tlc in solvent B. The yellowish gummy product was refluxed for 20 min with 50 ml of 95% ethanol. After evaporation of the solvent under diminished pressure, the residue was taken into benzene and refluxed for 5 min and filtered. The filtrate was concentrated to a brownish yellow syrup which was applied to a silica gel column (40 × 1.5 cm) prepared in benzene. The column was eluted with 1 l. of benzene, which removed the olefinic contaminants. The column was then eluted with solvent C and the nucleoside fractions collected on a fraction collector. The nucleoside fractions containing both α-D and β-D anomers IVa and IVb were combined and concentrated to a foam (1.3 g) which was dissolved in 20 ml of hot ethyl acetate. On cooling, pure 1-(2,3,5-tri-*O*-benzoyl-4-thio-β-D-arabinofuranosyl)uracil (IVb) crystallized as small needles: yield 2.1 g; mp 208–209°; $[\alpha]^{25}D$ −13.8° (*c* 1, $CHCl_3$); ORD (*c* 0.004, $CHCl_3$) $[\phi]_{275}$ +4100°, $[\phi]_{247}$ −21,800°.

Anal. Calcd for $C_{30}H_{24}N_2O_8S$: C, 62.93; H, 4.22; N, 4.89; S, 5.60. Found: C, 63.03; H, 4.25; N, 4.87; S, 5.86.

The filtrate after separation of the β-D anomer IVb when examined by tlc in solvent D (plate developed three times) showed the presence of more β-D anomer (minor) and the α-D anomer (major). By repeated silica gel chromatography using solvent E as eluent the α-D anomer IVa (550 mg, 8.7%) and 300 mg more of the β-D anomer IVb were collected. Total yield of 1-(2,3,5-tri-*O*-benzoyl-4-thio-β-D-arabinofuranosyl)uracil (IVb) was 2.4 g, 42%. The α-D anomer IVa was recrystallized from ethanol: mp 127–128°; $[\alpha]^{25}D$ +12.3° (*c* 1, $CHCl_3$); ORD (*c* 0.004, $CHCl_3$) $[\phi]_{287}$ +14,900°, $[\phi]_{262}$ −29,500°.

Anal. Found: C, 62.92; H, 4.40; N, 4.77; S, 5.87.

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1-(4-Thio-α-D-arabinofuranosyl)uracil (Va).—To a solution of 50 mg of sodium in 10 ml of neat methanol was added a solution of compound IVa (700 mg) in 30 ml of warm neat methanol. This was stirred at 25° for 18 hr. The reaction mixture was deionized using methanol-washed Amberlite IR 120 (H^+) resin and filtered. The filtrate was concentrated under diminished pressure to a solid which was triturated with absolute ether to remove methyl benzoate and filtered. The precipitate was recrystallized from neat methanol to yield 266 mg of 1-(4-thio-α-D-arabinofuranosyl)uracil (Va): mp 214–215°; $[\alpha]^{25}D$ +57.7° (*c* 1, H_2O); uv $\lambda_{max}^{H_2O}$ mμ (ε, pH) 265 (10,000, 3.2), 265 (10,700, 7.0), 265 (9600, 9.6), 267 (8600, 14.0); ORD (*c* 0.004, $CHCl_3$) $[\phi]_{285}$ +9740°, $[\phi]_{251}$ −14,430°,

Anal. Calcd for $C_9H_{12}N_2O_5S$: C, 41.49; H, 4.65; N, 10.77; S, 12.33. Found: C, 41.58; H, 4.83; N, 10.86; S, 12.11.

1-(4-Thio-β-D-arabinofuranosyl)uracil (Vb).—The β-D anomer was debenzoylated in a manner similar to that used for the α-D-anomer. 1-(4-Thio-β-D-arabinofuranosyl)uracil (Vb) was crystallized from neat methanol to yield 600 mg: mp 194–195°; $[\alpha]^{25}D$ +117.8° (*c* 1, H_2O); uv $\lambda_{max}^{H_2O}$ mμ (ε, pH) 264 (10,700, 3.2), 264 (10,400, 7.0), 264 (11,400, 9.6), 266 (9200, 14.0); ORD (*c* 0.004, $CHCl_3$) $[\phi]_{286}$ +4740°, $[\phi]_{262}$ −4410°.

Anal. Found: C, 41.26; H, 4.65; N, 10.71; S, 12.09.

Anomeric 1-(4-Thio-D-arabinofuranosyl)thymines (VIIa and VIIb).—In a procedure similar to that described above for 1-(2,3,5-tri-*O*-benzoyl-4-thio-D-arabinofuranosyl)uracils, the bromo sugar II (5.41 g, 0.01 mol) was condensed with bis(trimethylsilyl)-thymine (4.05 g, 0.015 mol). After chromatographic purification on silica gel, 3.1 g of the anomeric 1-(2,3,5-tri-*O*-benzoyl-4-thio-D-arabinofuranosyl)thymines (VIa and VIb) was obtained. Debenzoylation with a catalytic amount of sodium methoxide followed by deionization with methanol-washed Amberlite IR 120 (H^+) resin gave the anomeric mixture of 1-(4-thio-D-arabinofuranosyl)thymines (VIIa and VIIb). Crystallization from neat methanol gave 0.76 g (27.7%) of pure 1-(4-thio-β-D-arabinofuranosyl)thymine (VIIb): mp 209–210°; $[\alpha]^{25}D$ +136° (*c* 1, H_2O); uv $\lambda_{max}^{H_2O}$ mμ (ε, pH) 270 (10,900, 3.2), 270 (10,400, 7.0), 270 (10,200, 9.6), 271 (8500, 14.0); ORD (*c* 0.004, $CHCl_3$) $[\phi]_{290}$ +10,900°, $[\phi]_{247}$ −22,600°.

Anal. Calcd for $C_{10}H_{14}N_2O_5S$: C, 43.78; H, 5.14; N, 10.22; S, 11.69. Found: C, 44.26; H, 5.05; N, 10.40; S, 11.93.

Anomeric 1-(2,3,5-Tri-*O*-benzoyl-4-thio-D-arabinofuranosyl)-*N*-acetylcytosines (VIIIa and VIIIb).—Bis(trimethylsilyl)-*N*-acetylcytosine and the bromo sugar II (5.41 g, 0.01 mol) were condensed as described for 1-(2,3,5-tri-*O*-benzoyl-4-thio-D-arabinofuranosyl)uracils. After chromatographic purification using solvent F, the nucleoside fractions were collected to give 1.5 g of the mixture of the α-D and β-D anomers VIIIa and VIIIb. A thin layer chromatogram developed five times in solvent D showed the two distinct anomers. Recrystallization from ethyl acetate gave 1.23 g of 1-(2,3,5-tri-*O*-benzoyl-4-thio-β-D-arabinofuranosyl)-*N*-acetylcytosine (VIIIb): mp 226–227°; $[\alpha]^{25}D$ +15.8° (*c* 1, $CHCl_3$); ORD (*c* 0.004, $CHCl_3$) $[\phi]_{267}$ +19,000°, $[\phi]_{248}$ −27,700°.

Anal. Calcd for $C_{32}H_{27}O_8N_3S$: C, 62.63; H, 4.44; N, 6.85; S, 5.22. Found: C, 62.41; H, 4.42; N, 6.80; S, 5.43.

1-(4-Thio-β-D-arabinofuranosyl)cytosine (IXb).—A solution of compound VIIIb (1.2 g) in 50 ml of absolute methanol was saturated with dry NH_3 gas at 0° and kept in the refrigerator for 2 days. The mixture was then evaporated to dryness and triturated with dry ether three times to remove benzamide and methyl benzoate. The residual solid was recrystallized from dry methanol to give 450 mg of 1-(4-thio-β-D-arabinofuranosyl)cytosine (IXb): mp 210–211°; $[\alpha]^{25}D$ +143° (*c* 1, H_2O). uv $\lambda_{max}^{H_2O}$ mμ (ε, pH) 280 (12,100, 3.2), 274 (9700, 7.0), 274 (10,600, 9.6), 275 (9600, 14).

Anal. Calcd for $C_9H_{13}O_4N_3S$: C, 41.69; H, 5.05; N, 16.20; S, 12.38. Found: C, 41.45; H, 5.07; N, 16.19; S, 12.40.

1-(2,3,5-Tri-*O*-benzoyl-4-thio-β-D-arabinofuranosyl)-4-thiouracil (X).—A mixture containing 6.292 g (0.011 mol) of IVb, 10.77 g of phosphorus pentasulfide, and 150 ml of reagent grade pyridine was refluxed for 5 hr. About half of the pyridine was removed under diminished pressure and the dark brown colored solution was poured into stirred water where compound X started solidifying. The solid product was filtered and the precipitate was taken into chloroform and filtered from insoluble material. The chloroform solution was washed twice with water and dried over anhydrous sodium sulfate. After filtration the chloroform solution was concentrated to a yellow solid foam which was crystallized from hot ethanol to give 4.96 g of compound X as yellow needles: mp 156–157°; $[\alpha]^{24}D$ +6.4° (*c* 1, $CHCl_3$).

Anal. Calcd for $C_{30}H_{24}O_7N_2S_2$: C, 61.21; H, 4.11; N, 4.76; S, 10.89. Found: C, 61.37; H, 4.11; N, 4.89; S, 10.86.

1-(4-Thio-β-D-arabinofuranosyl)cytosine (IXb).—Compound X (1.178 g, 0.002 mol) was treated with 160 ml of anhydrous methanolic ammonia (previously saturated at −5 to 0°) in a sealed tube at 110–115° for 18 hr. After the tube was opened, the contents were transferred to a round-bottomed flask and concentrated under reduced pressure to a solid. The solid was triturated with ether to remove benzamide and the residual solid dissolved in hot methanol and decolorized with charcoal. The methanolic solution was filtered and then concentrated under diminished pressure to a solid which was recrystallized from hot methanol to give 0.37 g of compound IXb: mp 210–211°; $[\alpha]^{25}D$ +143° (*c* 1, H_2O).

Registry No.—I, 26527-29-7; II, 26527-30-0; III, 26527-31-1; IVa, 26527-32-2; IVb 26527-33-3; Va, 26527-34-4; Vb, 26527-35-5; VIIb, 26527-36-6; VIIIb, 26527-37-7; IXb, 26599-17-7; X, 26527-38-8.