REACTIVITY OF 2',3'-ANHYDRO PYRIMIDINE NUCLEOSIDES TOWARD TRIMETHYLALUMINUM

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Abstract — Treatment of 2',3'-anhydro pyrimidine nucleoside derivatives (**1**) with trimethylaluminum afforded 1-(3-deoxy-3-methyl-β-D-arabinofuranosyl)pyrimidine derivatives (**2**) and 1-(2-deoxy-2-methyl-β-D-xylofuranosyl)pyrimidine derivatives (**3**) as a mixture in approximately 2 : 1 – 3 : 1 ratio *via* ring-opening of the epoxide involving the nucleophilic attack of trimethylaluminum at the 3' or 2'-position of **1**.

Nucleosides modified in the sugar moiety have been recognized as attractive synthetic targets for the development of potential antiviral agents[1] and synthetic oligonucleotide probes.[2] 2',3'-Anhydro-β-D-lixofuranosyl pyrimidine nucleoside derivatives (**1**) first synthesized by Fox *et al.*[3,4] are useful key intermediates for the synthesis of biologically interesting pyrimidine nucleosides. A large number of reactions of **1** with a variety of nucleophiles have been investigated.[3-11] It is well known that nucleophilic addition of **1** gave a mixture of 2' and 3'-adducts in most cases.[3-11] However, the reaction with trialkylaluminum as a carbon-nucleophile have not been carried out until recently.[11] Further, the nucleophilic reaction of even non-nucleoside epoxides with trialkylaluminum was also rather exceptional, although a few examples have been reported.[12,13] On the other hand, the regioselective ring-opening reaction of 2,3-epoxy-1-alkanols using trialkylaluminum was reported by Ohshima *et al.*[12] The regioselective outcome of the reaction was interpreted by the conversion of the hydroxy group into aluminum alkoxide and the coordination of the epoxy-oxygen to an aluminum atom (Figure 1). As 1-(2,3-anhydro-β-D-lyxofuranosyl)uracil (**1a**)[4,6] also possesses a 2,3-epoxy alcohol moiety within the molecule, we applied **1** to regioselective methylation. We report here the reaction of 2',3'-anhydro pyrimidine nucleoside derivatives (**1**) with trimethylaluminum.

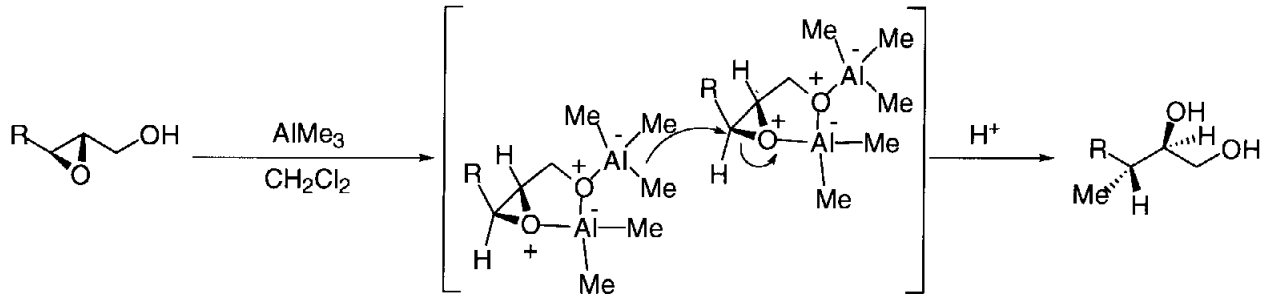
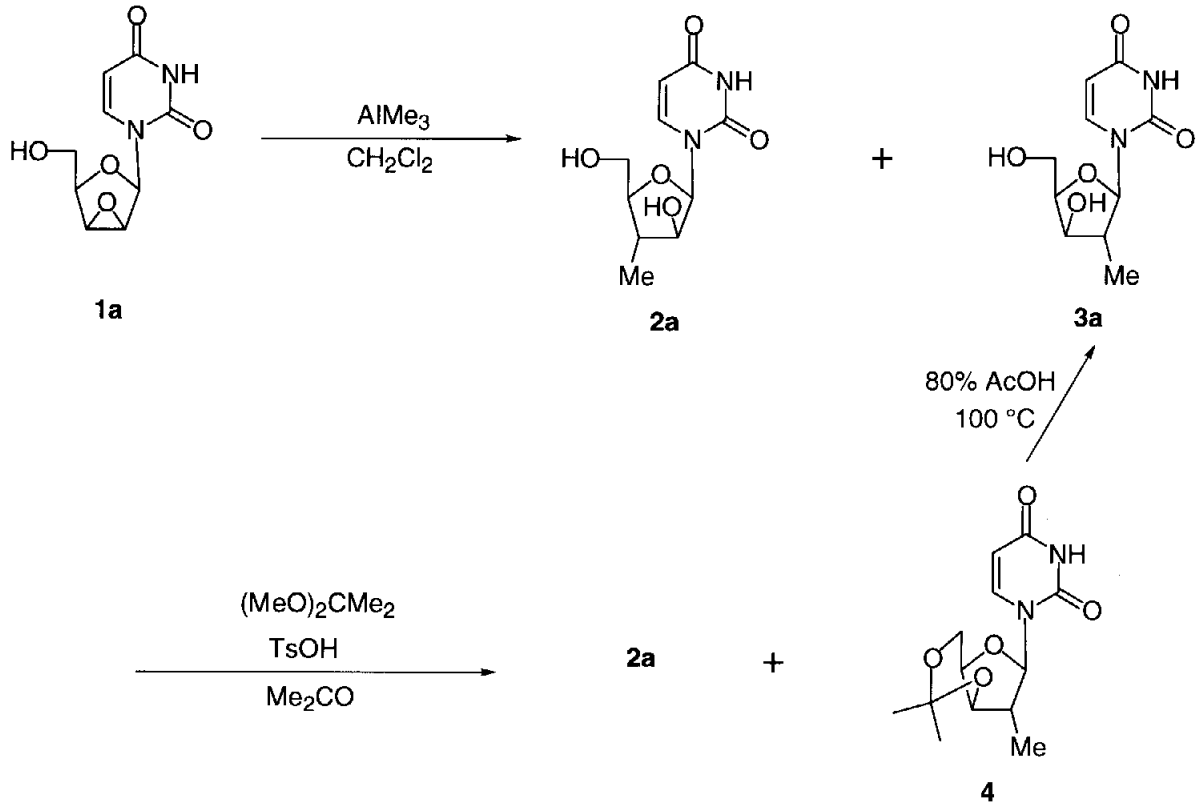


Figure 1



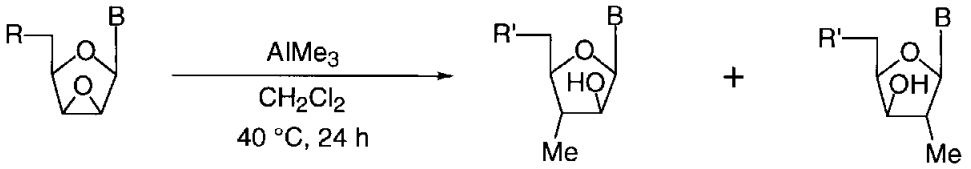
Scheme 1

1-(2,3-Anhydro-β-D-lyxofuranosyl)uracil (**1a**) readily obtained in four steps from uridine[4,6] was treated with trimethylaluminum (5 equiv.) in CH_2Cl_2 to afford a mixture of 1-(3-deoxy-3-methyl-β-D-arabinofuranosyl)uracil (**2a**)[6,7] and 1-(2-deoxy-2-methyl-β-D-xylofuranosyl)uracil (**3a**)[8] in the ratio of 2 : 1 together with 10% of recovered **1a** (Scheme 1 and Table 1, Entry 1). The expected regioselective addition did not proceed. The yields of **2a** and **3a** were estimated by the integration ratios of the ^{1}H-NMR spectra of the mixture. Products (**2a**) and (**3a**) could be separated by further modification as follows. The reaction

of the mixture (**2a** and **3a**) with 2,2-dimethoxypropane in the presence of TsOH afforded 1-(2-deoxy-3,5-*O*-isopropyridene-2-methyl-β-D-xylofuranosyl)uracil (**4**)[8] along with unreacted (recovered) pure **2a**. Finally, the isopropylidene product (**4**) easily underwent deprotection upon treatment with 80% AcOH at 100 ℃ to give pure **3a** in 60% yield.

When 1-(2,3-anhydro-β-D-lyxofuranosyl)thymine (**1b**)[4,6] was allowed to react with trimethylaluminum under analogous conditions, the corresponding 1-(3-deoxy-3-methyl-β-D-arabinofuranosyl)thymine (**2b**)[6,7] (35%) and 1-(2-deoxy-2-methyl-β-D-xylofuranosyl)thymine (**3b**)[8] (11%) were obtained as a mixture together with recovered **1b** (8%).

Table 1. Reaction of 2',3'-anhydropyrimidine nucleosides (**1a-e**) with trimethylaluminum.



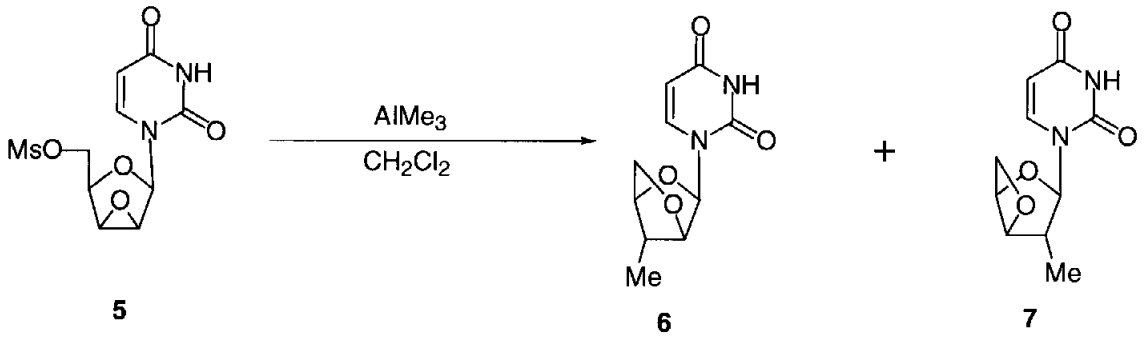
1 **2** **3**

Entry	Substrate	B	R	$AlMe_3$ (equiv.)	Products (%)[1]		R'	Recovery (%)
1	**1a**	U	OH	5	**2a** (40)	**3a** (19)	OH	10
2	**1b**	T	OH	5	**2b** (35)	**3b** (11)	OH	8
3	**1c**	U	OBz	10	**2a** (47)	**3a** (24)	OH	ND[3]
4	**1d**	U	OTr	10	**2a** (45)	**3a** (18)	OH	ND[3]
5	**1e**	U	I	10	**2c** (52)	**3c** (26)	I	ND[3]

[1]The yields were estimated by ^{1}H NMR. [2]Isolated yield. [3]Not detectable.

In order to investigate the effect of the 5'-hydroxy group (or oxygen atom) of **1a** on the regioselectivity, 5'-*O*-benzoyl (**1c**), 5'-*O*-trityl (**1d**) and 5'-deoxy-5'-iodo derivatives (**1e**) of **1a** were employed as substrates. Although the use of 10 equivalents of trimethylaluminum was necessary to obtain better yield, 1-(2,3-

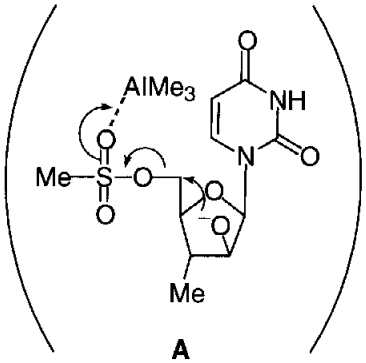
anhydro-5-*O*-benzoyl-β-D-lyxofuranosyl)uracil (**1c**)[4] or 1-(2,3-anhydro-5-*O*-trityl-β-D-lyxofuranosyl)uracil (**1d**)[4] possessing no hydroxy group at the 5-position of the sugar moiety also easily underwent the ring-opening methylation reaction along with the debenzoylation or detritylation to give **2a** and **3a** as a mixture in similar product ratios (Table 1, Entry 3 and 4). Upon treatment with 1-(2,3-anhydro-5-deoxy-5-iodo-β-D-lyxofuranosyl)uracil (**1e**),[3,4] which possesses no oxygen atom at the 5-position, 1-(3,5-dideoxy-5-iodo-3-methyl-β-D-arabinofuranosyl)uracil (**2c**)[9] (52%) and 1-(2,5-dideoxy-5-iodo-2-methyl-β-D-xylofuranosyl)uracil (**3c**) (26%) were similarly obtained as a mixture (Table 1, Entry 5). As shown in Table 1, the formation ratio of products (**2**) and (**3**) by the reaction of 2',3'-anhydro pyrimidine nucleosides (**1a-e**) with trimethylaluminum was approximately 2 : 1 and good regioselective synthesis could not achieved. These results indicate that the hydroxy group (or oxygen atom) at the 5'-position of **1a** and **1b** is not concerned in the control for the regioselective methyl attack on the 3'-position *via* the coordination to an aluminum atom.



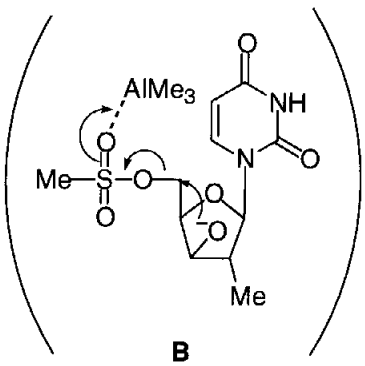
5 **6** **7**

Scheme 2

The ring-opening methylation was also studied using 1-(2,3-anhydro-5-*O*-mesyl-β-D-lyxofuranosyl)uracil (**5**).[4] As shown in Scheme 2, 1-(2,5-anhydro-3-deoxy-3-methyl-β-D-arabinofuranosyl)uracil (**6**) (39%) and 1-(3,5-anhydro-2-deoxy-2-methyl-β-D-xylofuranosyl)uracil (**7**) (19%) were obtained as a mixture although the degree of regioselectivity of the ring-opening of epoxide was not changed (approximately 2 : 1). Formation of **6** and **7** could be induced by the nucleophilic attack of the resulting 2'- or 3'-oxy anion (**A** or **B**) on the 5'-position.[14] This observation can be explained on the basis of the activation of the 5'-*O*-mesyl group by trimethylaluminum since the formation of **6** or **7** was not observed in the reaction of **1e** that possesses a 5-iodo group.



A



B

EXPERIMENTAL

Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. All column chromatography was carried out with silica gel (230–400 mesh, Wakogel C-300). All reactions were monitored by TLC performed on glass-backed silica gel 60 F254, 0.2 mm plates (MERCK), and compounds were visualized under UV light (254 nm). Melting points were determined on a Yanagimoto micro hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were determined with a JEOL JNM-GX-270 spectrometer in DMSO-d_6. Coupling constants (J) are reported in Hertz (Hz). UV spectra were obtained from EtOH solutions on a Shimadzu UV-260 spectrophotometer. MS (EI$^+$) were obtained in a JEOL JMS-D 300 machine operating at 70 eV. Microanalyses were carried out at the Microanalytical Laboratory of our University.

Reaction of 1-(2,3-anhydro-β-D-lyxofuranosyl)uracil (1a)[4,6] with $AlMe_3$. To a stirred mixture of **1a** (226 mg, 1.00 mmol) in dry CH_2Cl_2 (15 mL) was added 1*N* $AlMe_3$ in hexane (5.00 mL, 5.00 mmol) at reflux under argon atmosphere. The reaction mixture was refluxed for 24 h and the mixture was partitioned between $CHCl_3$ (30 mL) and water (30 mL). The aqueous layer was filtered using a celite® cake and the filtrate was concentrated *in vacuo*. The residue was subjected to silica gel column chromatography ($CHCl_3$: MeOH = 10 : 1) to give 1-(3-deoxy-3-methyl-β-D-arabinofuranosyl)uracil (**2a**)[6,7] (96 mg, 40%) and 1-(2-deoxy-2-methyl-β-D-xylofuranosyl)uracil (**3a**)[8] (46 mg, 19%) as a mixture along with recovered **1a** (10% recovery). **2a** and **3a** were identical with the samples prepared below. Yields were estimated by the integration ratios of the ^{1}H-NMR spectra of the mixture.

1-(3-deoxy-3-methyl-β-D-arabinofuranosyl)uracil (2a)[6,7] and 1-(2-deoxy-3,5-*O*-isopropylidene-2-methyl-β-D-xylofuranosyl)uracil (4).[8] A solution of the above mixture (242 mg, 1.00 mmol; **2a** : **3a** = 2 : 1) and *p*-toluenesulfonic acid (25 mg, 0.15 mmol) in dry acetone (50 mL) and 2,2-dimethoxypropane (2 mL) was stirred at rt for 12 h. To a stirred solution was added anhydrous K_2CO_3 (1.00 g, 7.30 mmol) and the mixture was stirred at rt. The mixture was filtered and concentrated followed by silica gel column chromatography ($CHCl_3$: MeOH = 10 : 1) to give 1-(2-deoxy-3,5-*O*-isopropylidene-2-methyl-β-D-xylofuranosyl)uracil (**4**) (82 mg, 87% from **3a**) together with recovered **2a** (87 mg, 46%).

2a: mp 211–213 °C; λ$_{max}$ (EtOH) 263 nm; MS *m/z* 242 (M$^+$); ^{1}H NMR δ 1.08 (d, 3H, *J* = 6 Hz), 2.01 (s,

1H, J = 6 Hz), 3.60 (m, 2H), 3.75 and 4.06 (each m, 1H), 5.17 (t, 1H, J = 5 Hz, deuterium exchangeable), 5.61 (m, 1H, deuterium exchangeable), 5.62 (d, 1H, J = 8 Hz), 6.04 (d, 3H, J = 6 Hz), 7.95 (d, 1H, J = 8 Hz), 11.29 (br, 1H, deuterium exchangeable). *Anal.* Calcd for $C_{10}H_{14}N_2O_5$: C, 49.57; H, 5.83; N, 11.56. Found: C, 49.35; H, 5.82; N, 11.47.

4: mp 149–151 °C; λ_{max}(EtOH) 263 nm; MS *m/z* 282 (M^+); ^{1}H NMR δ 1.11 (d, 3H, J = 8 Hz), 1.26 and 1.41 (each s, 3H), 2.23 (q, 1H, J = 8 Hz), 4.06 (m, 2H), 4.13 and 4.16 (each m, 1H), 5.50 (s, 1H), 5.65 and 8.01 (d, 1H, J = 8 Hz), 11.31 (br, 1H, deuterium exchangeable). *Anal.* Calcd for $C_{13}H_{18}N_2O_5$: C, 55.31; H, 6.43; N, 9.92. Found: C, 55.03; H, 6.46; N, 9.78.

1-(2-deoxy-2-methyl-β-D-xylofuranosyl)uracil (3a).[8] A solution of **4** (480 mg, 1.70 mmol) in 80% AcOH (5 mL) was stirred at 100 °C for 24 h. The solvent was evaporated *in vacuo* and a small amount of the remaining AcOH was removed as the toluene azeotrope. The residue was subjected to silica gel column chromatography ($CHCl_3$: MeOH = 10 : 1) to afford **3a** (288 mg, 60%): mp 140–141 °C; λ_{max}(EtOH) 262 nm; MS *m/z* 242 (M^+); ^{1}H NMR δ 1.05 (d, 3H, J = 7 Hz), 2.16 (q, 1H, J = 7 Hz), 3.67 (m, 2H), 3.87 and 3.99 (each m, 1H), 4.69 (t, 1H, J = 6 Hz, deuterium exchangeable), 5.26 and 5.57 (each d, 1H, J = 4 Hz deuterium exchangeable), 5.63 and 7.85 (each d, 1H, J = 8 Hz), 11.25 (br s, 1H, deuterium exchangeable). *Anal.* Calcd for $C_{10}H_{14}N_2O_5$: C, 49.57; H, 5.83; N, 11.56. Found: C, 49.51; H, 5.95; N, 11.32.

Reaction of 1-(2,3-anhydro-β-D-lyxofuranosyl)thymine (1b)[4,6] with $AlMe_3$. **1b** (240 mg, 1.00 mmol) was treated with 1*N* $AlMe_3$ in hexane (5.00 mL, 5.00 mmol) in dry CH_2Cl_2 (15 mL) under similar conditions to those employed for the reaction of **1a** with $AlMe_3$ to give 1-(3-deoxy-3-methyl-β-D-arabinofuranosyl)thymine (**2b**)[6,7] (89 mg, 35%) and 1-(2-deoxy-2-methyl-β-D-xylofuranosyl)thymine (**3b**)[8] (28 mg, 11%) as a mixture along with recovered **1b** (8% recovery). Yields were estimated by the integration ratios of the ^{1}H-NMR spectra of the mixture.

A mixture of **2b** and **3b**: MS *m/z* 256 (M^+).

2b: ^{1}H NMR δ 1.00 (d, 3H, J = 6 Hz), 1.76 (s, 3H), 1.98 (q, 1H, J = 6 Hz), 3.63 (m, 2H), 3.73 and 3.93 (each m, 1H), 5.11 (t, 1H, J = 5 Hz, deuterium exchangeable), 5.45 (m, 1H, deuterium exchangeable), 5.95 (d, 1H, J = 6 Hz), 7.78 (s, 1H), 11.18 (br s, 1H, deuterium exchangeable).

3b: ^{1}H NMR δ 1.13 (d, 3H, J = 7 Hz), 1.71 (s, 3H), 2.25 (q, 1H, J = 7 Hz), 3.67 (m, 2H), 3.95 and 4.19 (each m, 1H), 4.79 (t, 1H, J = 6 Hz, deuterium exchangeable), 5.35 (d, 1H, J = 4 Hz, deuterium exchangeable), 5.60 (d, 1H, J = 4 Hz), 7.79 (s, 1H), 11.29 (br s, 1H, deuterium exchangeable).

Reaction of 1-(2,3-anhydro-5-*O*-benzoyl-β-D-lyxofuranosyl)uracil (1c)[4] with $AlMe_3$. **1c** (165 mg, 0.50 mmol) was treated with 1*N* $AlMe_3$ in hexane (5.00 mL, 5.00 mmol) in dry CH_2Cl_2 (10 mL) under similar conditions to those employed for the reaction of **1a** with $AlMe_3$ to give **2a** (57 mg, 47%) and **3a** (29 mg, 24%) as a mixture, which were identical with the samples prepared above. Yields were estimated by the integration ratios of ^{1}H-NMR spectra of the mixture.

Reaction of 1-(2,3-anhydro-5-*O*-trityl-β-D-lyxofuranosyl)uracil (1d)[4] with $AlMe_3$. **1d** (1112 mg, 2.40 mmol) was treated with 1*N* $AlMe_3$ in hexane (24.00 mL, 24.00 mmol) in dry CH_2Cl_2 (15 mL) under similar conditions to those employed for the reaction of **1a** with $AlMe_3$ to give **2a** (262 mg, 45%)

and **3a** (105 mg, 18%) as a mixture, which were identical with the samples prepared above. Yields were estimated by the integration ratios of ^{1}H-NMR spectra of the mixture.

Reaction of 1-(2,3-anhydro-5-deoxy-5-iodo-β-D-lyxofuranosyl)uracil (1e)[3,4] with $AlMe_3$. **1e** (168 mg, 0.50 mmol) was treated with 1*N* $AlMe_3$ in hexane (5.00 mL, 5.00 mmol) in dry CH_2Cl_2 (10 mL) under similar conditions to those employed for the reaction of 1-(2,3-anhydro-β-D-lyxofuranosyl)uracil (**1a**) with $AlMe_3$ to yield 1-(3,5-dideoxy-5-iodo-3-methyl-β-D-arabinofuranosyl)uracil (**2c**)[9] (91 mg, 52%) and 1-(2,5-dideoxy-5-iodo-2-methyl-β-D-xylofuranosyl)uracil (**3c**) (46 mg, 26%) as a mixture. Yields were estimated by the integration ratios of the ^{1}H-NMR spectra of the mixture.

A mixture of **2c** and **3c**: MS *m/z* 352 (M^+).

2c: ^{1}H NMR δ 1.15 (d, 3H, *J* = 7 Hz), 1.92 (q, 1H, *J* = 7 Hz), 3.52 (m, 2H), 3.71 and 4.12 (each m, 1H), 5.66 (m, 1H, deuterium exchangeable), 5.68 (d, 1H, *J* = 8 Hz), 6.10 (d, 1H, *J* = 6 Hz), 7.63 (d, 1H, *J* = 8 Hz), 11.39 (br s, 1H, deuterium exchangeable).

3c: ^{1}H NMR δ 1.13 (d, 3H, *J* = 6 Hz), 2.32 (q, 1H, *J* = 6 Hz), 3.52 (m, 2H), 3.98 and 4.34 (each m, 1H), 5.64 (m, 1H, deuterium exchangeable), 5.65 (d, 1H, *J* = 4 Hz), 5.72 and 7.85 (each d, 1H, *J* = 8 Hz), 11.39 (br s, 1H, deuterium exchangeable).

Reaction of 1-(2,3-anhydro-5-*O*-mesyl-β-D-lyxofuranosyl)uracil (5)[4] with $AlMe_3$. 1-(2,3-anhydro-5-*O*-mesyl-β-D-lyxofuranosyl)uracil (**5**) (304 mg, 1.00 mmol) was treated with 1*N* $AlMe_3$ in hexane (10.00 mL, 10.00 mmol) in dry CH_2Cl_2 (10 mL) under similar conditions to those employed for the reaction of **1a** with $AlMe_3$ to give 1-(2,5-anhydro-3-deoxy-3-methyl-β-D-arabinofuranosyl)uracil (**6**) (87 mg, 39%) and 1-(3,5-anhydro-2-deoxy-2-methyl-β-D-xylofuranosyl)uracil (**7**) (43 mg, 19%) as a mixture. Yields were estimated by the integration ratios of the ^{1}H-NMR spectra of the mixture.

A mixture of **6** and **7**: MS *m/z* 224 (M^+).

6: ^{1}H NMR δ 1.14 (d, 3H, *J* = 7 Hz), 2.45 (q, 1H, *J* = 7 Hz), 3.78 and 3.93 (each d, 1H, *J* = 9 Hz), 4.31 and 4.55 (each s, 1H), 5.57 (d, 1H, *J* = 8 Hz), 5.84 (s, 1H), 7.77 (d, 1H, *J* = 8 Hz), 11.39 (br s, 1H, deuterium exchangeable).

7: ^{1}H NMR δ 0.98 (d, 3H, *J* = 7 Hz), 2.78 (q, 1H, *J* = 7 Hz), 4.08 (d, 1H, *J* = 8 Hz), 4.66 (dd, 1H, *J* = 4 and 8 Hz), 5.01 (each s, 1H), 5.07 (d, 1H, *J* = 4 Hz), 5.72 (d, 1H, *J* = 8 Hz), 5.98 (d, 1H, *J* = 2 Hz), 8.14 (d, 1H, *J* = 8 Hz), 11.36 (br s, 1H, deuterium exchangeable).

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