SYNTHESIS OF DEOXY, DIDEOXY AND DIDEHYDRODIDEOXY ANALOGS OF 9-(β-D-HEXOFURANOSYL)ADENINE

Hubert HREBABECKY, Jan DOCKAL and Antonin HOLY

Institute of Organic Chemistry and Biochemistry,
Academy of Sciences of the Czech Republic, 166 10 Prague 6, The Czech Republic

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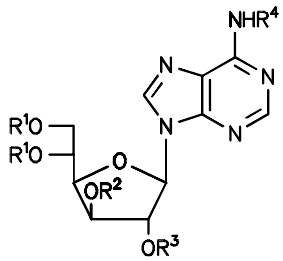
Condensation of 1,2-di-*O*-acetyl-3,5,6-tri-*O*-benzoyl-D-glucofuranose with N^6-benzoyladenine, catalyzed with tin tetrachloride, afforded nucleoside *I*. Partial deacetylation of *I*, followed by mesylation, gave 9-(3,5,6-tri-*O*-benzoyl-2-*O*-methanesulfonyl-β-D-glucofuranosyl)adenine (*III*). 9-(2,5,6-Tri-*O*-acetyl-3-*O*-methanesulfonyl-β-D-glucofuranosyl)-N^6-benzoyladenine (*IV*) was prepared by condensation of 1,2,5,6-tetra-*O*-acetyl-3-*O*-methanesulfonyl-D-glucofuranose with N^6-benzoyladenine. Reaction of mesyl derivative *III* with methanolic sodium methoxide and of mesyl derivative *IV* with methanolic ammonia led to 2′,3′-anhydronucleosides *V* and *VI* which were acetylated to give the respective 9-(5,6-di-*O*-acetyl-2,3-anhydro-β-D-mannofuranosyl)adenine (*VII*) and 9-(5,6-di-*O*-acetyl-2,3-anhydro-β-D-allofuranosyl)adenine (*VIII*). Epoxy derivative *VII* was cleaved with bromotrimethylsilane, affording a mixture of 9-(5,6-di-*O*-acetyl-2-bromo-2-deoxy-β-D-glucofuranosyl)adenine (*Xa*) and 9-(5,6-di-*O*-acetyl-3-bromo-3-deoxy-β-D-altrofuranosyl)adenine (*XIa*), epoxy derivative *VIII* was cleaved analogously to give 9-(5,6-di-*O*-acetyl-3-bromo-3-deoxy-β-D-glucofuranosyl)adenine (*XIIa*). Their dehalogenation with tributylstannane and subsequent deacetylation led to 9-(2-deoxy-β-D-*arabino*-hexofuranosyl)adenine (*Xc*), 9-(3-deoxy-β-D-*arabino*-hexofuranosyl)adenine (*XIc*) and 9-(3-deoxy-β-D-*ribo*-hexofuranosyl)adenine (*XIIc*). 9-(2,5,6-Tri-*O*-acetyl-3-bromo-3-deoxy-β-D-glucofuranosyl)adenine (*XIId*), which was prepared by acetylation of *XIIa*, on reductive elimination with Cu/Zn couple and subsequent deacetylation gave 9-(2,3-dideoxy-β-D-*erythro*-hex-2-enofuranosyl)-adenine (*XIV*). 9-(2,3-Dideoxy-β-D-*erythro*-hexofuranosyl)adenine (*XVI*) was obtained either by catalytic hydrogenation of bromo derivative *XIId* followed by deacetylation, or by catalytic hydrogenation of didehydro derivative *XIV*. The synthesized nucleosides were tested for antiviral activity.

This communication represents a continuation of our previous studies dealing with the synthesis of hexofuranosyl analogs[1,2] of 3′-azido-2′,3′-dideoxy-, 2′,3′-dideoxy- and 2′,3′-didehydro-2′,3′-dideoxynucleosides active against HIV (see refs[1,2] and references therein). The present study concerns the synthesis of the above-mentioned analogs, containing adenine as the nucleoside base.

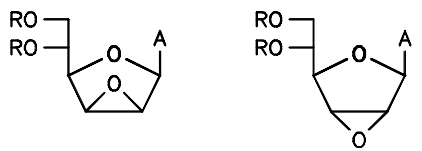
As the key compounds for the synthesis of deoxy compounds derived from 9-(β-D-hexofuranosyl)adenine we have chosen 2′,3′-anhydronucleosides, which are easily accessible from the mesyl derivatives.

Condensation of 1,2-di-*O*-acetyl-3,5,6-tri-*O*-benzoyl-D-glucofuranose[3] with N^6-benzoyladenine in acetonitrile under catalysis with tin tetrachloride afforded nucleoside *I*. Its deacetylation with hydrazine hydrate in a mixture of acetic acid and pyridine[4] gave derivative *II* with free hydroxy group in position 2′ which was converted into mesyl



I, $R^1 = R^2 = R^4 = Bz$; $R^3 = Ac$
II, $R^1 = R^2 = Bz$; $R^3 = R^4 = H$
III, $R^1 = R^2 = Bz$; $R^3 = Ms$; $R^4 = H$
IV, $R^1 = R^3 = Ac$; $R^2 = Ms$; $R^4 = Bz$

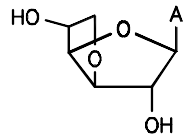
derivative *III*. Starting compound for the preparation of mesyl derivative *IV* was 5,6-di-*O*-acetyl-1,2-*O*-isopropylidene-3-*O*-methanesulfonyl-D-glucofuranose[5]. It was acetolyzed to 1,2,5,6-tetra-*O*-acetyl-3-*O*-methanesulfonyl-D-glucofuranose which was condensed with N^6-benzoyladenine to give nucleoside *IV*. Mesyl derivative *III* reacted with 0.5 M methanolic sodium methoxide and the mesyl derivative *IV* with methanolic ammonia to give 2′,3′-anhydronucleosides *V* and *VI*. Reaction of mesyl derivative *IV* with methanolic



V, R = H *VI*, R = H
VII, R = Ac *VIII*, R = Ac
A = adenin-9-yl

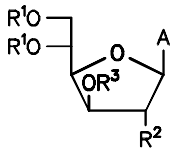
sodium methoxide afforded 3′,6′-anhydronucleoside *IX* instead of the expected epoxide *VI*. In this case the 6′-alkoxide anion attacks intramolecularly the position 3′ of the primarily arising epoxy derivative *VI* under formation of anhydronucleoside *IX*. This assumption is supported by the fact that epoxy derivative *VI* on treatment with sodium methoxide also affords the derivative *IX*.

Epoxy derivatives *V* and *VI* were acetylated with acetic anhydride in acetonitrile under catalysis with 4-dimethylaminopyridine to give acetyl derivatives *VII* and *VIII*. The anhydride was added gradually in order to prevent acetylation of the base. The

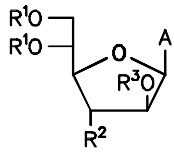


IX, A = adenin-9-yl

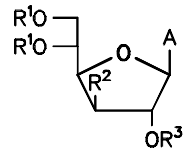
protected epoxides were cleaved with bromotrimethylsilane in the presence of boron trifluoride etherate. It is known that reaction of hydrogen halides with 9-(2,3-anhydro-β-D-lyxofuranosyl)adenine[6,7] and 9-(2,3-anhydro-β-D-ribofuranosyl)adenine[7,8] leads to 3′-halogeno derivatives. Also oxirane *VIII* is cleaved with the same reagents to give 3′-bromo derivative *XIIa*. In the case of the *manno* epoxide *VII*, this reaction leads to a mixture of 2′-isomer *Xa* and 3′-isomer *XIa* with the latter slightly predominating.



X



XI



XII

Xa – *XIIa*, R^1 = Ac; R^2 = Br; R^3 = H
Xb – *XIIb*, R^1 = Ac; R^2 = R^3 = H
Xc – *XIIc*, R^1 = R^2 = R^3 = H
XIId, R^1 = R^3 = Ac; R^2 = Br

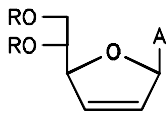
A = adenin-9-yl

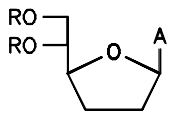
Bromo derivatives *Xa*, *XIa* and *XIIa* were reduced with tributylstannane under catalysis with 2,2′-azobis(2-propionitrile). The obtained deoxy compounds *Xb*, *XIb* and *XIIb* were deacetylated with methanolic ammonia to the respective free deoxy derivatives *Xc*, *XIc* and *XIIc*.

The 2′- and 3′-deoxy derivatives are easily distinguishable by ^{1}H NMR spectroscopy. Spectrum of 2′-deoxy derivative *XIIc* exhibits two multiplets of 2′-methylene protons:

one doublet of doublets at 2.23 ppm and a multiplet centered at 2.76 ppm. 3′-Deoxy derivatives display one or two multiplets in the region 1.82 – 2.37 ppm (*XIc*: 2.02 – 2.30 m; *XIIc*: 1.82 – 1.95 m, 2.22 – 2.37 m). Spectra of the synthesized deoxynucleosides are in accord with those of 2′-deoxyadenosine[9], 9-(2-deoxy-β-D-*threo*-pentofuranosyl)adenine[10], 9-(3-deoxy-β-D-*erythro*-pentofuranosyl)adenine[11], 9-(3-deoxy--β-D-*threo*-pentofuranosyl)adenine[12] and also with spectra of pyrimidine analogs[1,2].

The UV spectra of deoxy derivatives *XIc* and *XIIc* exhibit absorption maximum at 260 nm. Its position proves that the sugar component is bound in position N^9 of the adenine moiety. In the condensation of sugar 1-*O*-acetyl derivatives with N^6-benzoyladenine we did not observe any N^3-isomer whose formation was described[13] in the reaction of protected ribofuranosyl bromide with adenine. Under conditions of the tin tetrachloride-catalyzed reaction the primarily formed N^3-isomer rearranges immediately into the N^9-isomer.





XIII, R = Ac ***XV***, R = Ac

XIV, R = H ***XVI***, R = H

A = adenin-9-yl

The 2′,3′-didehydro-2′,3′-dideoxy derivative *XIII* was prepared by Zn/Cu couple reductive elimination[14] of tri-*O*-acetylbromo derivative *XIId*, which in turn was prepared by acetylation of bromonucleoside *XIIa*. Because of low stability of purine didehydrodideoxynucleosides and also because the reaction with 3′,5′-di-*O*-acetyl-2′-bromo-2′-deoxyuridine[15] is accompanied by significant cleavage of the nucleoside bond, we performed the reaction at 0 °C, the solution of the bromo derivative being slowly added to suspension of the Zn/Cu couple. In this way, we were able to prepare the 2′,3′-unsaturated nucleoside *XIII* in 89% yield. The free nucleoside *XIV* was obtained by methanolysis with methanolic ammonia. Hydrogenation of nucleoside *XIV* over Pd/C afforded dideoxynucleoside *XVI* in an only 48% yield because the hydrogenation was accompanied with significant cleavage of the nucleoside bond. Therefore, we also tried an alternative, already described, procedure[1] consisting in catalytic hydrogenation of bromo derivative *XIId*. In this case, the yield of dideoxynucleoside *XV* was 72%. The free nucleoside *XVI* was obtained from compound *XV* by methanolysis.

None of the synthesized compounds exhibited activity against HIV. The anhydro derivative *IX* was significantly active against vaccinia virus with low cytotoxicity[16].

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. ^{1}H NMR spectra (δ, ppm; *J*, Hz) were measured on a Varian XL-200 (200 MHz) instrument in hexadeuteriodimethyl sulfoxide with tetramethylsilane as internal standard. UV spectra were measured on a Beckman DU-65 spectrometer. Column chromatography was performed on silica gel (particle size 30 – 60 μm; Service Laboratories of this Institute) and thin-layer chromatography (TLC) on Silufol UV 254 sheets (Kavalier, Votice, The Czech Republic) in the following systems: S1, ethyl acetate–toluene (4 : 1); S2, ethyl acetate–acetone–ethanol–water (19 : 3 : 2 : 1); S3, ethyl acetate–acetone–ethanol–water (32 : 6 : 7 : 5); S4, ethyl acetate. The solvents were evaporated at bath temperature 30 – 60 °C/2 kPa and the compounds were dried over phosphorus pentoxide at 13 Pa.

9-(2-*O*-Acetyl-3,5,6-tri-*O*-benzoyl-β-D-glucofuranosyl)-N^6- benzoyladenine (*I*)

Finely ground N^6-benzoyladenine (2.39 g, 10 mmol) was added to a solution of 1,2-di-*O*-acetyl-3,5,6-tri-*O*-benzoyl-D-glucofuranose[3] (5.76 g, 10 mmol) in acetonitrile (20 ml). The suspension formed was mixed with tin tetrachloride (2.2 ml, 19 mmol) and the stirring was continued until the mixture became homogeneous. After standing overnight at room temperature, the mixture was added dropwise into 10% aqueous sodium hydrogen carbonate solution (300 ml). The product was taken up in ethyl acetate (2 × 100 ml), the ethyl acetate solution was washed with 10% aqueous sodium hydrogen carbonate (60 ml), dried over magnesium sulfate and the solvent was evaporated. The residue was chromatographed on a column of silica gel (800 g) in ethyl acetate–toluene (3 : 1) to give 6.0 g (79%) of compound *I* as a solid foam; R_F 0.54 (S1). For $C_{41}H_{33}N_5O_{10}$ (755.7) calculated: 65.16% C, 4.40% H, 9.27% N; found: 64.98% C, 4.32% H, 9.11% N. ^{1}H NMR spectrum: 2.17 s, 3 H (CH_3CO); 4.59 dd, 1 H, *J*(6a′,5′) = 5.8, *J*(6a′,6b′) = 12.2 (H-6a′); 4.91 dd, 1 H, *J*(6b′,5′) = 2.2 (H-6b′); 5.06 dd, 1 H, *J*(4′,3′) = 4.6, *J*(4′,5′) = 9.0 (H-4′); 5.87 m, 1 H (H-5′); 5.97 dd, 1 H, *J*(3′,2′) = 1.8 (H-3′); 6.28 dd, 1 H, *J*(2′,1′) = 3.1 (H-2′); 6.52 d, 1 H (H-1′); 7.38 – 8.07 m, 20 H (H-arom.); 8.60 s, 1 H (H-2); 8.79 s, 1 H (H-8); 11.26 s, 1 H (NH).

9-(3,5,6-Tri-*O*-benzoyl-β-D-glucofuranosyl)adenine (*II*)

Hydrazine hydrate (80%, 1.8 ml) was added to a solution of acetyl derivative *I* (7.56 g, 10 mmol) in a mixture of acetic acid and pyridine (1 : 4, 90 ml). After standing at room temperature for 2 days, acetone (20 ml) was added to the mixture and after 2 h the solvent was evaporated. The residue was dissolved in ethyl acetate (250 ml) and the solution was washed successively with water (3 × 50 ml), 2% hydrochloric acid to acid reaction of the aqueous layer, water (50 ml) and 10% aqueous sodium hydrogen carbonate (2 × 50 ml). After drying over magnesium sulfate, the solution was concentrated and the residue was chromatographed on a column of silica gel (500 g) in ethyl acetate, yielding 5.1 g (83%) of compound *II* as a solid foam; R_F 0.57 (S4). For $C_{32}H_{27}N_5O_8$ (609.6) calculated: 63.05% C, 4.47% H, 11.49% N; found: 62.90% C, 4.70% H, 11.24% N. ^{1}H NMR spectrum: 4.61 dd, 1 H, *J*(6a′,5′) = 5.7, *J*(6a′,6b′) = 12.9 (H-6a′); 4.89 – 5.09 m, 3 H (H-2′, H-4′, H-6b′); 5.63 dd, 1 H, *J*(3′,2′) = 1.5, *J*(3′,4′) = 2.5 (H-3′); 5.86 m, 1 H (H-5′); 6.12 s, 1 H (H-1′); 6.56 d, 1 H, *J*(OH,2′) = 4.7 (2′-OH); 7.35 – 7.94 m, 17 H (H-arom., NH_2); 8.09 s, 1 H (H-2); 8.48 s, 1 H (H-8).

9-(3,5,6-Tri-*O*-benzoyl-2-*O*-methanesulfonyl-β-D-glucofuranosyl)adenine (*III*)

Methanesulfonyl chloride (3 ml, 39 mmol) was added dropwise under ice-cooling to a stirred solution of nucleoside *II* (6.10 g, 10 mmol) in pyridine (50 ml). After standing at room temperature for 5 h, the mixture was cooled to 0 °C, water (2 ml) was added and after standing for 15 min the solvent

was evaporated. The residue was partitioned between water (50 ml) and ethyl acetate (400 ml), the organic layer was washed with water (2 × 100 ml), dried over magnesium sulfate and concentrated. Column chromatography of the residue on silica gel (400 g) in ethyl acetate afforded 5.30 g (77%) of mesyl derivative *III* as a solid foam; R_F 0.32 (S1). For $C_{33}H_{29}N_5O_{10}S$ (687.7) calculated: 57.63% C, 4.25% H, 10.18% N, 4.66% S; found: 57.34% C, 4.40% H, 9.92% N, 4.70% S. ^{1}H NMR spectrum: 3.38 s, 3 H (CH_3SO_2); 4.57 dd, 1 H, *J*(6a′,5′) = 5.5, *J*(6a′,6b′) = 12.5 (H-6a′); 4.90 dd, 1 H, *J*(6b′,5′) = 2.4 (H-6b′); 5.07 dd, 1 H, *J*(4′,3′) = 4.8, *J*(4′,5′) = 9.1 (H-4′); 5.92 m, 1 H (H-5′); 6.03 dd, 1 H, *J*(3′,2′) = 2.6 (H-3′); 6.26 dd, 1 H, *J*(2′,1′) = 3.9 (H-2′); 6.52 d, 1 H (H-1′); 7.36 – 7.92 m, 17 H (NH_2, H-arom.); 8.00 s, 1 H (H-2); 8.51 s, 1 H (H-8).

9-(2,5,6-Tri-*O*-acetyl-3-*O*-methanesulfonyl-β-D-glucofuranosyl)-N^6-benzoyladenine (*IV*)

Sulfuric acid (1.1 ml) was added dropwise during 30 min to a stirred and ice-cooled mixture of 5,6-di-*O*-acetyl-1,2-*O*-isopropylidene-3-*O*-methanesulfonyl-D-glucofuranose[5] (3.82 g, 10 mmol), acetic acid (12 ml) and acetic anhydride (3.5 ml). The mixture was stirred at room temperature until it became homogeneous, left to stand overnight, poured on ice (100 g) and neutralized with solid sodium hydrogen carbonate. After extraction with ethyl acetate (3 × 50 ml), the combined extracts were washed with 10% solution of sodium hydrogen carbonate until the evolution of carbon dioxide ceased. The aqueous layer was extracted with ethyl acetate (2 × 50 ml) and all the combined extracts were dried over magnesium sulfate. The solvent was evaporated, the residue was dried in vacuo (13 Pa) at 40 °C for 3 h, dissolved in acetonitrile (20 ml) and mixed with N^6-benzoyladenine (2.39 g, 10 mmol). Tin tetrachloride (2.3 ml, 20 mmol) was added dropwise under stirring. The mixture was stirred to dissolution of benzoyladenine, set aside overnight and added dropwise to 10% solution of sodium hydrogen carbonate solution (150 ml). After extraction with ethyl acetate (3 × 100 ml), the combined extracts were washed with 10% sodium hydrogen carbonate solution (60 ml), the aqueous layer was washed with ethyl acetate (50 ml) and all the combined extracts were dried over magnesium sulfate. The solvent was evaporated and the residue was chromatographed on a column of silica gel (400 g). Elution with ethyl acetate recovered the unreacted sugar derivative, elution with ethyl acetate–2-propanol (4 : 1) afforded 4.96 g (82%) of compound *IV* as a solid foam; R_F 0.47 (S4). For $C_{25}H_{27}N_5O_{11}S$ (605.6) calculated: 49.58% C, 4.49% H, 11.57% N, 5.29% S; found: 49.65% C, 4.67% H, 11.44% N, 5.10% S. ^{1}H NMR spectrum: 2.01 s, 3 H (CH_3CO); 2.04 s, 3 H (CH_3CO); 2.16 s, 3 H (CH_3CO); 3.31 s, 3 H (CH_3SO_2); 4.10 dd, 1 H, *J*(6a′,5′) = 3.6, *J*(6a′,6b′) = 12.3 (H-6a′); 4.55 dd, 1 H, *J*(6b′,5′) = 2.3 (H-6b′); 4.67 dd, 1 H, *J*(4′,3′) = 4.0, *J*(4′,5′) = 9.2 (H-4′); 5.34 m, 1 H (H-5′); 5.46 dd, 1 H, *J*(3′,2′) = 1.5 (H-3′); 6.00 dd, 1 H, *J*(2′,1′) = 2.4 (H-2′); 6.41 d, 1 H (H-1′); 7.50 – 7.69 m and 8.02 – 8.09 m, 3 H and 2 H (H-arom.); 8.56 s, 1 H (H-2); 8.79 s, 1 H (H-8).

9-(2,3-Anhydro-β-D-mannofuranosyl)adenine (*V*)

A solution of mesyl derivative *III* (3.44 g, 5 mmol) in 0.5 M methanolic sodium methoxide (30 ml) was set aside at room temperature overnight. After neutralization with acetic acid and evaporation of the solvent, the residue was crystallized from water to give 810 mg (58%) of anhydro nucleoside *V*, m.p. 221 – 222 °C; R_F 0.31 (S3). For $C_{11}H_{13}N_5O_4$ (279.3) calculated: 47.31% C, 4.69% H, 25.08% N; found: 47.21% C, 4.75% H, 24.97% N. ^{1}H NMR spectrum: 3.27 – 3.42 m, 1 H (H-6a′); 3.46 – 3.68 m, 2 H (H-5′, H-6b′); 3.97 d, 1 H, *J*(4′,5′) = 8.5 (H-4′); 4.14 d, 1 H, *J*(3′,2′) = 3.1 (H-3′); 4.27 d, 1 H (H-2′); 4.54 t, 1 H, *J*(OH,6′) = 5.6 (6′-OH); 5.15 d, 1 H, *J*(OH,5′) = 5.8 (5′-OH); 6.24 s, 1 H (H-1′); 7.36 s, 2 H (NH_2); 8.14 s, 1 H (H-2); 8.17 s, 1 H (H-8); after exchange with D_2O: 3.32 dd, 1 H, *J*(6a′,5′) = 5.6, *J*(6a′, 6b′) = 11.4 (H-6a′); 3.50 dd, 1 H, *J*(6b′,5′) = 2.6 (H-6b′); 3.63 m, 1 H (H-5′).

9-(2,3-Anhydro-β-D-allofuranosyl)adenine (*VI*)

A solution of mesyl derivative *IV* (3.03 g, 5 mmol) in methanolic ammonia (saturated at 0 °C, 50 ml) was allowed to stand at room temperature for 50 h. The separated crystalline compound *VI* was collected (1.09 g, 78%) and the mother liquors were concentrated to one third of the original volume to give further 80 mg (6%) of the same product, m.p. 168 – 170.5 °C; R_F 0.41 (S3). For $C_{11}H_{13}N_5O_4$ (279.3) calculated: 47.31% C, 4.69% H, 25.08% N; found: 47.20% C, 4.72% H, 25.01% N. ^{1}H NMR spectrum: 3.15 – 3.40 m, 2 H (H-5′, H-6a′); 3.56 m, 1 H, *J*(6b′,5′) = 5.4, *J*(6b′,6a′) = 11.0 (H-6b′); 4.11 d, 1 H, *J*(4′,5′) = 6.3 (H-4′); 4.31 d, 1 H, *J*(3′,2′) = 2.7 (H-3′); 4.45 d, 1 H (H-2′); 4.65 t, 1 H, *J*(OH, 6a′) = *J*(OH,6b′) = 4.5 (6′-OH); 5.28 d, 1 H, *J*(OH,5′) = 5.2 (5′-OH); 6.20 s, 1 H (H-1′); 7.33 s, 2 H (NH_2); 8.17 s, 1 H (H-2); 8.33 s, 1 H (H-8).

9-(5,6-Di-*O*-acetyl-2,3-anhydro-β-D-mannofuranosyl)adenine (*VII*)

4-Dimethylaminopyridine (250 mg) and acetic anhydride (0.5 ml) were added to a stirred suspension of epoxide *V* (1.40 g, 5 mmol) in acetonitrile (15 ml). After 3 h, another portion of acetic anhydride (0.5 ml) was added and the mixture was stirred at room temperature overnight. The separated crystalline compound was filtered and washed with ethanol; yield 1.42 g (78%) of acetyl derivative *VII*. The combined mother liquors and washings were concentrated, the residue was dissolved in chloroform (20 ml), washed with water (2 × 2 ml) and dried over magnesium sulfate. Evaporation of the solvent and crystallization from 2-propanol afforded further 190 mg (10%) of the product, m.p. 215 – 218 °C; R_F 0.65 (S3). For $C_{15}H_{17}N_5O_6$ (363.3) calculated: 49.58% C, 4.72% H, 19.28% N; found: 49.32% C, 4.71% H, 19.37% N. ^{1}H NMR spectrum: 2.01 s, 3 H (CH_3CO); 2.09 s, 3 H (CH_3CO); 4.04 dd, 1 H, *J*(6a′,5′) = 6.1, *J*(6a′,6b′) = 12.4 (H-6a′); 4.23 d, 1 H, *J*(3′,2′) = 2.9 (H-3′); 4.29 d, 1 H, *J*(4′,5′) = 7.5 (H-4′); 4.35 d, 1 H (H-2′); 4.41 dd, 1 H, *J*(6b′,5′) = 2.8 (H-6b′); 5.25 m, 1 H (H-5′); 6.31 s, 1 H (H-1′); 7.41 s, 2 H (NH_2); 8.16 s, 1 H (H-2); 8.18 s, 1 H (H-8).

9-(5,6-Di-*O*-acetyl-2,3-anhydro-β-D-allofuranosyl)adenine (*VIII*)

Epoxide *VI* (1.40 g, 5 mmol) was acetylated as described for the preparation of acetyl derivative *VII*; yield 1.66 g (91%) of compound *VIII*, m.p. 194 – 195 °C; R_F 0.71 (S3). For $C_{15}H_{17}N_5O_6$ (363.3) calculated: 49.58% C, 4.72% H, 19.28% N; found: 49.49% C, 4.69% H, 19.41% N. ^{1}H NMR spectrum: 1.92 s, 3 H (CH_3CO); 2.02 s, 3 H (CH_3CO); 3.80 dd, 1 H, *J*(6a′,5′) = 4.6, *J*(6a′,6b′) = 12.0 (H-6a′); 4.12 dd, 1 H, *J*(6b′,5′) = 2.8 (H-6b′); 4.32 d, 1 H, *J*(4′,5′) = 8.0 (H-4′); 4.38 d, 1 H, *J*(3′,2′) = 2.8 (H-3′); 4.58 d, 1 H (H-2′); 5.23 m, 1 H (H-5′); 6.27 s, 1 H (H-1′); 7.35 s, 2 H (NH_2); 8.12 s, 1 H (H-2); 8.25 s, 1 H (H-8).

9-(3,6-Anhydro-β-D-glucofuranosyl)adenine (*IX*)

A. A solution of mesyl derivative *IV* (606 mg, 1 mmol) in 1 M methanolic sodium methoxide (5 ml) was allowed to stand at room temperature overnight. After neutralization with acetic acid, the separated crystalline compound was collected on filter and recrystallized from water to give 200 mg (72%) of compound *IX*. The residue after concentration of the mother liquors on crystallization from water gave 13 mg (5%) of the same product, m.p. 228 – 229 °C; R_F 0.36 (S3). For $C_{11}H_{13}N_5O_4$ (279.3) calculated: 47.31% C, 4.69% H, 25.08% N; found: 47.25% C, 4.71% H, 24.89% N. ^{1}H NMR spectrum: 3.56 dd, 1 H, *J*(6a′,5′) = 7.8, *J*(6a′,6b′) = 8.2 (H-6a′); 3.84 dd, 1 H, *J*(6b′,5′) = 6.4 (H-6b′); 4.21 m, 1 H (H-5′); 4 44 dd, 1 H, *J*(3′,2′) = 2.3, *J*(3′,4′) = 4.7 (H-3′); 4.60 t, 1 H, *J*(4′,5′) = 4.7 (H-4′); 4.21 m, 1 H (H-2′); 5.18 d, 1 H, *J*(OH,5′) = 6.1 (5′-OH); 5.93 d, 1 H, *J*(1′,2′) = 4.3 (H-1′); 5.96 d, 1 H, *J*(OH,2′) = 4.9 (2′-OH); 7.32 s, 2 H (NH_2); 8.16 s, 1 H (H-2); 8.31 s, 1 H (H-8).

B. A suspension of epoxide *VI* (100 mg, 0.36 mmol) in 0.1 M methanolic sodium methoxide (8 ml) was stirred at room temperature overnight. The mixture was neutralized with acetic acid and the separated product was collected and washed on filter with water and ether. Yield 86 mg (86%) of anhydronucleoside *IX*, m.p. 228 – 229 °C.

9-(5,6-Di-*O*-acetyl-2-bromo-2-deoxy-β-D-glucofuranosyl)adenine (*Xa*)
and 9-(5,6-Di-*O*-acetyl-3-bromo-3-deoxy-β-D-altrofuranosyl)adenine (*XIa*)

Bromotrimethylsilane (1 ml) and boron trifluoride etherate (2 ml) were added to a solution of epoxide *VII* (1.82 g, 5 mmol) in dioxane (25 ml) and the mixture was stirred at room temperature for 3 h. After addition of 1 M triethylammonium hydrogen carbonate (20 ml), the mixture was concentrated to half of the original volume and extracted with chloroform (2 × 50 ml). The chloroform extracts were combined, dried over magnesium sulfate and the solvent was evaporated. The residue was chromatographed on a column of silica gel (300 g) in chloroform–methanol (10 : 1). The first fraction afforded 916 mg (41%) of bromo derivative *Xa* as a solid foam; R_F 0.59 (S2). For $C_{15}H_{18}BrN_5O_6$ (444.2) calculated: 40.55% C, 4.08% H, 17.99% Br, 15.77% N; found: 40.23% C, 4.21% H, 17.50% Br, 15.49% N. ^{1}H NMR spectrum: 2.01 s, 3 H (CH_3CO); 2.02 s, 3 H (CH_3CO); 4.12 dd, 1 H, *J*(6a′,5′) = 5.5, *J*(6a′,6b′) = 12.4 (H-6a′); 4.45 – 4.58 m, 3 H (H-3′, H-4′, H-6b′); 4.92 dd, 1 H, *J*(2′,1′) = 3.0, *J*(2′,3′) = 1.9 (H-2′); 5.37 m, 1 H, *J*(5′,6b′) = 2.4 (H-5′); 6.41 d, 1 H (H-1′); 6.61 d, 1 H, *J*(OH,3′) = 5.3 (3′-OH); 7.41 s, 2 H (NH_2); 8.17 s, 1 H (H-2); 8.30 s, 1 H (H-8).

The second fraction gave 1.05 g (47%) of bromo derivative *XIa* as a solid foam; R_F 0.57 (S2). For $C_{15}H_{18}BrN_5O_6$ (444.2) calculated: 40.55% C, 4.08% H, 17.99% Br, 15.77% N; found: 40.27% C, 4.19% H, 17.48% Br, 15.46% N. ^{1}H NMR spectrum: 2.01 s, 3 H (CH_3CO); 2.05 s, 3 H (CH_3CO); 4.11 dd, 1 H, *J*(6a′,5′) = 6.7, *J*(6a′,6b′) = 12.2 (H-6a′); 4.41 t, 1 H, *J*(4′,3′) = *J*(4′,5′) = 6.4 (H-4′); 4.43 dd, 1 H, *J*(6b′,5′) = 3.0 (H-6b′); 4.65 m, 1 H, *J*(2′,1′) = 5.5, *J*(2′,3′) = 6.4, *J*(2′,OH) = 5.7 (H-2′); 4.80 t, 1 H (H-3′); 5.43 m, 1 H (H-5′); 6.37 d, 1 H (H-1′); 6.39 d, 1 H (2′-OH); 7.30 s, 2 H (NH_2); 8.14 s, 1 H (H-2); 8.24 s, 1 H (H-8).

9-(5,6-Di-*O*-acetyl-3-bromo-3-deoxy-β-D-glucofuranosyl)adenine (*XIIa*)

Bromotrimethylsilane (1 ml, 7.6 mmol) and boron trifluoride etherate (2 ml, 16.3 ml) were added to a stirred suspension of epoxide *VIII* (1.82 g, 5 mmol) in dioxane (30 ml). After stirring at room temperature for 3 h, the mixture was neutralized with 1 M triethylammonium hydrogen carbonate solution (25 ml), concentrated to one third of the original volume and extracted with chloroform (150 ml). The chloroform layer was washed with water (10 ml), dried over magnesium sulfate and concentrated. Crystallization of the residue from 2-propanol afforded 2.20 g (99%) of bromo derivative *XIIa*, m.p. 122 – 124 °C; R_F 0.56 (S2). For $C_{15}H_{18}BrN_5O_6$ (444.2) calculated: 40.55% C, 4.08% H, 17.99% Br, 15.77% N; found: 40.15% C, 4.15% H, 18.23% Br, 15.54% N. ^{1}H NMR spectrum: 2.03 s, 3 H (CH_3CO); 2.04 s, 3 H (CH_3CO); 4.17 dd, 1 H, *J*(6a′,5′) = 3.7, *J*(6a′,6b′) = 12.4 (H-6a); 4.50 – 4.60 m, 3 H (H-2′, H-4′, H-6b′); 5.01 m, 1 H (H-3′); 5.27 m, 1 H (H-5′); 5.94 d, 1 H, *J*(1′,2′) = 2.4 (H-1′); 6.68 d, 1 H, *J*(OH,2′) = 4.4 (2′-OH); 7.36 s, 2 H (NH_2); 8.17 s, 1 H (H-2); 8.33 s, 1 H (H-8).

9-(5,6-Di-*O*-acetyl-2-deoxy-β-D-*arabino*-hexofuranosyl)adenine (*Xb*)

A solution of tributylstannane in toluene (1 M, 4 ml), followed by 2,2′-azobis(2-propionitrile) (50 mg), was added at 100 °C to a solution of bromo derivative *Xa* (888 mg, 2 mmol) in dioxane (6 ml). The mixture was heated for 20 min and filtered while hot. After cooling, the solution deposited crystals which were collected and washed on filter with toluene. Yield 231 mg (32%) of deoxy derivative *Xb*. The filtrate was concentrated and the residue was dissolved in 2-propanol (3 ml). On standing over-

night at 4 °C, the solution deposited crystals which were washed with 2-propanol; this afforded further 263 mg (36%) of compound *Xb*, m.p. 185.5 – 187.5 °C; R_F 0.28 (S2). For $C_{15}H_{19}N_5O_6$ (365.3) calculated: 49.31% C, 5.24% H, 19.17% N; found: 49.52% C, 5.19% H, 19.29% N. ^{1}H NMR spectrum: 1.99 s, 3 H (CH_3CO); 2.01 s, 3 H (CH_3CO); 2.32 dd, 1 H, *J*(2a′,1′) = 1.8, *J*(2a′,2b′) = 14.6 (H-2a′); 2.84 m, 1 H, *J*(2b′,1′) = 5.8, *J*(2b′,3′) = 8.8 (H-2b′); 3.98 dd, 1 H, *J*(6a′,5′) = 5.5, *J*(6a′,6b′) = 12.2 (H-6a′); 4.06 dd, 1 H, *J*(4′,3′) = 3.3, *J*(4′,5′) = 7.9 (H-4′); 4.35 m, 1 H (H-3′); 4.47 dd, 1 H, *J*(6b′,5′) = 2.4 (H-6b′); 5.23 m, 1 H (H-5′); 6.30 m, 2 H (H-1′, 3′-OH); 7.38 s, 2 H (NH_2); 8.15 s, 1 H (H- 2); 8.15 s, 1 H (H-8).

9-(2-Deoxy-β-D-*arabino*-hexofuranosyl)adenine (*Xc*)

A solution of acetyl derivative *Xb* (183 mg; 0.5 mmol) in methanolic ammonia was allowed to stand at room temperature overnight. The solvent was evaporated and the residue on crystallization from 2-propanol afforded 110 mg (78%) of compound *Xc*, m.p. 175 – 177.5 °C; R_F 0.21 (S3). For $C_{11}H_{15}N_5O_4$ (281.3) calculated: 46.97% C, 5.38% H, 24.90% N; found: 46.94% C, 5.33% H, 24.92% N. ^{1}H NMR spectrum: 2.23 dd, 1 H, *J*(2a′,1′) = 1.8, *J*(2a′,2b′) = 14.6 (H-2a′); 2.76 m, 1 H, *J*(2b′,1′) = 8.5, *J*(2b′,3′) = 5.5 (H-2b′); 3.34 m, 1 H, *J*(6a′,5′) = 5.5, *J*(6a′,6b′) = 11.3, *J*(6a′,OH) = 5.8 (H-6a′); 3.55 m, 1 H, *J*(6b′,5′) = 2.1, *J*(6b′,OH) = 5.8 (H-6b′); 3.69 dd, 1 H, *J*(4′,3′) = 2.7, *J*(4′,5′) = 8.5 (H-4′); 4.37 m, 1 H (H-3′); 4.45 t, 1 H (6′-OH); 4.72 d, 1 H, *J* = 5.5 (OH); 5.88 d, 1 H, *J* = 5.5 (OH); 6.25 dd, 1 H (H-1′); 7.33 s, 2 H (NH_2); 8.14 s, 1 H (H-2); 8.35 s, 1 H (H-8).

9-(5,6-Di-*O*-acetyl-3-deoxy-β-D-*arabino*-hexofuranosyl)adenine (*XIb*)

A solution of tributylstannane in toluene (1 M, 4 ml), followed by 2,2′-azobis(2-propionitrile) (50 mg), was added at 100 °C to a solution of bromo derivative *XIa* (888 mg, 2 mmol) in dioxane (6 ml). The mixture was heated for 20 min and filtered while hot. After evaporation of the solvent, the residue was dissolved in 2-propanol. The solution deposited 490 mg (67%) of deoxy derivative *XIb*, m.p. 130 – 131 °C; R_F 0.37 (S2). For $C_{15}H_{19}N_5O_6$ (365.3) calculated: 49.31% C, 5.24% H, 19.17% N; found: 49.21% C, 5.15% H, 19.01% N. ^{1}H NMR spectrum: 2.01 s, 3 H (CH_3CO); 2.03 s, 3 H (CH_3CO); 2.08 m, 1 H, *J*(3a′,3b′) = 12.6 (H-3a′); 2.44 m, 1 H (H-3b′); 4.06 dd, 1 H, *J*(6a′,5′) = 6.4, *J*(6a′,6b′) = 12.2 (H-6a′); 4.21 m, 1 H, *J*(4′,3a′) = *J*(4′,3b′) = 6.3, *J*(4′,5′) = 5.6 (H-4′); 4.42 dd, 1 H, *J*(6b′,5′) = 2.7 (H-6b′); 4.48 m, 1 H (H-2′); 5.27 m, 1 H (H-5′); 5.56 d, 1 H, *J*(OH,2′) = 4.6 (2′-OH); 6.17 d, 1 H, *J*(1′,2′) = 4.9 (H-1′); 7.26 s, 2 H (NH_2); 8.14 s, 1 H (H-2); 8.15 s, 1 H (H-8).

9-(3-Deoxy-β-D-*arabino*-hexofuranosyl)adenine (*XIc*)

Methanolysis of acetyl derivative *XIb* (183 mg, 0.5 mmol) with methanolic ammonia gave 121 mg (86%) of compound *XIc*, m.p. 160 – 161 °C; R_F 0.24 (S3). For $C_{11}H_{15}N_5O_4$ (281.3) calculated: 46.97% C, 5.38% H, 24.90% N; found: 47.15% C, 5.41% H, 24.81% N. UV spectrum (water): λ_{max} 260 nm, ε_{max} 15 100. ^{1}H NMR spectrum: 2.02 – 2.30 m, 2 H (2 × H-3′); 3.36 t, 2 H, *J*(6′,5′) = *J*(6′,OH) = 5.8 (2 × H-6′); 3.76 m, 1 H, *J*(2′,1′) = 5.6, *J*(2′,3a′) = *J*(2′,3b′) = 5.2 (H-2′); 4.08 m, 1 H (H-4′); 4.50 m, 1 H (H-5′); 4.64 t, 1 H (6′-OH); 5.37 d, 1 H, *J* = 4.8 (OH); 5.38 d, 1 H, *J* = 5.8 (OH); 6.12 d, 1 H (H-1′); 7.21 s, 2 H (NH_2); 8.11 s, 1 H (H-2); 8.30 s, 1 H (H-8).

9-(5,6-Di-*O*-acetyl-3-deoxy-β-D-*ribo*-hexofuranosyl)adenine (*XIIb*)

Reaction of bromo derivative *XIIa* (444 mg, 1 mmol) with tributylstannane, followed by column chromatography on silica gel (40 g) in ethyl acetate–acetone–ethanol–water (38 : 6 : 3 : 3) and crystallization from 2-propanol–ether afforded 285 mg (78%) of deoxy derivative *XIIb*, m.p. 85 – 87 °C;

R_F 0.41 (S2). For $C_{15}H_{19}N_5O_6$ (365.3) calculated: 49.31% C, 5.24% H, 19.17% N; found: 49.02% C, 5.36% H, 18.94% N. ^{1}H NMR spectrum: 1.92 s, 3 H (CH_3CO); 1.99 s, 3 H (CH_3CO); 1.98 – 2.10 m, 1 H (H-3a′); 2.40 – 2.53 m, 1 H (H-3b′); 4.02 dd, 1 H, *J*(6a′,5′) = 6.4, *J*(6a′,6b′) = 12.2 (H-6a′); 4.31 dd, 1 H, *J*(6b′,5′) = 3.1 (H-6b′); 4.46 m, 1 H, *J*(4′,3a′) = 6.2, *J*(4′,3b′) = 8.6, *J*(4′,5′) = 5.2 (H-4′); 4.80 m, 1 H (H-2′); 5.22 m, 1 H (H-5′); 5.75 d, 1 H, *J*(OH,2′) = 4.3 (2′-OH); 5.87 d, 1 H, *J*(1′,2′) = 2.1 (H-1′); 7.31 s, 2 H (NH_2); 8.15 s, 1 H (H-2); 8.22 s, 1 H (H-8).

9-(3-Deoxy-β-D-*ribo*-hexofuranosyl)adenine (*XIIc*)

Methanolysis of acetyl derivative *XIIb* (183 mg, 0.5 mmol) with methanolic ammonia gave 123 mg (87%) of compound *XIIc*, m.p. 243 °C (decomp); R_F 0.33 (S3). For $C_{11}H_{15}N_5O_4$ (281.3) calculated: 46.97% C, 5.38% H, 24.90% N; found: 46.77% C, 5.32% H, 24.89% N. UV spectrum (water): λ_{max} 260 nm, ε_{max} 15 200. ^{1}H NMR spectrum: 1.82 – 1.95 m, 1 H (H-3a′); 2.22 – 2.37 m, 1 H (H-3b′); 3.35 t, 2 H, *J*(6′,5′) = 5.8, *J*(6′,OH) = 5.6 (2 × H-6′); 3.77 m, 1 H, *J*(5′,4′) = 3.6, *J*(5′,OH) = 4.6 (H-5′); 4.33 - 4.42 m, 1 H (H-4′); 4.50 – 4.58 m, 1 H (H-2′); 4.64 t, 1 H, *J*(OH,6′) = 5.6 (6′-OH); 5.40 d, 1 H (5′-OH); 5.64 d, 1 H, *J*(OH,2′) = 4.0 (2′-OH); 5.85 d, 1 H, *J*(1′,2′) = 2.4 (H-1′); 7.30 s, 2 H (NH_2); 8.14 s, 1 H (H-2); 8.37 s, 1 H (H-8).

9-(2,5,6-Tri-*O*-acetyl-3-bromo-3-deoxy-β-D-glucofuranosyl)adenine (*XIId*)

Acetic anhydride (0.3 ml) and 4-dimethylaminopyridine (150 mg) were added to a stirred mixture of bromo derivative *XIIa* (2.22 g, 5 mmol) and acetonitrile (20 ml). After 2 h another portion of acetic anhydride (0.3 ml) was added and after further 5 h the mixture was mixed with methanol (1 ml) and stirred for additional 10 min. The solvent was evaporated, the residue was dissolved in chloroform (80 ml) and the solution was washed with water (2 × 5 ml) and dried over magnesium sulfate. After evaporation of the solvent, the residue was crystallized from 2-propanol to give 1.99 g (82%) of acetyl derivative *XIId*, m.p. 176 – 177 °C; R_F 0.52 (S2). For $C_{17}H_{20}BrN_5O_7$ (486.3) calculated: 41.99% C, 4.15% H, 16.43% Br, 14.40% N; found: 42.07% C, 4.18% H, 16.38% Br, 14.62% N. ^{1}H NMR spectrum: 2.04 s, 6 H (2 × CH_3CO), 2.14 s, 3 H (CH_3CO); 4.18 dd, 1 H, *J*(6a′,5′) = 4.4, *J*(6a′,6b′) = 12.6 (H-6a′); 4.50 – 4.60 m, 2 H (H-4′, H-6b′); 4.88 dd, 1 H, *J*(3′,2′) = 1.1, *J*(3′,4′) = 4.0 (H-3′); 5.20 – 5.29 m, 1 H (H-5′); 5.90 dd, 1 H (H-2′); 6.24 d, 1 H, *J*(1′,2′) = 2.1 (H-1′); 7.37 s, 2 H (NH_2); 8.16 s, 1 H (H-2); 8.35 s, 1 H (H-8).

9-(5,6-Di-*O*-acetyl-2,3-dideoxy-β-D-*erythro*-hex-2-enofuranosyl)adenine (*XIII*)

A solution of bromo derivative *XIId* (486 mg, 1 mmol) in dimethylformamide (7 ml) was added at 0 °C during 30 min to a stirred suspension of Cu/Zn couple (prepared from 0.55 g of cupric acetate and 3.4 g of zinc dust according to ref.[14]). The mixture was stirred at 0 °C for further 15 min and then filtered through Celite. The insoluble material was washed with dimethylformamide (7 ml) and the combined filtrates were diluted with chloroform (250 ml). The solution was washed successively with saturated solution of ethylenediaminetetraacetic acid disodium salt (2 × 15 ml), 10% aqueous sodium hydrogen carbonate (15 ml), dried over magnesium sulfate and the solvent was evaporated. The residue was codistilled with xylene and dissolved in a minimum amount of methanol. Upon slow addition of ether, the solution deposited 309 mg (89%) of crystalline compound *XIII*, m.p. 169.5 – 172.5 °C; R_F 0.39 (S2). For $C_{15}H_{17}N_5O_5$ (347.3) calculated: 51.87% C, 4.93% H, 20.16% N; found: 51.62% C, 5.01% H, 20.02% N. ^{1}H NMR spectrum: 1.98 s, 3 H (CH_3CO); 1.99 s, 3 H (CH_3CO); 4.04 dd, 1 H, *J*(6a′,5′) = 5.9, *J*(6a′,6b′) = 12.1 (H-6a′); 4.29 dd, 1 H, *J*(6b′,5′) = 3.2 (H-6b′); 5.03 – 5.16 m, 2 H (H-4′, H-5′); 6.32 m, 1 H, *J*(3′,1′) = 1.5, *J*(3′,2′) = 5.9, *J*(3′,4′) = 1.8 (H-3′);

6.63 dt, 1 H, $J(2',1') = J(2',4') = 1.5$ (H-2′); 6.93 m, 1 H (H-1′); 7.33 s, 2 H (NH_2); 7.99 s, 1 H (H-2); 8.17 s, 1 H (H-8).

9-(2,3-Dideoxy-β-D-*erythro*-hex-2-enofuranosyl)adenine (*XIV*)

Methanolysis of acetyl derivative *XIII* (174 mg, 0.5 mmol) with methanolic ammonia, followed by crystallization from 2-propanol afforded 110 mg (84%) of compound *XIV*, m.p. 175 – 176 °C; R_F 0.30 (S3). For $C_{11}H_{13}N_5O_3$ (263.3) calculated: 50.18% C, 4.98% H, 26.60% N; found: 50.10% C, 5.04% H, 26.59% N. ^{1}H NMR spectrum: 3.41 m, 2 H (2 × H-6′); 3.61 m, 1 H, $J(5',6a') = J(5',6b') = J(5',4') = 4.8$ (H-5′); 4.70 t, 1 H, $J(OH,6') = 5.6$ (6′-OH); 4.90 m, 1 H (H-4′); 5.28 d, 1 H, $J(OH,5') = 4.8$ (5′-OH); 6.12 m, 1 H, $J(3',1') = 1.5$, $J(3',2') = 6.1$, $J(3',4') = 2.1$ (H-3′); 6.55 m, 1 H, $J(2',1') = 1.8$, $J(2',4') = 1.5$ (H-2′); 6.92 m, 1 H, $J(1',4') = 3.0$ (H-1′); 7.30 s, 2 H (NH_2); 8.14 s, 1 H (H-2); 8.18 s, 1 H (H-8).

9-(5,6-Di-*O*-acetyl-2,3-dideoxy-β-D-*erythro*-hexofuranosyl)adenine (*XV*)

A mixture of bromo derivative *XIId* (486 mg, 1 mmol), dimethylformamide (3 ml), magnesium oxide (80 mg) and 10% Pd/C (50 mg) was hydrogenated at room temperature and atmospheric pressure for 30 h. The solids were removed by filtration through Celite, washed with dimethylformamide, the combined filtrates were concentrated and the residue was chromatographed on a column of silica gel (50 g) in ethyl acetate–acetone–ethanol–water (19 : 3 : 2 : 1). Crystallization from 2-propanol gave 253 mg (72%) of dideoxy derivative *XV*, m.p. 155 – 156 °C; R_F 0.35 (S2). For $C_{15}H_{19}N_5O_5$ (349.3) calculated: 51.57% C, 5.48% H, 20.05% N; found: 51.47% C, 5.42% H, 19.94% N. ^{1}H NMR spectrum: 1.91 s, 3 H (CH_3CO); 1.98 s, 3 H (CH_3CO); 2.10 – 2.69 m, 4 H (2 × H-2′, 2 × H-3′); 3.97 dd, 1 H, $J(6a',5') = 6.4$, $J(6a',6b') = 12.2$ (H-6a′); 4.23 m, 1 H (H-4′); 4.29 dd, 1 H, $J(6b',5') = 3.1$ (H-6b′); 5.18 m, 1 H, $J(5',4') = 5.2$ (H-5′); 6.21 dd, 1 H, $J(1',2a') = 6.7$, $J(1',2b') = 3.7$ (H-1′); 7.27 s, 2 H (NH_2); 8.14 s, 1 H (H-2); 8.25 s, 1 H (H-8).

9-(2,3-Dideoxy-β-D-*erythro*-hexofuranosyl)adenine (*XVI*)

A. Methanolysis of acetyl derivative *XV* (175 mg, 0.5 mmol) with methanolic ammonia and subsequent crystallization from 2-propanol afforded 104 mg (78%) of dideoxy derivative *XVI*, m.p. 178 – 179.5 °C; R_F 0.26 (S3). For $C_{11}H_{15}N_5O_3$ (265.3) calculated: 49.80% C, 5.70% H, 26.40% N; found: 49.83% C, 5.71% H, 26.27% N. ^{1}H NMR spectrum: 1.90 – 2.44 m, 4 H (2 × H-2′, 2 × H-3′); 3.35 t, 2 H, $J(6',5') = J(6',OH) = 5.6$ (2 × H-6′); 3.70 m, 1 H, $J(5',4') = 4.3$, $J(5',OH) = 4.6$ (H-5′); 4.09 m, 1 H, $J(4',3a') = J(4',3b') = 6.7$ (H-4′); 4.59 t, 1 H (6′-OH); 5.26 d, 1 H (5′-OH); 6.20 dd, 1 H, $J(1',2a') = 4.9$, $J(1',2b') = 5.5$ (H-1′); 7.27 s, 2 H (NH_2); 8.12 s, 1 H (H-2); 8.36 s, 1 H (H-8).

B. Didehydro derivative *XIV* (100 mg, 0.38 mmol) in dimethylformamide (2.5 ml) was hydrogenated over 10% Pd/C (10 mg) at room temperature for 30 h. The catalyst was removed by filtration through Celite, washed with dimethylformamide and the combined filtrates were taken down. The residue, which contained a significant amount of adenine in addition to the product *XVI* (TLC in S3), was dissolved in hot 2-propanol, the solution was filtered and set aside overnight. Yield 48 mg (48%) of dideoxy derivative *XVI*, identical with the product obtained by procedure *A*.

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