sodium bicarbonate (2 × 25 mL) and water (2 × 25 mL) and then dried over magnesium suflate. The solution was filtered, the solvent evaporated, and the crude product purified by column chromatography (40 g of Merck H silica) using 15:85 ethyl acetate–petroleum ether (bp 60–80 °C) as eluent to give lactone **2a** (1.18 g) as a white crystalline solid: mp 65–70 °C; IR ($CHCl_3$) 1737 (s, C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.88 (m, H-2 (exo)), 2.62 (d, CH_2CO_2), 2.50–1.90 (m, 5 H), 1.60–0.90 (m, 4 H).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.82; H, 7.95.

2-(2-*endo*-Hydroxynorborn-6-*endo*-yl)ethanol (6). Lithium aluminium hydride (76 mg, 2.0 mmol) was suspended in tetrahydrofuran (10 mL) at 0 °C, and a solution of the lactone **2a** (100 mg, 0.66 mmol) in tetrahydrofuran (10 mL) was added. The mixture was stirred at 0 °C for 2 h, and stirring was then continued overnight while the temperature was allowed to rise to room temperature. The reaction was then quenched by the addition of methanol (2 mL), water (25 mL) was added, and the mixture was acidified with dilute hydrochloric acid to pH 2. The mixture was extracted with ether (5 × 25 mL), and the combined extracts were dried over $MgSO_4$, filtered, and evaporated to afford a residue which was purified by sublimation at 0.15 mmHg followed by recrystallization from hexane to give the diol **6** as white crystals (60 mg, 0.395 mmol): mp 71–72 °C; IR ($CHCl_3$) 3400 (OH) cm^{-1}; ^1H NMR (60 MHz) δ 4.62–3.58 (m, 5 H), 2.57–1.66 (m, 7 H), 1.45–0.78 (m, 4 H); ^1H NMR (90 MHz) δ 4.27 (pentet, H-2 (exo)), 4.08 (m, 2 OH), 3.73 (m, H-9), 2.42 (m, H-1), 2.16 (m, H-4), 1.98 (m, H-8, H-3 (exo), H-5 (exo)), 1.78 (m, H-6 (exo)), 1.34 (m, H-7), 0.97 (m, H-3 (endo), H-5 (endo)); $J_{1,2(exo)} = 3.5$ Hz, $J_{2(exo),3(exo)} = 9.5$ Hz, $J_{2(exo),3(endo)} = 4.2$ Hz; on addition of D_2O the peak at δ 4.08 disappeared.

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.99; H, 10.32.

The identical compound (**6**) could be prepared from **2a** by using the procedure of Nickon[1] to convert it into the keto ester **4b** which was then reduced with lithium aluminium hydride.

Acknowledgment. Support from the Science Research Council and Glaxo Group Research, Ltd., is gratefully acknowledged.

Registry No. 2a, 14734-16-8; **2b**, 26433-43-2; **6**, 73395-76-3.

Synthesis of 5-Amino-9-(β-D-ribofuranosyl)-*v*-triazino[4,5-*b*]-pyrimido[4,5-*d*]pyrrol-4-one and Unusual Ring Opening of This New Ring System with the Vilsmeier-Haack Reagent

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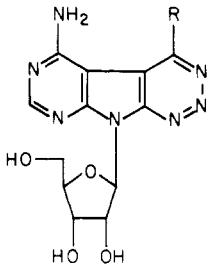
It has been reported[1b] that certain bicyclic nucleosides containing a *v*-triazine ring (e.g., 2-azaadenosine) display some in vivo activity against L-1210 mouse leukemia. In view of this fact, we initiated research designed to synthesize "linear" tricyclic nucleosides in which analogues of 2-azapurine are incorporated into a tricyclic heterocycle. The structure of this type of nucleoside (**1**) can be viewed as resembling adenosine on one side of the molecule and a 2-azapurine nucleoside analogue on the other side. The interesting structural features of **1** should prove to be valuable for studying the relationship that substrate structure has to the interaction of enzymes in purine nucleoside metabolism.



1

The chemical syntheses and reactions of *v*-triazines (1,2,3-triazines) have been the subject of several extensive reviews.[2] The more commonly employed methods for the synthesis of the *v*-triazine ring use intramolecular coupling reactions via a diazotization. In the field of nucleoside chemistry, this type of ring annulation has been employed[3] for the synthesis of 2-azapurine nucleosides from 5-amino-1-(β-D-ribofuranosyl)imidazole-4-carboxamide (AICA riboside). Therefore, for the synthesis of the desired tricyclic nucleosides we elected to use 6-aminosangivamycin[4] (**2**) as our starting material.

Selective diazotization of the exocyclic amino group at the 6-position of **2** furnished the unique [6,5,6] "linear" tricyclic nucleoside, 5-amino-9-(β-D-ribofuranosyl)-*v*-triazino[4,5-*b*]pyrimido[4,5-*d*]pyrrol-4-one (**3**) (see Scheme I), which not only provided the desired nucleoside but also a derivative of a new ring system. However, our attempts to prepare the 4-chloro analogue of **1** (R = Cl) resulted in the discovery of an interesting ring opening of the *v*-triazino ring. The isolation and identification of the ring-opened product has offered some insight into the mechanism of this interesting ring-opening reaction.

Results and Conclusions

Treatment of 6-aminosangivamycin (**2**) with nitrous acid at ice-bath temperature furnished a moderate yield of a product, after column chromatography, which we assumed to be **3**. Evidence that ring closure had taken place was found in the ^1H NMR spectrum of **3** which displayed a broad 1-proton singlet at δ 15.53 for a lactam (NH) group and only one signal (doublet) that could be assigned to an amino group. The signal for the amino group was split into two 1-proton singlets (δ 7.20 and 7.76), indicating that strong hydrogen bonding may exist between one of the amino protons and the 4-one group. Although the empirical formula for **3** was established by elemental analysis and by the mass spectrum, these data do not establish the direction in which the ring annulation had taken place. If ring closure had occurred between the 4-amino group and the carboxamide group, then a "triangular" tricyclic nucleoside such as **8**, with a seven-membered ring, would have been formed instead of **3**. The possible formation of **8** was excluded by the following: (1) The ring-closed product (**3**) shows a significant bathochromic shift in the ultraviolet spectrum (λ_{max} (MeOH) = 343 nm) in comparison[4] to **2** (λ_{max} (MeOH) = 293 nm). This large bathochromic shift has been found to be characteristic for all the "linear" tricyclic nucleosides derived from bicyclic pyrrolo[2,3-*d*]-

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(4) Schram, K. H.; Townsend, L. B. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1253.

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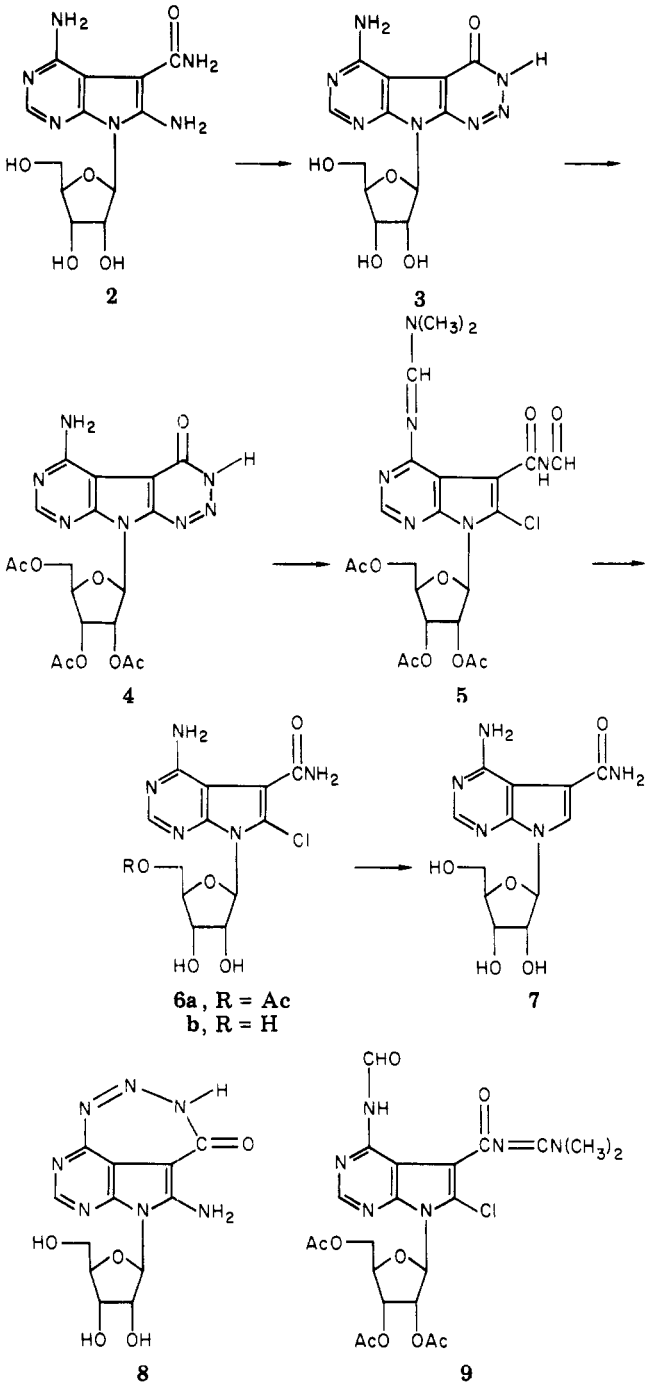
Scheme I



pyrimidine nucleoside precursors in this study.[5] (2) The amino group residing at the 6-position of the pyrrolo[2,3-*d*]pyrimidine ring of **2** appears considerably upfield in the ^{1}H NMR spectrum when compared to the chemical shift for an amino group at the 4-position of the pyrrolo[2,3-*d*]pyrimidine[4] ring. This would suggest that the 6-amino group is more basic than the 4-amino group because it is attached to a relatively electron-rich pyrrole ring, and that the diazotization reaction should take place more readily with the 6-amino group than with the 4-amino group. (3) There is a significant downfield chemical shift of the 2′-H of the ribose moiety observed in **3** (from δ 4.67 for **2** to δ 5.12 for **3**). Such downfield shifts for the 2′-H proton have not been observed[5] when bicyclic nucleosides are converted into certain "nonlinear" tricyclic nucleosides. This downfield chemical shift of 2′-H can be attributed to the anisotropic effect of either N-1 or N-8.[5] Only in a "linear" geometry of the aglycone would the 2′-H of the ribose experience[5] such effects regardless of the anti or syn conformation of the nucleosides. (4) Attempts to ring close sangivamycin[6] under the same or even more stringent conditions have resulted[5] in the recovery of sangivamycin.

One of our goals in this area was to prepare the 4-chloro derivative from **3**. This 4-chloro derivative could then be functionalized to furnish several potentially active anticancer agents. We therefore examined the reaction of **4** under mild chlorinating conditions in an attempt to avoid the cleavage of the glycosyl bond. Another reason for using mild conditions was that it has been reported[7] that the reaction of 1,2,3-benzotriazin-4-one with a mixture of phosphorus oxychloride and phosphorus pentachloride results in the formation of *o*-chlorobenzonitrile, presumably via the formation and then decomposition of a 4-chlorotriazine intermediate into a diazonium salt which subsequently reacts with chloride ion to give the observed product.

The 2′,3′,5′-tri-*O*-acetyl derivative **4** was prepared (83.3% yield) by treatment of **3** with acetic anhydride in pyridine at room temperature in an effort to protect the hydroxy groups of the sugar from the chlorinating reagent. The nucleoside **4** was then allowed to react with dimethylformamide–thionyl chloride[8] in methylene chloride at reflux. After the reaction mixture was washed with saturated aqueous sodium bicarbonate, the solvent was removed in vacuo to yield a homogeneous product after column chromatography. The chemical-ionization mass spectrum (isobutane) of the product showed a molecular ion (MH^+) at *m/e* 553, whereas the electron-impact mass spectrum showed a peak at *m/e* 524 indicating loss of CO from the molecule. The mass spectra also showed isotope patterns indicating the presence of a chlorine atom. The ^{1}H NMR spectrum of this product clearly indicated the presence of a *N*-(dimethylamino)methylene group as well as a 1-proton doublet for the proton of a formyl group at δ 9.75. The addition of D_2O caused a collapse of the 1-proton doublet into a 1-proton singlet, and this revealed that the formyl proton was coupled to an exchangeable proton which appeared at δ 13.52. A marked hypsochromic shift in the UV spectrum suggested that ring opening had occurred. However, the absence of an absorption for a cyano group in the 2200-cm^{-1} region of the infrared spectrum ruled out the possibility of the formation of an *o*-chloro nitrile such as that obtained[7] during chlorination of the benzotriazinone. On the basis of the spectroscopic data, the structure of this product was tentatively assigned as 6-chloro-4-[*N*-[(dimethylamino)methylene]amino]-5-(*N*-formylcarboxamido)-7-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)pyrrolo[2,3-*d*]pyrimidine (**5**). An alternate structure for the product that would also fit the spectroscopic data is **9**. However, it is well-known[9] that the Vilsmeier–Haack reagent[8] (dimethylchloroforminium chloride) readily reacts with unprotected amino groups to form *N*-[(dimethylamino)methylene]amino groups, and it

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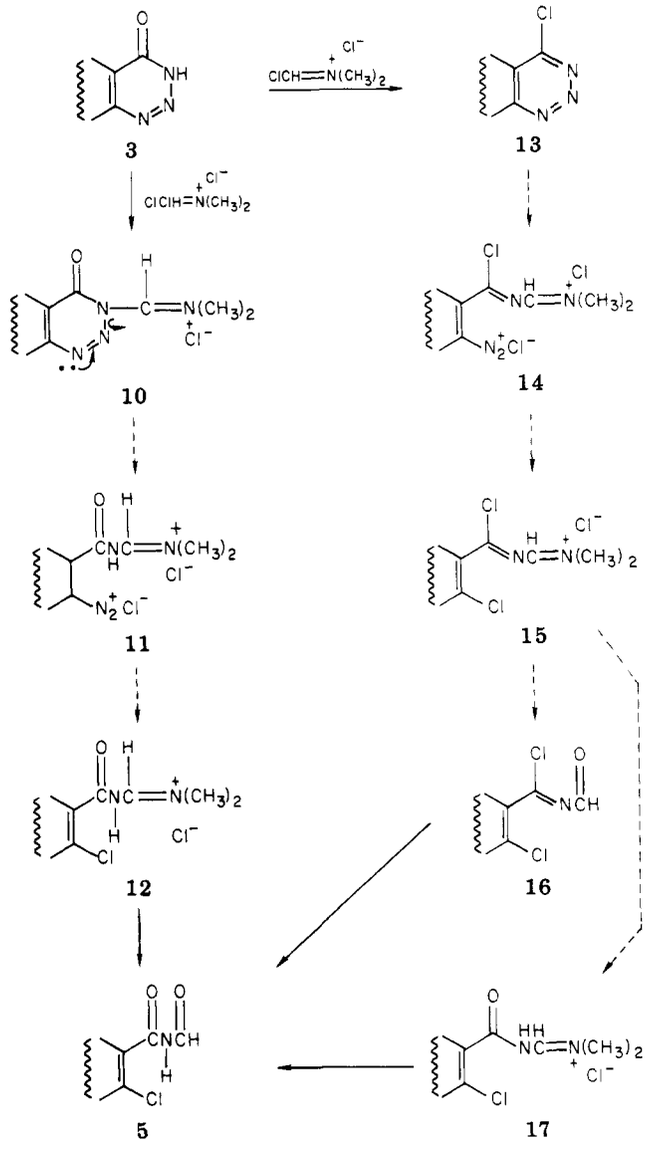
is likely that the 5-amino group of **4** reacts with the Vilsmeier–Haack reagent before ring opening takes place.

Treatment of **5** with dilute ethanolic ammonia at room temperature gave 5′-*O*-acetyl-6-chlorosangivamycin (**6a**). Evidence for the structure of **6a** was supplied by the ^{1}H NMR and mass spectral data as well as by the elemental analysis. The ^{1}H NMR spectrum of **6a** displays a 3-proton singlet at δ 2.00 and a marked downfield chemical shift for the 5′-protons which is indicative of a 5′-*O*-acetylated nucleoside. The completely deblocked nucleoside **6b** (6-chlorosangivamycin) was obtained in 68% yield when **6a** was treated with ammonium hydroxide on a steam bath for 10 min. The structure of **6b** was confirmed by its mass and UV spectra as well as by its elemental analysis. As would be expected, the UV spectrum of **6b** (λ_{max} (MeOH) = 283.5 nm) was nearly identical with that reported[10] for 6-bromosangivamycin (λ_{max} (EtOH) = 285 nm). Finally, **6b** was subjected to catalytic hydrogenation which gave a single product that was found to be identical in all respects with an authentic sample of sangivamycin.[6]

Studies have not been carried out to determine the mechanism of the chlorination–ring-opening reaction. However, the structure of the isolated product **5** suggests that the ring-opening reaction is initiated by attack on N-3 of **3** by the Vilsmeier–Haack reagent to give the intermediate **10** (see Scheme II). Cleavage of the bond between N-3 and N-2 of **10** would then result in a formation of the diazonium salt **11**. Nucleophilic attack by chloride ion on the diazonium group of **11** would then provide the 6-chloro intermediate **12** which would hydrolyze during workup to give **5**. An alternative mechanism[11] could involve the initial formation of a 4-chlorotriazine derivative (**13**) with the subsequent formation of **14**. Displacement of the diazonium group by chloride ion would provide **15** which could then furnish **5** by hydrolysis during workup via **16** or **17**. Another pathway might involve an initial attack at the exocyclic oxygen atom at C-4 followed by an attack at N-3 with ring opening between N-2 and N-3. Displacement of the diazonium group by chloride ion followed by hydrolysis during workup would also furnish **5**.

Scheme II



Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian A-60 or an EM-390 spectrophotometer with Me_2SO-d_6 as solvent and sodium 4,4-dimethyl-4-silapentane-1-sulfonate as internal standard or in $CDCl_3$ with tetramethylsilane as an internal standard. Mass spectra were obtained with an LKB 9000 S instrument and a Varian MAT 112 S/SS100 C data system. Nonvolatile samples were derivatized by using bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS). Samples were introduced by direct probe with an ionizing energy of 70 eV for the electron-ionization (EI) mass spectra. Characteristic nucleoside peaks from the mass spectra are given as follows: ((*m*/*e*) relative intensity), with b = base moiety and M = molecular ion. Thin-layer chromatography was carried out by using microscope slides coated with chromatographic grade silica gel (SilicAR-7GF) obtained from Mallinckrodt. Spots were detected by using short-range (254 nm) ultraviolet light or by spraying the TLC plates with 10% sulfuric acid and then heating at 120 °C. Silica gel suitable for column chromatography was purchased from J. T. Baker Chemical Co. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

5-Amino-9-(β-D-ribofuranosyl)-*v*-triazino[4,5-*b*]pyrimido[4,5-*d*]pyrrol-4-one (3). A dilute aqueous solution of sodium nitrite (55.2 mg, 0.80 mmol in 10 mL of water) was added dropwise with stirring into an ice-cold solution of 6-aminosangivamycin (**2**, 200 mg, 0.62 mmol), water (50 mL), and 2 N HCl (0.5 mL) over a period of 10 min. The resulting dark red solution was stirred at 0 °C for another 30 min and then neutralized with concentrated ammonium hydroxide to pH 7.5. The clear solution was evaporated to dryness in vacuo in the presence of silica gel (1 g). The solid was then applied to the top of a column (2 × 25 cm) of silica gel (23 g), and the column was eluted with chloroform–ethanol (7:3, v/v). Fractions containing the product (as indicated by TLC) were collected and evaporated to dryness in vacuo to afford a crude product. This crude product was recrystallized from methanol–water (7:3, v/v) to furnish 85 mg (41.0%) of **3**: mp 250 °C; dec $[\alpha]^{27}_D$ −40.5° (*c* 1.00, Me_2SO); ^{1}H NMR (Me_2SO-d_6) δ 5.12 (t, 1, H_2, $J_{2',1'}$ = 6, $J_{2',3'}$ = 6 Hz), 6.43 (d, 1, H_1, $J_{1',2'}$ = 6 Hz), 7.76 (br s, 1, NH**H**), 8.20 (br s, 1, **NH**H), 8.39 (s, 1, H_2); mass spectrum (*m*/*e*/relative intensity, EI), M + 5 Me_3Si (695/4), b + 2 Me_3Si + 2 H (348/24), b + 2 Me_3Si + CH_2O (376/45).

Anal. Calcd for $C_{12}H_{13}N_7O_5 \cdot H_2O$: C, 40.80; H, 4.25; N, 27.76. Found: C, 41.09; H, 4.33; N, 27.94.

5-Amino-9-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)-*v*-triazino[4,5-*b*]pyrimido[4,5-*d*]pyrrol-4-one (4). **3** (200 mg, 0.60 mmol) was suspended in pyridine (15 mL) at room temperature (a solution gradually occurred with stirring). Acetic anhydride (0.4 mL, 4.21 mmol) was then added (dropwise) into the solution with stirring and, after 7 h, the solvent was evaporated in vacuo to dryness. The residue was coevaporated with ethanol (2 × 15 mL) and then toluene (2 × 15 mL) to yield 230 mg (83.3%) of

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(11) We thank a referee for suggesting this very plausible alternative mechanism.

4: mp 162 °C (foaming); ^{1}H NMR (Me_2SO-d_6) δ 2.05, 2.09, and 2.14 (3 s, 9, 3 $COCH_3$), 6.67 (d, 1, H_1, $J_{1',2'}$ = 5 Hz), 7.61 (br s, 1, NHH), 8.17 (br s, 1, NHH), 8.48 (s, 1, H_2).

Anal. Calcd for $C_{18}H_{19}N_7O_8$: C, 46.85; H, 4.12; N, 21.26. Found: C, 46.94; H, 4.25; N, 20.90.

6-Chloro-4-[*N*-[(dimethylamino)methylene]amino]-5-(*N*-formylcarboxamido)-7-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)pyrrolo[2,3-*d*]pyrimidine (5). 4 (300 mg, 0.65 mmol) was dissolved in dry methylene chloride (40 mL). The solution was heated at reflux temperature and stirred under a blanket of nitrogen while a solution of thionyl chloride (0.66 mL, 9.08 mmol) and dimethylformamide (0.33 mL, 10.5 mmol) in methylene chloride (10 mL) was added dropwise during 20 min. After the addition was completed, the reaction mixture was heated at reflux for another 2.5 h. The reaction mixture was then cooled to room temperature and poured into a cold (0 °C), saturated, sodium bicarbonate solution, followed by vigorous stirring for 15 min. The methylene chloride layer was separated, and the aqueous layer was then extracted with methylene chloride (2 × 10 mL). The combined methylene chloride solutions were washed with saturated aqueous sodium bicarbonate solution (2 × 15 mL) and water (2 × 20 mL). The methylene chloride solution was then dried overnight (magnesium sulfate). The solution was concentrated in vacuo to a foam which was dissolved in chloroform (3 mL) and then applied to the top of a column (2 × 20 cm) of silica gel (19 g). The column was eluted with chloroform–ethyl acetate–ethanol (12:7:1, v/v/v). The fractions containing the product were collected, and the solvent was evaporated to afford 250 mg (70.0%) of **5** as a light yellow foam: mp 160 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.06, 2.11, 2.17 (3 s, 9, 3 $COCD_3$), 3.30 (s, 3, NCH_3), 3.36 (s, 3, NCH_3), 6.36 (s, 1, $H_{1'}$), 8.50 (s, 1, H_2 or N=CHN), 8.74 (s, 1, N=CHN or H_2), 9.75 (d, 1, CONHCHO, J = 10.0 Hz), 13.52 (d, 1, CONHCHO, J = 10.0 Hz); mass spectrum ((*m*/*e*)/relative intensity, CI), M + H (553/0.91), M + H + 2 (555/0.37); (EI) M − CO (524/3.00), M + 2 − CO (526.1.34).

Anal. Calcd for $C_{22}H_{25}N_6O_9Cl{\cdot}H_2O$: C, 46.28; H, 4.73; N, 14.72. Found: C, 46.21; H, 4.76; N, 14.63.

5'-*O*-Acetyl-6-chlorosangivamycin (6a). **5** (250 mg, 0.45 mmol) was dissolved in ethanolic ammonia (16 mL, ethanol–ammonia, 15:1, v/v) and the solution was then stirred for 20 h at 25 °C. A white solid separated from solution and was collected by filtration. This solid was recrystallized from water (30 mL) to furnish 100 mg (57.4%) of **6a**: mp 140 °C; $[\alpha]^{27}_D$ −48.5° (*c* 1.00, Me_2SO); ^{1}H NMR (Me_2SO-d_6) δ 2.00 (s, 3, $COCH_3$), 5.10 (t, 1, $H_{2'}$), 6.20 (d, 1, $H_{1'}$, $J_{1',2'}$ = 5.0 Hz), 7.73 (s, 2, NH_2), 7.87 (d, 2, $CONH_2$), 8.12 (s, 1, H_2); mass spectrum ((*m*/*e*)/relative intensity, EI), M + 4 Si (673/6), b + 2 Me_3Si + 2 H (354/86), b + 2 Me_3Si + CH_2O (384/82).

Anal. Calcd for $C_{14}H_{16}N_5O_6Cl{\cdot}H_2O$: C, 41.63; H, 4.46; N, 17.35. Found: C, 41.46; H, 4.44; N, 17.46.

6-Chlorosangivamycin (6b). 5'-*O*-Acetyl-6-chlorosangivamycin (**6a**, 25 mg, 0.06 mmol) was treated with dilute ammonium hydroxide (10%, 15 mL) on a steam bath for 10 min. The solvent was evaporated in vacuo and the residual solid was recrystallized from water (10 mL) to afford 15 mg (68%) of **6b**, mp 174 °C. An analytical sample was obtained by recrystallization from water (10 mL) followed by drying in vacuo at 110 °C for 8 h: ^{1}H NMR (Me_2SO-d_6) δ 5.03 (t, 1, $H_{2'}$, $J_{2',1'}$ = 6.0 Hz, $J_{2',3'}$ = 6 Hz), 6.00 (d, 1, $H_{1'}$, $J_{1',2'}$ = 6.0 Hz), 7.80–7.97 (m, 4 H, NH_2 and $CONH_2$), 8.10 (s, 1, H_2); mass spectrum ((*m*/*e*)/relative intensity, EI) M + 5 Me_3Si (703/2), M + 5 Me_3Si − CH_2O (673/47), b + 2 Me_3Si + 2 H (356/100), b + 2 Me_3Si + CH_2O (386/93).

Anal. Calcd for $C_{12}H_{14}N_5O_5Cl$: C, 41.92; H, 4.08; N, 20.38. Found: C, 41.73; H, 4.17; N, 20.24.

Reduction of 6-Chlorosangivamycin (6b). 6-Chlorosangivamycin (**6b**, 70 mg, 0.2 mmol) was dissolved in 20% aqueous ethanol (50 mL). To this solution was added 5% Pd/C (50 mg) and 1 N aqueous sodium hydroxide (0.2 mL). The reaction mixture was agitated under 40 psi of hydrogen for 4.5 h. The reaction mixture was filtered, and the filter cake was washed with hot water (2 × 20 mL). The filtrate and washings were combined and evaporated in vacuo to afford a white solid which was crystallized from water (20 mL) to furnish 45 mg of the product. This product (73%) was shown to be identical with an authentic sample of sangivamycin[6] by a comparison of UV, ^{1}H NMR, TLC, and mixture melting point.

Acknowledgment. This investigation was supported by Drug Research and Development Contract NIH NCI-CM-77142 from the Division of Cancer Treatment, National Cancer Institute, National Institutes of Health, Public Health Service.

Registry No. **2**, 57071-59-7; **3**, 73210-45-4; **4**, 73210-46-5; **5**, 73210-47-6; **6a**, 73210-48-7; **6b**, 73210-49-8; **7**, 18417-89-5; dimethylchloroforminium chloride, 3724-43-4.

Improved Synthesis of Methoxy-1,4-phenanthraquinones

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Recent work by Rosen and Weber[1] has demonstrated that a variety of substituted 1,4-phenanthraquinones can be prepared by the Diels–Alder addition of the appropriate styrenes to 1,4-benzoquinone. Subsequent treatment of these intermediates with 1,3-butadiene gave benz[*a*]anthracene-7,12-diones, useful in the preparation of substituted analogues of the potent carcinogen 7,12-dimethylbenz[*a*]anthracene.[2,3] The authors did not observe the formation of 5-methoxy-1,4-phenanthraquinone and suggested that the Diels–Alder method could not be employed to synthesize this sterically crowded molecule. The Diels–Alder additions of styrenes to 1,4-naphthoquinone have been used to form the sterically crowded compounds 1-chlorobenz[*a*]anthracene-7,12-dione and 1,4-dimethylbenz[*a*]anthracene-7,12-dione[4] as well as the benz[*a*]anthracene-7,12-dione possessing similar steric interactions, namely, 1-methoxybenz[*a*]anthracene-7,12-dione.[5]

Using conditions similar to those employed in the benz[*a*]anthracene-7,12-dione syntheses, we have prepared methoxy-1,4-phenanthraquinones and obtained products substituted in the 5-position. We heated a toluene solution of the methoxystyrene, excess benzquinone, and catalytic amounts of trichloroacetic acid[6] in a 100 °C oil bath for periods varying from 30 to 150 h. In all cases, yields superior to those obtained with the above-cited method were obtained. However, the major product of the reaction of 3-methoxystyrene and excess *p*-benzoquinone was a dihydro form of 7-methoxy-1,4-phenanthraquinone.[7] Attempted dehydrogenation by *p*-benzoquinone or chloranil in refluxing xylene failed. Successful conversion did occur under treatment with a refluxing solution of pyridine in nitrobenzene.[8]

The reaction method gave surprisingly good yields for the 5-methoxy- and 5,8-dimethoxyphenanthraquinones The lower yield of 5-methoxy compound was not unex-

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