tyldimethylsilyl)oxy]-1-(tributylstannyl)-1-octene (3) was prepared as previously described.[13] (*R*)-4-((*tert*-butyldimethylsilyl)oxy]-2-cyclopentenone (2)[14] and methyl 7-hydroxy-5-heptynoate (7)[18] were prepared as previously described. All other reagents were used as received.

Silyl Enol Ether (5). To a dry 25-mL flask was added copper(I) cyanide (0.116 g, 1.30 mmol) and a magnetic stirring bar. The flask was capped with a rubber septum and heated with a heat gun under high vacuum to remove any traces of water, allowed to cool, and filled with nitrogen. THF (3 mL) was added, and the suspension was cooled to 0 °C and vacuum purged with nitrogen under stirring. Methyllithium (2.00 mL, 2.80 mmol, 1.40 M) was added via syringe, and stirring continued for 15 min during which time the suspension became homogeneous. Stannane 3 (0.731 g, 1.40 mmol) dissolved in 1 mL of THF was added in one portion, and stirring continued for 60 min at 25 °C. The cuprate formation was followed by TLC in hexanes. There was a small amount of 3 left unreacted, R_f = 0.70, a large amount of demetalated alkane due to quenching, R_f = 0.57, and a small amount of unknown side product, R_f = 0.17. The resulting cuprate solution was cooled to −70 °C and treated with a solution of enone 2 (0.212 g, 1.00 mmol) in 1 mL of THF added over 1 min. After 5 min chlorotrimethylsilane (0.543 g, 5.00 mmol) was added dropwise, stirring was continued for 15 min, and triethylamine (1.01 g, 10.0 mmol) was added. The cooling bath was removed, and the mixture was allowed to warm to 0 °C when it was poured into a mixture of 50 mL of deionized water and 100 mL of hexanes. The aqueous layer was extracted with 50 mL of hexanes, and the combined organic solutions were dried over magnesium sulfate. Filtration and concentration gave a clear oil, which was taken into 50 mL of toluene and concentrated under high vacuum to give 1.10 g of 5 as a clear oil (195%). In addition to the desired enol ether 5 this material contains methyltributyltin, unreacted 3, and side products due to decomposition of the cuprate: IR (neat) 1640, 1454, 1250, 1065, 837 cm^{-1}; ^1H NMR 2.23 (m, 1 H), 2.55 (m, 1 H), 3.09 (m, 1 H), 4.04 (m, 2 H), 4.47 (d, J = 2.0 Hz, 1 H), 4.48 (dd, J = 4.2 Hz, J = 11 Hz, 2 H); MS m/z 526 (M^+), 469, 394, 337, 311, 285, 215.

5,6-Didehydro-11,15-*O*-bis(*tert*-butyldimethylsilyl)-PGE$_2$, Methyl Ester (1). The synthesis of triflate 8 (reaction A) and enolate 6 (reaction B) must be conducted simultaneously as described in dry apparatus.

Reaction A. A 25-mL flask equipped with an efficient magnetic stirring bar was charged with 3 mL of dichloromethane, cooled to −23 °C (CCl_4, solid CO_2), and vacuum purged with nitrogen. Trifluoromethanesulfonic anhydride (0.502 g, 1.78 mmol) was added with stirring followed by the dropwise addition of a mixture of alcohol 7 (0.265 g, 1.70 mmol) and di-*tert*-butylpyridine (0.344 g, 1.80 mmol) in 1.5 mL of dichloromethane over a 3-min period. The sample vial was rinsed with 0.5 mL of dichloromethane, and stirring was continued for 5 min.

Reaction B. During this 5-min period a 50-mL flask containing enol ether 5 (1.10 g, 1 mmol) dissolved in 10 mL of dry THF was vacuum purged with nitrogen and placed in a cooling bath at −23 °C.

Reaction A. After the 5-min stirring period the mixture was treated dropwise with hexanes (10 mL) and then placed in a −70 °C bath (IPA, solid CO_2) with vigorous stirring for 10 min.

Reaction B. During this 10-min period the solution was treated with methyllithium (1.10 mL, 1.54 mmol, 1.40 M), added at once with stirring. Stirring was continued for 13 min.

Reaction A. After the 10-min stirring period the thick suspension was filtered through a 2-mm pad of anhydrous sodium sulfate into a precooled (−70 °C) 25-mL pear-shaped flask, and the filtrate was rinsed with 3 mL of hexanes. This flask was quickly vacuum purged with nitrogen and the clear solution was stored at (−70 °C) until used.

Reaction B. After 13 min of stirring the yellow anion solution was placed in a −70 °C bath with stirring for 4 min when the contents of the flask from reaction A was added rapidly via cannula. The resulting solution was stirred 5 min at −70 °C and 10 min at −23 °C and quenched with 5 mL of saturated aqueous ammonium chloride. After warming to ambient temperature the mixture was poured into 30 mL of saturated aqueous ammonium chloride and extracted with 100 mL of diethyl ether. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solution was concentrated in vacuo, and the residue was chromatographed on 50 g of silica, eluting with 5:95 ethyl acetate–hexanes. Fractions containing 1 (R_f = 0.50, 15:85 ethyl acetate–hexanes) were combined to give 0.385 g of clear oil (65%): IR (neat) 1747, 1252, 837, 775 cm^{-1}; $[\alpha]^{22}_D$ −13.3° (*c* 0.21, CH_3OH); ^1H NMR ($CDCl_3$) δ 0.03, 0.04, and 0.05 (each s, 12 H), 0.88 (s, 18 H), 0.91 (t, 3 H, J = 6.5 Hz), 1.2–1.4 (m, 6 H) 1.45–1.60 (m, 2 H), 1.73–1.79 (quint, 2 H, J = 7.1 Hz), 2.01–2.09 (m, 1 H), 2.17–2.25 (m, 4 H), 2.39 (t, 2 H, J = 7.5 Hz), 2.65–2.76 (m, 2 H), 2.78–2.85 (m, 1 H), 3.65 (s, 3 H), 4.14 (m, 2 H), 5.48–5.64 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.7, −4.5 (2 C), −4.2, 13.6, 14.0, 16.8, 18.0, 18.2, 22.6, 24.2, 25.1, 25.8 (3 C), 25.9 (3 C), 31.9, 32.8, 38.5, 47.8, 51.5, 51.8, 52.9, 72.7, 73.1, 77.3, 80.9, 128.1, 136.9, 173.7, 213.9; MS m/z 592 (M^+), 577, 561, 535, 429, 403, 297; HRMS m/z calcd for $C_{29}H_{51}O_5Si_2$ ($M^+ - C_4H_9$) 535.3275, found 535.3284.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra for compound 1 (2 pages). Ordering information is given on any current masthead page.

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Stereospecific Vorbrüggen-like Reactions of 1,2-Anhydro Sugars. An Alternative Route to the Synthesis of Nucleosides

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Recently we described the oxidative conversion of pyranose glycals to 1,2-anhydro sugars by reaction with 3,3-dimethyldioxirane (1).[1a] While this class of compounds had been known for many years,[2] the general use of such epoxides as glycosylating agents was rather limited.[3] With the advent of a straightforward method for the stereospecific synthesis of such systems came the encouragement to investigate the effects of resident protecting groups on the efficiency of 1,2-anhydropyranohexoses as glycal donors. It was found that in the presence of nonparticipating neighboring groups, systems such as 3 undergo inversion of configuration upon reaction with various alcohols, including secondary alcohols, in the presence of zinc chloride.[1b] In the work described herein, we addressed the question as to whether 1,2-anhydro sugars might glycosylate heterocyclic bases and, if so, what would be the stereoselectivity of such reactions. Given the useful role of nonnatural nucleosides in antiviral therapy[4] the problem of providing stereospecific access to this series is of particular topical interest.

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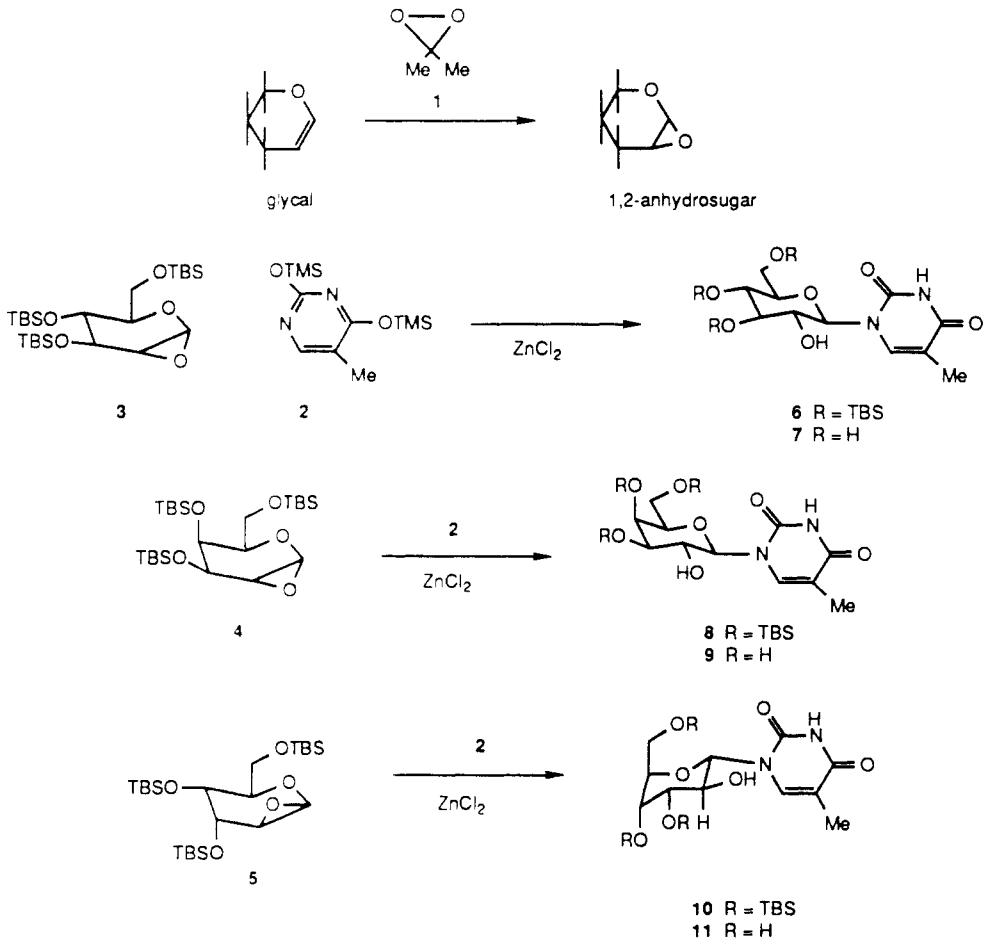
Scheme I



We began our inquiry with a study of the reaction of pyrimidine-based nucleophiles with 1,2-anhydro sugars derived from pyranohexoses. Given the pioneering advances of Nishimara[5] and Vorbrüggen[6] on the silatropic variation of the classical Hilbert–Johnson reaction[7] in the synthesis of nucleosides,[8] we first turned to the bis(siloxy)imidate **2**[9] as the nucleophile. Epoxides **3**, **4**, and **5** were fashioned from the corresponding glycals by reaction with **1** as previously described.[1b]

Reaction of epoxide **3** in dry THF with **2** (3 equiv) in the presence of ethereal zinc chloride occurred at room temperature. Although the yield of **6** was only 38%, we could find no evidence of the other anomer.[10] Deprotection of the silyl groups upon treatment with HF in acetonitrile led to an 84% yield of **7**.[11] Similarly, anhydro sugar **4**[1b] afforded **8** and, upon deprotection, the nucleoside **9**.[12] Once again, the oxidation and glycosylation steps were, apparently, stereospecific. An interesting extension to the allal series was achieved. The β-oxirane **5**, derived from the reaction of OTBS allal[13a] with **1**, reacted smoothly with **2** under zinc chloride catalysis. There was obtained a 79% yield of **10**, which, upon deprotection, gave **11**. NMR analysis indicates that the novel nucleoside analogues **10** and **11** exist in the conformations indicated.[13b]

The applicability of the method to furanose substrates was probed. For this purpose, we prepared glycals **12** and **13**.[14] The reaction of furanoid glycals with **1** had not previously been investigated.[15] As was the case with the pyranose-derived glycals,[1b] compound **12** reacted with **1** with high face selectivity. It was presumed that the resulting 1,2-anhydrofuranose was **14**. Reaction of the epoxide with **2** even in the absence of external Lewis acid provided an 82% yield of a mixture **15** (52%) and **16** (30%). The mixture was deprotected with TBAF in THF to afford **17**. Acetylation (Ac_2O–DMAP) afforded a 94% yield of the C_1 epiarabinonucleoside, triacetate **17a**.

It was of interest to investigate the possibility of altering the facial course of epoxidation by exploiting the directivity of a free hydroxyl group at C_3. The use of hydroxyl groups to direct the course of epoxidation by peroxy acids or by metal-catalyzed epoxidation with hydroperoxides is a well known implement in stereochemical control in cyclic[16] or

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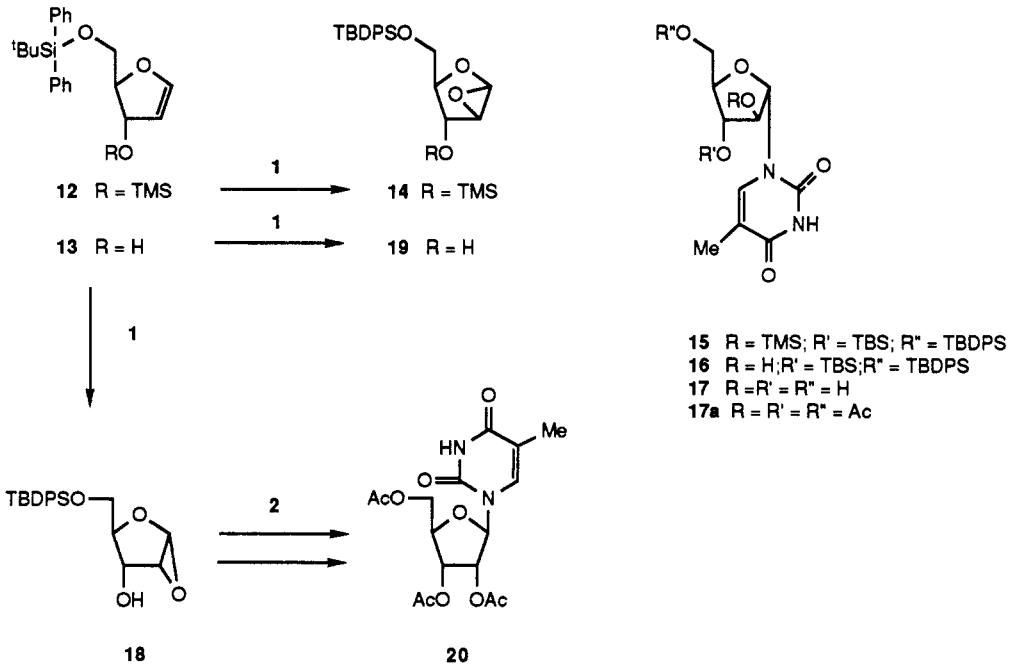
(10) Proton NMR of the crude reaction mixture showed none of the other anomer present.
(11) Yamazaki, T.; Matsuda, K.; Sugiyama, H.; Seto, S.; Yamaoka, N. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1654.
(12) Wittenburg, E. *Chem. Ber.* **1968**, *101*, 1095.
(13) Tris(*tert*-butyldimethylsilyl)allal was prepared in the following manner: 4,6-*O*-benzylidene-D-allal was treated with Na/NH_3 to afford D-allal. Subsequent reaction with 4 equiv of *tert*-butyldimethylsilyl chloride and 8 equiv of imidazole in CH_2Cl_2 at reflux gave tris(*tert*-butyldimethylsilyl)allal. (b) The coupling constants of the anomeric protons of **10** and **11** were 8.2 and 8.5 Hz, respectively. These values are consistent for axial–axial coupling.
(14) Furanoid glycals **12** and **13** were prepared by the procedure of Ireland. Ireland, R. E.; Wilcox, C. S.; Thaisrivongs, S. *J. Org. Chem.* **1978**, *43*, 786.
(15) Baertschi, S. W.; Raney, K. D.; Stone, M. P.; Harrb, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 7929.

Scheme II



acyclic[17] systems. It will be recalled[1b] that such directivity had not been observed in the reactions of the pyranose-derived glycals bearing a free hydroxyl at C_3. Reaction of furanoid glycal **13** with **1** in acetone with a minimal amount of dichloromethane afforded ca. 1:1 mixture of anhydro sugars **18** and **19**.[18] This result, while disappointing, did suggest that an allylic hydroxyl might have greater directing potential on the reaction of the 1,2-double bond with **1** in the furanoid relative to the pyranoid series. In the latter case there was virtually no difference between whether C_3 was protected or free. In either case reaction with **1** occurred anti to the substituent at C_3.

Given this small encouragement, we investigated the reaction of **13** with **1** in a solvent system where the acetone solution of **1** as described in the Murray protocols was diluted with methylene chloride such that the ratio of acetone/methylene chloride was ca. 6:1. The hope was that in such a medium the directivity of the free hydroxyl group at C_3 via hydrogen bonding would be increase, thereby favoring syn attack. In the event there was obtained a 9:1 mixture of epoxides **18** and **19**.[18] For purposes of nucleoside formation, the mixture was treated with **2** in acetonitrile. The resultant products were desilylated with TBAF in THF and then acetylated with acetic anhydride/DMAP. There was obtained a 36% yield of a 4:1 mixture of **20**:**17a**. The former could be purified by HPLC. *Thus, in the furanoid series, stereoselective syn oxidation by 1 under the influence of an allylic (C_3) alcohol is observed at least under these conditions.*[19]

In summary, it has been shown that 1,2-epoxides, in both the furanoid and pyranoid series, glycosylate compound **2** with clean inversion of configuration. Future studies will be directed to fine tuning these protocols with a view toward yield improvements. We also hope to investigate extensions of this strategy to the preparation of other nucleosides both of natural and unnatural structural types. In these connections, the issue of hydroxy directivity will be explored in greater detail.

Experimental Section

1-(3′,4′,6′-Tri-*O*-(*tert*-butyldimethylsilyl)-β-D-glucopyranosyl)-5-methyl-2,4(1*H*,3*H*)-pyrimidinedione (6). Tri-*O*-(*tert*-butyldimethylsilyl)glucal[1b] (0.50 g, 1.0 mmol) was dissolved in 5 mL of CH_2Cl_2. The solution was cool to 0 °C, whereupon 20 mL of a 61 mM solution (in acetone, 1.5 mmol) of dimethyldioxirane (**1**) was added. The reaction mixture was stirred at 0 °C for 1 h before being concentrated. Residue solvent was removed under vacuum (0.10 mmHg). The anhydro sugar **3** was dissolved in 25 mL of dry THF; 0.81 g (3.0 mmol) of bis-*O*-(trimethylsilyl)thymine (**2**) and 1.0 mL of a 1 M $ZnCl_2$ (in ether, 1.0 mmol) solution were added. After being stirred for 16.5 h at room temperature, the reaction mixture was quenched with 5% $NaHCO_3$. The resultant mixture was extracted with ethyl acetate (2×). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. SiO_2 chromatography (2:1 hexanes/ethyl acetate) afforded 0.23 g (37%) of **6**: mp 194–197 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 8.66 (br s, 1 H, N_3-H), 7.17 (d, J = 1.2 Hz, 1 H, C_6-H), 5.77 (d, J = 8.1 Hz, 1 H, $C_{1'}$-H), 3.78–3.84 (m, 4 H), 3.63–3.66 (br m, 1 H), 3.49–3.52 (br m, 1 H), 2.76 (d, J = 8.0 Hz, 1 H, $C_{2'}$-OH), 1.91 (d, J = 1.2 Hz, 3 H, C_5-CH_3), 0.94 (s, 9 H, SiC_4H_9), 0.93 (s, 9 H, SiC_4H_9), 0.90 (s, 9 H, SiC_4H_9), 0.15–0.17 (m, 12 H, $SiCH_3$), 0.04 (m (app s), 6 H, $SiCH_3$); IR 3420, 3180, 3040, 2960, 2940, 2900, 2860, 1790, 1480, 1260, 1110 cm^{-1}; MS m/z 573 ($M^+ - C_4H_9$); high-resolution MS for $C_{29}H_{58}N_2O_7Si_3$ (M^+ + H) calcd 631.3632, found 631.3581; $[\alpha]_D$ +20.1° (MeOH, c = 0.67). Anal. Calcd: C, 55.24; H, 9.21. Found: C, 55.46; H, 9.50.

1-(β-D-Glucopyranosyl)-5-methyl-2,4(1*H*,3*H*)-pyrimidinedione (7). Compound **6** (0.13 g, 0.21 mmol) was dissolved in 5 mL of a 5% HF/CH_3CN solution. After being stirring at room temperature for 8.5 h, the reaction mixture was filtered through a plug of neutral alumina. The eluent was concentrated, and the residue was subjected to SiO_2 chromatography (2:1 ethyl acetate/methanol) to afford 50 mg (84%) of **7**: ^1H NMR (250 MHz, CD_3OD) δ 7.57 (d, J = 1.2 Hz, 1 H, C_6-H), 5.55 (d, J = 8.9 Hz, 1 H, $C_{1'}$-H), 3.89 (dd, J = 12, 1.4 Hz, 1 H, $C_{6'}$-H), 3.67 (dd, J = 12, 4.6 Hz, 1 H, $C_{6'}$-H), 3.46–3.62 (m, 4 H), 3.46–3.62 (m, 4 H), 1.92 (d, J = 1.2 Hz, 3 H, C_5-CH_3); IR 3384, 1683, 1472, 1370, 1274, 1255, 1069 cm^{-1}; MS m/z 288 (M^+); high-resolution MS for $C_{11}H_{16}N_2O_7$ (M^+ + H) calcd 289.1036, found 289.1020; $[\alpha]_D$ +15.7° (H_2O, c = 0.64) (lit.[11] $[\alpha]^{25}_D$ +19° (c = 1.00, H_2O)).

1-(3′,4′,6′-Tri-*O*-(*tert*-butyldimethylsilyl)-β-D-galactopyranosyl)-5-methyl-2,4(1*H*,3*H*)-pyrimidinedione (8). Tri-

(16) Henbest, S. W.; Wilson, R. A. L. *J. Chem. Soc.* **1957**, 1958.
(17) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136.
(18) The stereochemistry of **18** and **19** were determined by methanolysis of the epoxides followed by desilylation to afford methylribose and methylarabinose, respectively.
(19) For reasons which are not obvious the ratio of nucleosides which are produced do not fully reflect the selectivity of the epoxidation.[18]

O-(*tert*-butyldimethylsilyl)galactal[1b] (0.44 g, 0.90 mmol) was dissolved in 5 mL of CH_2Cl_2. The solution was cool to 0 °C, whereupon 23.7 mL of a 57 mM solution (in acetone, 1.35 mmol) of **1** was added. The reaction mixture was stirred at 0 °C for 1 h before being concentrated. Residue solvent was removed under vacuum (0.10 mmHg). The anhydro sugar **4** was dissolved in 20 mL of dry THF; 0.73 g (2.7 mmol) of bis-*O*-(trimethylsilyl)thymine (**2**) and 0.90 mL of a 1 M $ZnCl_2$ (in ether, 0.90 mmol) solution were added. After being stirred for 12 h at room temperature, the reaction mixture was quenched with 5% $NaHCO_3$. The resultant mixture was extracted with ethyl acetate (3×). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. SiO_2 chromatography (2:1 hexanes/ethyl acetate) afforded 0.25 g (44%) of **8**, mp 113–115 °C: ^1H NMR (250 MHz, $CDCl_3$) δ 9.49 (br s, 1 H, N_3-H), 7.20 (s, 1 H, C_6-H), 5.71 (d, J = 8.7 Hz, 1 H, C_1-H), 4.04 (d, J = 1.8 Hz, 1 H), 3.83–3.93 (m, 1 H), 3.55–3.73 (m, 4 H), 3.17 (d, J = 6.0 Hz, 1 H, C_2-OH), 1.84 (s, 3 H, C_5-CH_3), 0.96 (s, 9 H, SiC_4H_9), 0.94 (s, 9 H, SiC_4H_9), 0.88 (s, 9 H, SiC_4H_9), 0.19 (s, 3 H, $SiCH_3$), 0.16 (m (app s), 6 H, $SiCH_3$), 0.14 (s, 3 H, $SiCH_3$), 0.05 (m (app s), 6 H, $SiCH_3$); IR 3410, 3160, 3040, 2940, 2920, 2880, 2850, 1790, 1520, 1250, 1110 cm^{-1}; MS m/z 573 ($M^+ - C_4H_9$); high-resolution MS for $C_{29}H_{58}N_2O_7Si_3$ (M^+ + H) calcd 631.3632, found 631.3612; $[\alpha]_D$ +17.9° (MeOH, c = 0.57). Anal. Calcd: C, 55.24; H, 9.21. Found: C, 55.44; H, 9.37.

1-(β-D-Galactopyranosyl)-5-methyl-2,4(1*H*,3*H*)-pyrimidinedione (9). Compound **8** (0.15 g; 0.24 mmol) was dissolved in 25 mL of a 2% HF/CH_3CN solution. After being stirred at room temperature for 7.5 h, the reaction mixture was filtered through a plug of neutral alumina. The eluent was concentrated, and the residue was subjected to SiO_2 chromatography (3:1 ethyl acetate/methanol) to afford 57 mg (83%) of **9**: ^1H NMR (250 MHz, CD_3OD) δ 7.67 (d, J = 1.1 Hz, 1 H, C_6-H), 5.51 (d, J = 9.2 Hz, 1 H, C_1-H), 3.93 (d, J = 3.2 Hz, 1 H), 3.59–3.84 (m, 5 H), 1.89 (d, J = 1.1 Hz, 3 H, C_5-CH_3); IR 3360, 1700, 1480, 1380, 1290, 1100 cm^{-1}; MS m/z 288 (M^+); high-resolution MS for $C_{11}H_{16}N_2O_7$ (M^+ + H) calcd 289.1036, found 289.1019; $[\alpha]_D$ +46.1° (CH_3OH, c = 0.74) (lit.[12] $[\alpha]^{25}_D$ +47.2° (c = 1.0, H_2O).

1-(3′,4′,6′-Tri-*O*-(*tert*-butyldimethylsilyl)-α-D-allopyranosyl)-5-methyl-2,4(1*H*,3*H*)-pyrimidinedione (10). Tri-*O*-(*tert*-butyldimethylsilyl)allal[13a] (0.70 g, 1.43 mmol) was dissolved in 10 mL of CH_2Cl_2. The solution was cool to 0 °C, whereupon 36.5 mL of a 59 mM solution (in acetone, 2.15 mmol) of **1** was added. The reaction mixture was stirred at 0 °C for 1 h before being concentrated. Residue solvent was removed under vacuum (0.10 mmHg). The anhydro sugar **5** was dissolved in 30 mL of dry THF; 1.16 g (4.29 mmol) of bis-*O*-(trimethylsilyl)-thymine (**2**) and 1.43 mL of a 1 M $ZnCl_2$ (in ether, 1.43 mmol) solution were added. After being stirred for 17 h at room temperature, the reaction mixture was quenched with 5% $NaHCO_3$. The resultant mixture was extracted with ethyl acetate (3×). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. SiO_2 chromatography (2:1 hexanes/ethyl acetate) afforded 0.71 g (79%) of **10**, mp 115–117 °C: ^1H NMR (250 MHz, $CDCl_3$) δ 8.35 (br s, 1 H, N_3-H), 7.27 (s, 1 H, C_6-H), 5.89 (d, J = 8.2 Hz, 1 H, C_1-H), 3.75–4.14 (m, 6 H), 1.23 (br s, 1 H, C_2-OH), 1.91 (s, 3 H, C_5-CH_3), 0.92–0.96 (m, 27 H, SiC_4H_9), 0.09–0.14 (m, 18 H, $SiCH_3$); IR 3360, 3180, 3060, 2940, 2920, 2880, 2840, 1710, 1690, 1460, 1250, 1110, 1080 cm^{-1}; MS m/z 573 ($M^+ - C_4H_9$); high-resolution MS for $C_{29}H_{58}N_2O_7Si_3$ (M^+ + H) calcd 631.3632, found 631.3614; $[\alpha]_D$ −21.5° ($CHCl_3$, c = 0.79). Anal. Calcd: C, 55.24; H, 9.21. Found: C, 55.34; H, 9.45.

1-(α-D-Allopyranosyl)-5-methyl-2,4(1*H*,3*H*)-pyrimidinedione (11). Compound **10** (0.17 g, 0.27 mmol) was dissolved in 5 mL of a 5% HF/CH_3CN solution. After being stirred at room temperature for 5.5 h, the reaction mixture was filtered through a plug of neutral alumina. The eluent was concentrated, and the residue was subjected to SiO_2 chromatography (3:1 chloroform/methanol) to afford 78 mg (100%) of product **11**: ^1H NMR (250 MHz, CD_3OD) δ 7.67 (d, J = 0.6 Hz, 1 H, C_6-H), 5.77 (d, J = 8.5 Hz, 1 H, C_1-H), 4.00–4.04 (m, 2 H), 3.82–3.92 (m, 3 H), 3.72 (dd, J = 11.8, 5.4 Hz, 1 H), 1.90 (d, J = 0.6 Hz, 3 H, C_5-CH_3); IR 3380, 3160, 3040, 1700, 1410, 1115, 1060, 1025 cm^{-1}; MS m/z 288 (M^+); high-resolution MS for $C_{11}H_{16}N_2O_7$ (M^+ + H) calcd 289.1036, found 289.1046; $[\alpha]_D$ −0.9° (CH_3OH, c = 0.92).

1-(3′-(Trimethylsilyl)-5′-(*tert*-butyldiphenylsilyl)-α-D-arabinofuranosyl)-5-methyl-2,4(1*H*,3*H*)-pyrimidinedione. Furanoid glycal **12**[14] (55 mg, 0.13 mmol) was dissolved in 2 mL of CH_2Cl_2. The solution was cool to 0 °C, whereupon 4.5 mL of a 43 mM solution (in acetone, 0.20 mmol) of **1** was added. The reaction mixture was stirred at 0 °C for 0.5 h before being concentrated. Residue solvent was removed under vacuum (0.10 mmHg). The anhydro sugar **14** was dissolved in 2 mL of dry CH_3CN followed by the addition of 74 mg (0.27 mmol) of **2**. After being stirred for 18 h at room temperature, the reaction mixture was quenched with 5% $NaHCO_3$. The resultant mixture was extracted with ethyl acetate (3×). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. SiO_2 chromatography (15:1 chloroform/methanol) afforded 43 mg (52%) of the **15** and 22 mg (30%) of free C_2 alcohol **16**, which was carried further (see the next experiment). A sample of compound **16** was purified: ^1H NMR (250 MHz, $CDCl_3$) δ 9.23 (br s, 1 H, N_3-H), 7.38–7.71 (m, 11 H), 5.86 (br s, 1 H, C_1-H), 4.55 (d, J = 5.6 Hz, 1 H), 4.31 (m, 2 H), 4.14–4.16 (m, 1 H), 3.93 (dd, J = 11.2, 3.7 Hz, 1 H, C_5-H), 3.77 (dd, J = 11.2, 3.7 Hz, 1 H, C_5-H), 1.92 (s, 3 H, C_5-CH_3), 1.09 (s, 9 H, SiC_4H_9), 0.10 (s, 6 H, $SiCH_3$); IR 3380, 3180, 3010, 3000, 2950, 2920, 2860, 1690, 1470, 1430, 1260, 1110 cm^{-1}; MS m/z 511 ($M^+ - C_4H_9$); high-resolution MS for $C_{29}H_{40}N_2O_6Si_2$ (M^+ + H) calcd 569.2504, found 569.2506.

1-(α-D-Arabinofuranosyl)-5-methyl-2,4(1*H*,3*H*)-pyrimidinedione. The crude **15**–**16** mixture (25 mg) was dissolved in 5 mL of a 2% HF/CH_3CN solution. After being stirred at room temperature for 10.5 h, the reaction mixture was filtered through a plug of neutral alumina. The eluent was concentrated, and the residue was subjected to SiO_2 chromatography (5:1 ethyl acetate/methanol) to afford 10.7 mg (94%) of **17**: ^1H NMR (250 MHz, CD_3OD) δ 7.56 (d, J = 1.0 Hz, 1 H, C_6-H), 5.82 (d, J = 3.7 Hz, 1 H, C_1-H), 4.20–4.29 (m, 2 H), 4.08 (t, J = 4.3 Hz, 1 H), 3.64–3.78 (m, 2 H, C_5-H), 1.88 (d, J = 1.0 Hz, 3 H, C_5-CH_3); IR 3376, 1692, 1467, 1261, 1114, 1036 cm^{-1}; MS m/z 258 (M^+); high-resolution MS for $C_{10}H_{14}N_2O_6$ (M^+) calcd 258.0852, found 258.0838; $[\alpha]_D$ +19.7° (CH_3OH, c = 0.59).

Triacetate **17a**: ^1H NMR (250 MHz, $CDCl_3$) δ 9.01 (br s, 1 H, N_3-H), 7.13 (d, J = 1.1 Hz, 1 H, C_6-H), 5.99 (d, J = 3.8 Hz, 1 H, C_1-H), 5.50 (t, J = 3.4 Hz, 1 H), 5.25 (t, J = 3.6 Hz, 1 H), 4.56–4.62 (m, 1 H, C_4-H), 4.26–4.36 (m, 2 H, C_5-H), 2.15 (s, 3 H, C(O)CH_3), 2.14 (s, 3 H, C(O)CH_3), 2.12 (s, 3 H, C(O)CH_3), 1.95 (d, J = 1.0 Hz, 3 H, C_5-CH_3).

1-(2′,3′,5′-Tri-*O*-acetyl-β-D-ribofuranosyl)-5-methyl-2,4-(1*H*,3*H*)-pyrimidinedione. Furanoid glycal **13**[14] (76 mg, 0.21 mmol) was dissolved in 30 mL of CH_2Cl_2. The solution was cool to 0 °C, whereupon 5.1 mL of a 63 mM solution (in acetone, 0.32 mmol) of **1** was added. The reaction mixture was stirred at 0 °C for 40 min before being concentrated to 2 mL by passing a stream of nitrogen over the solution. CH_3CN (10 mL) was added, and the stream of nitrogen continued until the volume was reduced to 5 mL. To the resultant mixture of **18** and **19** was added compound **2** (0.17 g, 0.63 mmol). The reaction mixture was stirred at room temperature for 19.5 h before being quenched with 5% $NaHCO_3$. This was followed by extraction with ethyl acetate (3×). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. The residue was dissolved in 3 mL of THF; 1.0 mL of a 1 M solution of TBAF was added. After being stirred overnight the reaction mixture was concentrated and the residue was subjected to SiO_2 chromatography (10:1 chloroform/methanol). The product obtained was dissolved in 10 mL of THF; 0.34 mL of pyridine, 0.40 mL of Ac_2O, and a catalytic amount of DMAP were added. After being stirred at room temperature for 12 h, the reaction mixture was concentrated and the residue was subjected to SiO_2 chromatography (1:1 hexanes/ethyl acetate) to afford 29 mg (36% of a 4:1 mixture of **20**:**17a** (previous experiment). Ribonucleoside **20** was obtained by HPLC separation: ^1H NMR (250 MHz, $CDCl_3$) δ 8.11 (br s, 1 H, N_3-H), 7.19 (br s, 1 H, C_6-H), 6.08 (d, J = 5.2 Hz, 1 H, C_1-H), 5.32–5.35 (m, 2 H), 4.37–4.38 (m, 3 H), 2.17 (s, 3 H, C(O)CH_3), 2.14 (s, 3 H, C(O)CH_3), 2.11 (s, 3 H, C(O)CH_3), 1.96 (s, 3 H, C_5-CH_3); IR 1752, 1690, 1460, 1366 cm^{-1}; MS m/z 384 (M^+).

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