pared according to Isler,[9] Trippett,[10] and co-workers, respectively. The benzene used in all runs was anhydrous.

α-(2,4,6-Trinitrophenyl)-α-carbomethoxymethylenetriphenylphosphorane (IIa).—A mixture of 2.01 g (0.0060 mole) of Ia and 0.74 g (0.0030 mole) of picryl chloride in 20 ml of benzene was heated on the steam bath for 1 hr. The phosphonium chloride, which was filtered off, washed with benzene, and dried, had a weight of 1.01 g (91%). The filtrate was evaporated to dryness and the residue was recrystallized from methanol–water to yield 0.93 g (57%) of violet-red crystals of phosphorane IIa: mp 192–193°; $\lambda_{max}^{CHCl_3}$ 493 mμ (ε 3930); infrared bands at 1640 (conjugated ester), 1604, 1538, 1490, 1440, 1342, 1302, 1250, 1102, 978, and 934 cm^{-1}.

Anal. Calcd for $C_{27}H_{20}N_3O_8P$: C, 59.45; H, 3.69; N, 7.70; P, 5.68. Found: C, 59.72; H, 3.90; N, 7.78; P, 5.45.

α-(2,4,6-Trinitrophenyl)-α-cyanomethylenetriphenylphosphorane (IIb).—A mixture of 4.00 g (0.0132 mole) of Ib and 1.64 g (0.0066 mole) of picryl chloride in 120 ml of benzene was heated on the steam bath for 2 hr. The phosphonium chloride was filtered off and weighed 1.93 g (87%). Evaporation of the filtrate and recrystallization of the residue from methanol yielded 1.77 g (52%) of violet-brown crystals of phosphorane IIb: mp 245–246°; $\lambda_{max}^{CHCl_3}$ 465 mμ (ε 12,300); infrared bands at 2180 (conjugated nitrile), 1606, 1589, 1540, 1491, 1440, 1330, 1266, 1100, 1090, and 963 cm^{-1}.

Anal. Calcd for $C_{26}H_{17}N_4O_6P$: N, 10.93; P, 6.04. Found: N, 10.51; P, 6.30.

α-(2,4-Dinitrophenyl)-α-carbomethoxymethylenetriphenylphosphorane (IIIa).—A solution of 2.01 g (0.0060 mole) of Ia and 0.61 g (0.0030 mole) of 2,4-dinitro-1-chlorobenzene in 40 ml of benzene was allowed to reflux for 70 hr under an atmosphere of nitrogen. The phosphonium salt was filtered off and weighed 0.52 g (47%). To the filtrate was added an equal volume of petroleum ether (bp 30–60°). The red precipitate that formed was filtered off to yield 0.84 g of solid, mp 210–220°. The product was slurried in a small amount of methanol, filtered, and dried. There was obtained 0.39 g (26%) of the orange-red phosphorane IIIa, mp 230–231°. An analytical sample was recrystallized from methanol–water and had mp 231–232°; $\lambda_{max}^{CHCl_3}$ 453 mμ (ε 9800); infrared bands at 1640 (conjugated ester), 1600, 1538, 1518, 1482, 1440, 1342, 1320, 1249, 1151, 1107, 1090, and 840 cm^{-1}.

Anal. Calcd for $C_{27}H_{21}N_2O_6P$: N, 5.60; P, 6.19. Found: N, 5.73; P, 6.50.

When the above reaction was carried out in 50 ml of dimethylformamide at 100° for 4 hr, followed by addition of water, extraction with benzene, precipitation with petroleum ether, and washing with methanol, 0.45 g (30%) of IIIa was obtained, mp 229–230°.

α-(2,4-Dinitrophenyl)-α-cyanomethylenetriphenylphosphorane (IIIb).—A solution of 10.00 g (0.0332 mole) of Ib and 3.35 g (0.0166 mole) of 2,4-dinitro-1-chlorobenzene in 200 ml of benzene was heated at reflux for 70 hr under an atmosphere of nitrogen. After cooling, the precipitate was filtered off, thoroughly washed with water to remove the phosphonium chloride, and dried. This material was recrystallized from benzene–petroleum ether and then from chloroform–methanol to yield 2.30 g (30%) of orange phosphorane IIIb: mp 249–250°; $\lambda_{max}^{CHCl_3}$ 437 mμ (ε 21,100); infrared bands at 2180 (conjugated nitrile), 1606, 1582, 1535, 1508, 1484, 1440, 1338, 1318, 1248, 1105, 960, and 832 cm^{-1}.

Anal. Calcd for $C_{26}H_{18}N_3O_4P$: N, 8.99; P, 6.63. Found: N, 8.78; P, 7.35.

2,4-Dinitrobenzylidenetriphenylphosphorane (IV).—A solution of 10.0 g (0.0383 mole) of 2,4-dinitrobenzyl bromide[11] in 20 ml of benzene was added over 5 min to 10.1 g (0.0385 mole) of triphenylphosphine in 200 ml of benzene. The mixture was allowed to stand for 16 hr whereupon the phosphonium bromide separated out as a gum. The benzene solution was decanted and the gum was washed with two 50-ml portions of hot benzene. Attempted crystallization of the salt was not successful. The gum was treated with five 200-ml portions of hot water in order to dissolve it. The water solution was filtered, cooled to 15°, and treated with a 2 *N* sodium hydroxide solution until slightly basic. The dark red solid which precipitated was filtered, washed thoroughly with water, and dried. Recrystallization from chloroform–petroleum ether afforded 7.88 g (46%) of the dark red phosphorane IV: mp 209–210°; $\lambda_{max}^{CHCl_3}$ 455 mμ (ε 36,600); infrared bands at 1612, 1560, 1502, 1482, 1441, 1374, 1350, 1309, 1267, 1140, 1114, 1102, 940, and 900 cm^{-1}.

Anal. Calcd for $C_{25}H_{19}N_2O_4P$: N, 6.33; P, 7.00. Found: N, 6.26; P, 7.25.

When phosphorane IV was recrystallized from benzene, a 1:1 complex between IV and benzene was formed.

Anal. Calcd for $C_{25}H_{19}N_2O_4P \cdot C_6H_6$: C, 71.53; H, 4.84; N, 5.38; P, 5.95. Found: C, 71.34; H, 4.72; N, 5.16; P, 6.04.

From the treatment of 1.00 g of IV with hot methanol was isolated 0.34 g (82%) of 2,4-dinitrotoluene and 0.48 g (76%) of triphenylphosphine oxide.

Reaction of Phosphorane IV with Methyl Chloroformate.—A mixture of 1.33 g (0.0030 mole) of IV in 10 ml of methyl chloroformate and 50 ml of benzene was refluxed under an atmosphere of nitrogen for 40 hr. The solution was decanted hot and the phosphonium chloride gum was washed with hot benzene. The combined benzene layers were evaporated to dryness. The residue was slurried twice with 25-ml portions of benzene and filtered. The dark red solid which was collected was starting material (identified by infrared and mixture melting point) and weighed 0.66 g (42% recovery as the 1:1 benzene complex). Petroleum ether (150 ml) was added to the filtrate and the precipitated solid was filtered off. Upon washing with a small amount of methanol, 0.17 g (23%) of an orange-red phosphorane was obtained, mp 228–230°. The infrared spectrum of this compound was identical with the infrared spectrum of IIIa and mixture melting point with IIIa showed no depression.

Reaction of Phosphorane IV with Benzoyl Chloride.—A mixture of 1.09 g (0.00246 mole) of IV and 0.18 g (0.00128 mole) of benzoyl chloride in 50 ml of benzene was refluxed under an atmosphere of nitrogen for 16 hr. The phosphonium chloride formed as a gum on the sides of the flask. The benzene was decanted and the gum was washed with hot benzene. The combined benzene solutions were evaporated to dryness. A yellow solid was obtained weighing 0.56 g. The infrared spectrum of this material was practically identical with the infrared spectrum of a synthetic 1:1 mixture of (2,4-dinitrophenyl)phenylacetylene (VII) (using the pure acetylene below) and triphenylphosphine oxide. On this basis the yield is 83% (theory requires a 0.67-g mixture of the two components). The mixture was recrystallized from 5 ml of methanol to give 0.17 g (51%) of pure acetylene VII, mp 117–118° (lit.[12] mp 112–112.5°).

Anal. Calcd for $C_{14}H_8N_2O_4$: N, 10.44. Found: N, 10.12.

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A Convenient Synthesis of 1-β-D-Arabinofuranosylthymine[1]

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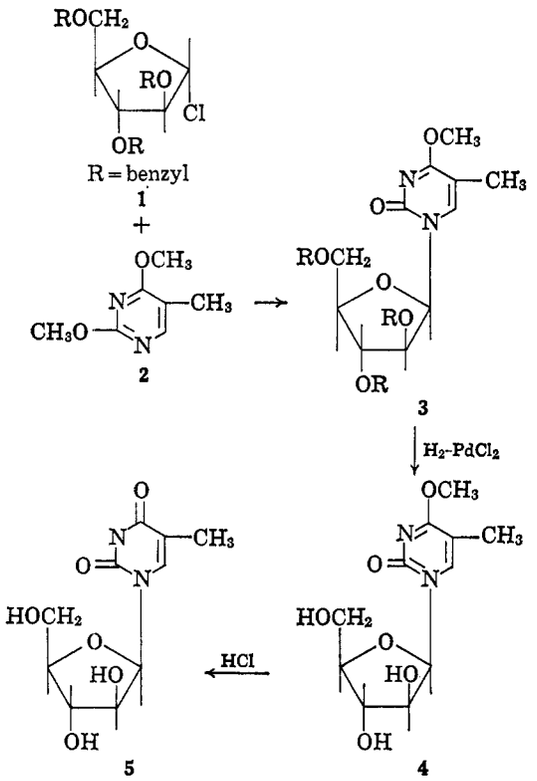
The natural product, 1-β-D-arabinofuranosylthymine, isolated from a species of sponge (*Cryptotethia crypta*),[2,3] is the prototype of a series of arabinofuranosyl nucleosides given the trivial name "spongo" nucleosides. 1-β-D-Arabinofuranosylthymine (**5**) has been synthesized previously from synthetic 1-β-D-ribofuranosyl-

SCHEME I



thymine[4] *via* a cyclonucleoside intermediate[5] in approximately 10% yield. An alternate improved synthesis from 1,2,diacetyl-5-methoxycarbonyl-3-(*p*-toluenesulfonyl)-D-xylofuranose in an over-all yield of 11% has also been recorded.[6] These syntheses served to unequivocally establish the structure of "spongothymidine" as being 1-β-D-arabinofuranosylthymine; however, the low yields realized by these routes has made its preparation in quantities sufficient for more extensive biological evaluation a difficult task. The extension of the Glaudemans and Fletcher[7] synthesis of 9-β-D-arabinofuranosyladenine from 2,3,5-tri-O-benzyl-D-arabinofuranosyl chloride to use in the synthesis of pyrimidine nucleosides by the Hilbert–Johnson method has recently been reported by Shen, Lewis, and Ruyle,[8a] who synthesized 1-β-D-arabinofuranosylcytosine and 1-β-D-arabinofuranosyl-5-trifluoromethyluracil in approximately 50% over-all yield by this procedure. This method has now been applied to the preparation of 1-β-D-arabinofuranosylthymine (**5**) (see Scheme I), resulting in an over-all yield of 38% based upon 2,3,5-tri-O-benzyl-β-D-arabinofuranose. The blocked halo sugar, 2,3,5-tri-O-benzyl-α-D-arabinofuranosyl chloride (**1**),[8b] was allowed to react with 2,4-dimethoxy-5-methylpyrimidine for 120 hr at ambient temperature. The reaction mixture was evaporated *in vacuo* to give the crude condensation product 1-(2′,3′,5′-tri-O-benzyl-β-D-arabinofuranosyl)-4-methoxy-5-methyl-2(1H)-pyrimidinone (**3**) as an oil which was debenzylated ($PdCl_2$–H_2) without further purification to give 1-β-D-arabinofuranosyl)-4-methoxy-5-methyl-2-(1H)-pyrimidinone (**4**) as a well-defined crystalline solid. The enol ether was readily hydrolyzed to give 1-β-D-arabinofuranosylthymine (**5**) by treatment with dilute methanolic hydrogen chloride. The product separated as analytically pure material, mp 246–248°, $[\alpha]^{27}D$ +97.9°, which was homogeneous upon paper chromatography.[9] As was noted by Shen, Lewis, and Ruyle,[8a] the product of this reaction is all or preponderantly the β anomer. No α anomer was isolated or detected.

Experimental Section

1-(β-D-Arabinofuranosyl)-4-methoxy-5-methyl-1H-pyrimidin-2-one (**4**).—2,3,5-Tri-O-benzyl-1-(*p*-nitrobenzoyl)-D-arabinofuranose[10] (545 g, 1.005 moles), prepared in 90% yield from 2,3,5-tri-O-benzyl-β-D-arabinofuranose,[11] was added to dry methylene chloride (10 l.) which had been saturated with hydrogen chloride at 0°. The solution was allowed to stand at 0° for 5 hr with the exclusion of moisture and was rapidly filtered through a sintered-glass funnel to remove the *p*-nitrobenzoic acid which had separated in quantitative yield. The filtrate was concentrated to dryness *in vacuo* (bath 40°) and evacuated (0.1 mm) for 16 hr (25°). The residual chloro sugar was diluted with dry methylene chloride (6 l.) and a solution of 2,4-dimethoxy-5-methylpyrimidine[12] (**2**) (200 g, 1.3 moles) in methylene chloride (1.5 l.) was added. The mixture was stirred for 5 days at ambient temperature (23–27°) protected by a drying tube. The solvent was removed *in vacuo*, yielding an oily residue (596.4 g) which was debenzylated without further purification. A portion of the above residue (100 g) was dissolved in dry methanol (molecular sieves,[13] 1 l.) and added to a suspension of palladium chloride (25 g) in dry methanol (2 l.) which had been prereduced just prior to the addition of the crude blocked nucleoside. The mixture was hydrogenated in a 2-gal stirred autoclave at an initial pressure of 10 atm with reduction being completed in 25–30 min. The above hydrogenation was carried out four times and the products were recovered in two batches. The reduction mixtures were filtered free of catalyst; the filtrates from two of the above hydrogenations were combined and neutralized by stirring with Dowex 2 × 8 (HCO_3^-) ion-exchange resin. The neutralized solutions were filtered free of resin, the resin was washed with a small amount of methanol, and the combined filtrate and wash were concentrated to dryness *in vacuo* (30° bath). The residue from each run was crystallized by dissolving in methanol (750 ml), filtering from a small amount of insolubles, adding an equal volume of ethyl ether, and diluting with hexane (3 l.). The product, **4** (93.2 g, 49%), mp 187–191°, was of satisfactory purity for use in the subsequent step. A portion of the material was recrystallized as above: mp 189–190.5°, $[\alpha]^{27.3}D$ +121.0° (*c* 1.0, DMF), λ_{max}^{EtOH} 284 mμ (ε 6560), λ_{min}^{EtOH} 243 mμ (ε 868). For analysis the material was vacuum dried at 25°.

Anal. Calcd for $C_{10}H_{16}N_2O_6 \cdot H_2O$ (290.27): C, 45.51; H, 6.25; N, 9.65; O, 38.58. Found: C, 45.59; H, 6.12; N, 9.55; O, 39.05.

1-(β-D-Arabinofuranosyl)thymine (**5**).—A portion of the above 4-O-methyl nucleoside **4** (81.6 g, 0.281 mole) was dissolved in a

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freshly prepared 1.0 *N* solution of hydrogen chloride in methanol (2.0 l.) and allowed to stand at ambient temperature for 6 days. The precipitate which formed was collected by filtration, washed with a small amount of methanol, and vacuum dried to give 1-(β-D-arabinofuranosyl)thymine (65.4 g, 0.242 mole, 86%): mp 246–248°, $[\alpha]^{27.0}D$ +97.9° (*c* 0.5, H_2O), $\lambda_{max}^{pH\ 1}$ 268 mμ (ε 9810), $\lambda_{min}^{pH\ 1}$ 229 mμ (ε 1750), $\lambda_{max}^{pH\ 7}$ 268 mμ (ε 9890), $\lambda_{min}^{pH\ 7}$ 234 mμ (ε 2320), $\lambda_{max}^{pH\ 13}$ 269 mμ (ε 8130), $\lambda_{min}^{pH\ 13}$ 246 mμ (ε 4130); lit.[6] mp 248–249°, $[\alpha]^{20}D$ +90° (*c* 0.5, H_2O), $\lambda_{max}^{pH\ 1}$ 268 mμ (ε 9590), $\lambda_{max}^{pH\ 7}$ 268 mμ (ε 9530), $\lambda_{max}^{pH\ 13}$ 270 mμ (ε 7870). The material was homogeneous in two paper chromatographic systems[9] with R_{Ad} 0.92 (*n*-BuOH–H_2O) and R_{Ad} 1.87 (5% Na_2HPO_4), respectively.

Anal. Calcd for $C_{10}H_{14}N_2O_6$ (258.2): C, 46.51; H, 5.47; N, 10.85; O, 37.18. Found: C, 46.82; H, 5.65; N, 10.76; O, 37.70.

The material could be recrystallized from 25% aqueous methanol with 80% recovery, mp 246–248°, $[\alpha]^{26}D$ +92° (*c* 0.5, water), with no appreciable change in spectral or microanalytical behavior.

Nucleosides and Related Substances. V. A Synthetic Procedure for Nucleosides with the Use of Phosphorus Pentoxide as Dehydrating Agent

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Fischer and Delbrück[1] first reported a procedure for the synthesis of β,β-trehalose by eliminating a water molecule from two molecules of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose with the use of phosphorus pentoxide (P_4O_{10}). Since then, the procedure has been applied to the synthesis of some oligosaccharides without significant success. After that, Schramm, Grötsch, and Pollmann[2] reported a more simplified method for the synthesis of *N*- and *O*-glycosides, which consisted of the direct condensation of aglycons with unsubstituted monosaccharides in *N*,*N*-dimethylformamide (DMF) in the presence of ethyl polyphosphate. Both methods seem to be based on a similar principle in that a molecule of water is eliminated during the condensation. It would be interesting to examine the synthesis of nucleosides by applying the method of Fischer and Delbrück,[1] because nucleosides might be obtained in higher yields than those reported by Schramm, Grötsch, and Pollmann.[2]

In the course of our recent work on the synthesis of polysaccharides with the use of P_4O_{10} as dehydrating agent,[3] not only the polymerization of monosaccharides but also the condensation of monosaccharides with aglycons was observed to occur. The present work describes the synthesis of some nucleosides in DMF in the presence of P_4O_{10}.

P_4O_{10} and SO_3 were effective as dehydrating agents for the synthesis of nucleosides, but concentrated H_2SO_4, $ZnCl_2$, P_4O_{10}–trace of HCl, and P_4O_{10}–trace of *p*-toluenesulfonic acid were ineffective. DMF was effective as solvent for the synthesis of nucleosides, but dimethyl sulfoxide (DMSO), chloroform, acetone, ethanol, formamide, dioxane, and dinitromethane were ineffective. In the reaction in DMSO in the presence of P_4O_{10}, the oxidation of hydroxyl groups in carbohydrate molecules[4] and the introduction of a $-CH_2SCH_3$ group into reactants[5] were observed to occur. The formation of nucleosides was observed with the reaction in DMF in the presence of P_4O_{10} or SO_3. The isolation of nucleosides was achieved in the yields as high as 37 and 48% in some reactions of purine bases with 2,3,4-tri-*O*-acetyl-D-xylopyranose, 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose, and 2,3,4-tri-*O*-acetyl-D-ribopyranose, respectively. In addition to the nucleosides described in the Experimental Section, some other nucleosides were observed by paper chromatographic examination to be produced in the following reactions: the reactions of theophylline with 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranose and 2,4-di-*O*-acetyl-D-glucurono-6,3-lactone, respectively, and the reactions of 6-benzamidopurine with tri-*O*-acetyl-D-arabinose, 2,4-di-*O*-acetyl-D-glucurono-6,3-lactone, and 2,3,5-tri-*O*-acetyl-D-ribofuranose, respectively. From these reaction mixtures, it was impossible to isolate the corresponding nucleosides because of very low yield. The method was also applied to the condensation of purine bases with unsubstituted monosaccharides of D-glucose, D-xylose, and D-fructose, but any of the corresponding nucleosides were not observed to be produced in these reactions. It was also observed not to produce any nucleosides in the reaction of 6-benzamidopurine with 2,3,4,6-tetra-*O*-benzoyl-α-D-fructofuranose.

Experimental Section

All melting points are uncorrected. All nmr spectra were recorded at 60 Mc and chemical shifts on the nmr spectra were expressed on δ scale in parts per million downfield displacement from tetramethylsilane or sodium 2,2-dimethyl-2-silapentane-5-sulfonate as internal standard. Paper chromatographic examination was carried out on Toyo Roshi No. 51 filter paper by the descending technique, using 1-butanol–water (86:14, v/v) as developing solvent.

7-β-D-Xylopyranosyltheophylline.—Theophylline (4.3 g) was dissolved at 40–50° in DMF (150 ml) containing P_4O_{10} (2.5 g). To the solution was added 2,3,4-tri-*O*-acetyl-D-xylopyranose (5.0 g) dissolved in DMF (50 ml.). The mixture was allowed to stand at 60–70° for 5 days with exclusion of moisture. After being allowed to cool at room temperature, the mixture was poured into about 300 ml of a mixture of ice–water and $CHCl_3$ (1:1, v/v), and this mixture was shaken vigorously. The chloroform layer was collected, washed three times with ice–water, dried with anhydrous Na_2SO_4, and finally concentrated under reduced pressure to a syrup. This was deacetylated in methanol saturated with ammonia according to the usual procedure. A crystalline product produced was collected by filtration and the filtrate was concentrated to a syrup. This was dissolved in a small volume of ethanol and the mixture was allowed to stand in a refrigerator overnight to produce a crystalline product. The combined crystalline products were recrystallized from hot ethanol: yield 2.1 g (37.2%); mp 255–256°; $[\alpha]^{21}D$ −23° (*c* 0.5, water); $\lambda_{max}^{H_2O}$ 274 mμ, $\lambda_{min}^{H_2O}$ 246 mμ; ν_{max}^{KBr} 3350–3450, 1700, 1670, 1630, 1600, 780, 760, and 740 cm^{-1}; nmr (in D_2O), δ 3.35 and 3.55 (CH_3N-1 and -3, 6 H), 8.28 (HC-8, 1 H), and 9.7 (HC-1′, 1 H), $J_{1',2'}$ = 9.0 cps; R_f 0.29.

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