Purines. XLVI.[1] Preparation of 1-Ethyladenine from Adenosine

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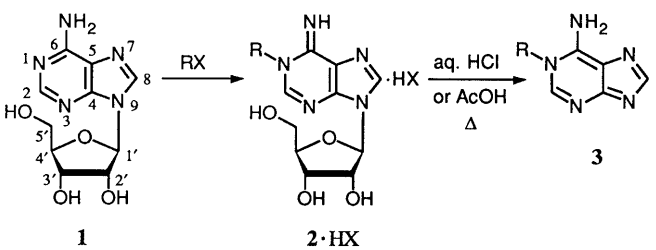
A detailed account is given of the synthesis and glycosidic cleavage of 1-ethyladenosine (2b), which established an alternative synthesis of 1-ethyladenine (3b). Ethylation of adenosine (1) with EtI in $AcNMe_2$ at 35—38 °C for 90 h gave 2b·HI in 54% yield. The hydriodide 2b·HI was readily converted into the perchlorate 2b·$HClO_4$ and into the free nucleoside 2b. Treatment of 2b·HI with 0.5 N aqueous HCl at 92—94 °C for 30 min or that of 2b·$HClO_4$ with boiling AcOH for 60 min produced the aglycone 3b in good yield. The free base easily formed the hydrochloride 3b·HCl, and the perchlorate 3b·$HClO_4$ as well.

Keywords adenosine; ethylation; 1-ethyladenosine; acid hydrolysis; glycosidic cleavage; 1-ethyladenine; UV; ^{1}H-NMR; acid dissociation constant

In previous work by us[2] on the Dimroth rearrangement of 1,9-dialkyladenines, it was necessary to prepare 1-ethyladenine (**3b**) in quantity. Although a few methods for the synthesis of **3b** were available at that time,[3] we prepared it from adenosine (**1**) through 1-ethyladenosine (**2b**) according to the general, two-step procedure first described by Jones and Robins[4] for the preparation of 1-methyladenine (**3a**), and subsequently utilized for securing many other 1-alkyladenines (type **3**).[5] The ethylation of **1**[2a,5b,g,j,k,6] and acid hydrolysis of **2b**[2a,5b,g,j,k,6b] leading to **3b** have been reported by us and by other research groups, but without experimental details or full characterization of the products. We present herein a detailed account of our synthetic procedure, in response to many requests for it.

Ethylation of **1** with an excess of EtI was effected in $AcNMe_2$ at 35—38 °C for 90 h, and the crude product was triturated with AcOH. The crystalline material that formed was then recrystallized from 70% (v/v) aqueous EtOH, giving **2b**·HI in 54% yield. Separate treatments of **2b**·HI in H_2O with Amberlite IRA-402 (ClO_4^-) and with Amberlite IRA-402 (HCO_3^-) produced the perchlorate **2b**·$HClO_4$ and the free nucleoside **2b** in 95% and 87% yields, respectively. The correctness of the structures of **2b**·HI, **2b**·$HClO_4$, and **2b** was supported by the way in which they had been generated, microanalytical data, and comparison of their ultraviolet (UV) spectra with that[2b,4] of known 1-methyladenosine (**2a**).

On treatment with 0.5 N aqueous HCl at 92—94 °C for 30 min, the hydriodide **2b**·HI underwent glycosidic hydrolysis to give the desired aglycone **3b** in 76% yield. The aglycone **3b** was characterized by its UV spectrum and two pK_a's (7.08 and 11.40 at 40 °C), indicative of a 1-substituted adenine.[3a,4] A similar hydrolysis of **2b**·HI in boiling 5% aqueous HBr for 10 min has been reported to give **3b**·HBr in 24% yield.[5j]



1 **2**·HX **3**

a: R = Me **b**: R = Et **c**: R = $PhCH_2$

d: R = CH_2=CH–CH_2 **e**: R = Me_2C=CH–CH_2

Chart 1

The glycosidic hydrolysis of 1-substituted adenosines (type **2**) with hot mineral acids sometimes encounters difficulties because it is accompanied with acid-catalyzed ring opening, although this is much slower,[5d,e] or dealkylation [as in the case of the 1-(3-methyl-2-butenyl) analogue **2e**][5c] of the resulting aglycones (type **3**). Our previous, improved procedure using hot AcOH instead of hot aqueous HCl,[5i] as exemplified in the cases of the benzyl analogue **2c**·HBr and the allyl analogues **2d,e**·HBr, may overcome such difficulties. Thus, the effectiveness of the AcOH procedure was then tested in the glycosidic cleavage of the 1-ethylated nucleoside (**2b**) and its salts **2b**·HI and **2b**·$HClO_4$. It may be seen from Table I that the glycosidic cleavage of the free nucleoside **2b** in boiling AcOH proceeds to some extent, but slows down in aqueous AcOH. The presence of potassium halide causes the reaction to speed up to a certain extent, regardless of the kind of halide ion. The glycosidic cleavage of the perchlorate salt **2b**·$HClO_4$ proceeds much faster than that of the free nucleoside **2b**. Interestingly, it is accelerated in the presence of halide ion, and this salt effect increases in the order of KCl < KI < KBr. These results suggest that the glycosidic cleavage of **2** or

TABLE I. The Glycosidic Hydrolysis of 1-Ethyladenosine (**2b**) and Its Salts (**2b**·HI and **2b**·$HClO_4$) in AcOH

Substrate	Additive	Reaction conditions[a]	Product (**3b**) Yield[b] (%)
2b	Nil	A	17
	H_2O[c]	A	5
	KCl (1 eq)	A	35
	KCl (2 eq)	A	49
	KBr (1 eq)	A	37
	KI (1 eq)	A	33
2b·HI	Nil	A[d]	—[e]
2b·$HClO_4$	Nil	A	87
	KCl (1 eq)	B	37
	KBr (1 eq)	B	83
	KBr (2 eq)	B	98
	KI (1 eq)	B	51

a) The letter A stands for refluxing a solution of the substrate (0.2 mmol) in AcOH (10 ml) with or without an additive for 30 min; B, heating a solution of the substrate (0.05 mmol) in AcOH (30 ml) with an additive at 110 °C for 30 min. *b*) Determined by UV spectrophotometry after paper electrophoretic separation. *c*) Contained in the solvent in the form of 50% (v/v) aqueous AcOH (10 ml). *d*) The hydriodide salt was sparingly soluble under these conditions. *e*) Unmeasurably low.

2·HX in AcOH proceeds by a complex mechanism rather than a simple A-1 mechanism.[5e,7] In the case of the hydriodide salt **2b**·HI, this AcOH procedure is not of practical value because of the extremely poor solubility of the substrate in boiling AcOH.

In a preparative run, **2b**·$HClO_4$ was heated in AcOH under reflux for 60 min, producing **3b**·$HClO_4$ in 71% yield. Alternatively, treatment of crude **2b**·HI, obtained from the above ethylation of **1**, with 0.5 N aqueous HCl at 95—100 °C for 45 min furnished, after basification, the free base **3b** in 80% overall yield (from **1**). The free base gave the hydrochloride (**3b**·HCl) and the perchlorate (**3b**·$HClO_4$) in the usual manner.

In conclusion, the AcOH procedure developed by us[5i] for the glycosidic cleavage of **2c—e**·HBr has proved to be also effective for that of the 1-ethyl analogue **2b**·HX. However, the conventional procedure using aqueous HCl may be recommended for preparation of 1-ethyladenine (**3b**) because of the overall simplicity of operation.

Experimental

General Notes All melting points were taken on a Yamato MP-1 capillary melting point apparatus and are corrected. UV spectra reported herein were recorded with a Hitachi EPS-2U or a Hitachi model 323 or 320 spectrophotometer on solutions in 95% (v/v) aqueous EtOH, 0.1 N aqueous HCl (pH 1), 0.005 M phosphate buffer (pH 7), and 0.1 N aqueous NaOH (pH 13). Spectrophotometric determinations were carried out with a Hitachi EPU-2A or a Hitachi model 320 spectrophotometer, and pH's were measured on a Toa HM-18ET pH meter. See ref. 1 for details of other instrumentation and measurements. Elemental analyses were performed by Mr. Y. Itatani and his associates at Kanazawa University. The following abbreviations are used: br = broad, d = doublet, m = multiplet, q = quartet, s = singlet, sh = shoulder, t = triplet.

1-Ethyladenosine Hydriodide (2b·HI) A mixture of adenosine (**1**) (6.70 g, 25.1 mmol) and EtI (39.5 g, 253 mmol) in $AcNMe_2$ (75 ml) was stirred at 35—38 °C for 90 h. The resulting brown solution was concentrated *in vacuo*, and the residue was triturated with AcOH (50 ml). The crystals that resulted were collected by filtration, washed successively with EtOH (20 ml) and ether (10 ml), and dried *in vacuo* over KOH pellets to afford crude **2b**·HI (10.5 g). This was recrystallized from 70% (v/v) aqueous EtOH to give **2b**·HI (5.73 g, 54%) as colorless needles, mp 200—201 °C (dec.). Further recrystallization from the same solvent provided an analytical sample as colorless needles, mp 200—201 °C (dec.) (lit.[5j] mp 208—209 °C); $[\alpha]_D^{22}$ −33.8° (*c* = 0.709, MeOH); UV $\lambda_{max}^{95\%\ EtOH}$ 260 nm (ε 12600); $\lambda_{max}^{H_2O}$ (pH 1) 259 (13400); $\lambda_{max}^{H_2O}$ (pH 7) 259 (13400); $\lambda_{max}^{H_2O}$ (pH 13) 261 (13700), 267 (sh) (12300), 289 (sh) (4100); ^{1}H-NMR (Me_2SO-d_6) δ: 1.35 (3H, t, *J* = 7 Hz, CH_2Me), 3.63 [2H, m, C(5′)-H_2], 3.99 [1H, m, C(4′)-H], 4.17 [1H, m, C(3′)-H], 4.33 (2H, q, *J* = 7 Hz, CH_2Me), 4.51 [1H, m, C(2′)-H], 5.06 (1H, t, *J* = 5 Hz, 5′-OH), 5.29 (1H, d, *J* = 5 Hz, 3′-OH), 5.56 (1H, d, *J* = 6 Hz, 2′-OH), 5.95 [1H, d, *J* = 5 Hz, C(1′)-H], 8.77 (2H, s, purine protons), 9.60 (2H, br, NH_2^+).[8] *Anal.* Calcd for $C_{12}H_{17}N_5O_4$·HI: C, 34.06; H, 4.29; N, 16.55. Found: C, 34.11; H, 4.35; N, 16.59.

1-Ethyladenosine Perchlorate (2b·$HClO_4$) A solution of **2b**·HI (1.69 g, 3.99 mmol) in H_2O (50 ml) was passed through a column packed with Amberlite IRA-402 (ClO_4^-) (40 ml), and the column was eluted with H_2O (150 ml). The eluates were combined and concentrated *in vacuo* to leave a solid (1.50 g, 95%). Recrystallization of the solid from EtOH afforded an analytical sample of **2b**·$HClO_4$ as colorless minute prisms, mp 158—159 °C (dec.); $[\alpha]_D^{22}$ −34.9° (*c* = 0.929, MeOH); UV $\lambda_{max}^{95\%\ EtOH}$ 260 nm (ε 13000); $\lambda_{max}^{H_2O}$ (pH 1) 259 (13100); $\lambda_{max}^{H_2O}$ (pH 7) 259 (13100); $\lambda_{max}^{H_2O}$ (pH 13) 261 (13500), 268 (sh) (12000), 290 (sh) (4000); ^{1}H-NMR (Me_2SO-d_6) δ: 1.35 (3H, t, *J* = 7 Hz, CH_2Me), 3.63 [2H, m, C(5′)-H_2], 3.99 [1H, m, C(4′)-H], 4.17 [1H, m, C(3′)-H], 4.32 (2H, q, *J* = 7 Hz, CH_2Me), 4.51 [1H, m, C(2′)-H], 5.06 (1H, t, *J* = 5 Hz, 5′-OH), 5.29 (1H, d, *J* = 5 Hz, 3′-OH), 5.56 (1H, d, *J* = 6 Hz, 2′-OH), 5.95 [1H, d, *J* = 5 Hz, C(1′)-H], 8.75 and 8.76 (1H each, s, purine protons), 9.57 (2H, br, NH_2^+). *Anal.* Calcd for $C_{12}H_{17}N_5O_4$·$HClO_4$: C, 36.42; H, 4.58; N, 17.70. Found: C, 36.47; H, 4.63; N, 17.64.

1-Ethyladenosine (2b) A solution of **2b**·HI (2.96 g, 6.99 mmol) in H_2O (100 ml) was passed through a column packed with Amberlite IRA-402 (HCO_3^-) (22 ml), and the column was eluted with H_2O (250 ml). The eluates were combined and concentrated *in vacuo* below 45 °C, leaving an oil. The oily residue was dissolved in MeOH (10 ml), and the solution was kept in a refrigerator for several hours. The precipitate that resulted was collected by filtration and dried to give **2b** (1.80 g, 87%). Recrystallization from MeOH afforded an analytical sample as colorless prisms, mp 198—200 °C (dec.); $[\alpha]_D^{23}$ −60° (*c* = 0.149, MeOH); UV $\lambda_{max}^{95\%\ EtOH}$ 254 nm (sh) (ε 11000), 260 (13300), 268 (11000), 288 (sh) (3900); $\lambda_{max}^{H_2O}$ (pH 1) 259 (13700); $\lambda_{max}^{H_2O}$ (pH 7) 259 (13700); $\lambda_{max}^{H_2O}$ (pH 13) 261 (14300), 268 (sh) (12800); 290 (sh) (4300); ^{1}H-NMR (Me_2SO-d_6) δ: 1.27 (3H, t, *J* = 7 Hz, CH_2Me), 3.59 [2H, m, C(5′)-H_2], 3.92 [1H, m, C(4′)-H], 4.05 [2H, q, *J* = 7 Hz, overlapped with a one-proton m [C(3′)-H], CH_2Me], 4.47 [1H, m, C(2′)-H], 5.09 (1H, t, *J* = 5 Hz, 5′-OH), 5.16 (1H, d, *J* = 5 Hz, 3′-OH), 5.43 (1H, d, *J* = 6 Hz, 2′-OH), 5.75 [1H, d, *J* = 6 Hz, C(1′)-H], 7.03 (1H, br, NH), 8.09 and 8.14 (1H each, s, purine protons).[9] *Anal.* Calcd for $C_{12}H_{17}N_5O_4$: C, 48.81; H, 5.80; N, 23.72. Found: C, 48.73; H, 5.84; N, 23.53.

1-Ethyladenine (3b) i) A solution of **2b**·HI (3.18 g, 7.51 mmol) in 0.5 N aqueous HCl (150 ml) was heated at 92—94 °C for 30 min. The reaction mixture was concentrated *in vacuo*, and the residue was dissolved in H_2O (100 ml). The resulting aqueous solution was passed through a column of Amberlite IRA-402 (HCO_3^-) (100 ml), and the column was eluted with H_2O (200 ml). The eluates were combined and concentrated *in vacuo* to a volume of *ca.* 15 ml and kept in a refrigerator to complete crystallization. The precipitate that resulted was collected by filtration and dried to give **3b**·1/2H_2O (985 mg, 76%) as a colorless solid, mp *ca.* 250 °C (dec.). Recrystallization from MeOH and drying over P_2O_5 at 2 mmHg and 50 °C for 21 h afforded an analytical sample of **3b**·1/2H_2O as colorless prisms, mp 252—254 °C (dec.)[10] (lit.[3c] mp 265—266 °C); UV $\lambda_{max}^{95\%\ EtOH}$ 227 nm (ε 22100), 274 (12300); $\lambda_{max}^{H_2O}$ (pH 1) 261 (11800); $\lambda_{max}^{H_2O}$ (pH 7) 267 (11400); $\lambda_{max}^{H_2O}$ (pH 13) 272 (14700); ^{1}H-NMR (Me_2SO-d_6) δ: 1.30 (3H, t, *J* = 7 Hz, CH_2Me), 3.46 (br, NH_2 and H_2O), 4.21 (2H, q, *J* = 7 Hz, CH_2Me), 7.85 and 8.18 (1H each, s, purine protons). *Anal.* Calcd for $C_7H_9N_5$·1/2H_2O: C, 48.83; H, 5.85; N, 40.67. Found: C, 48.75; H, 6.01; N, 40.58.

ii) A mixture of adenosine (**1**) (40.0 g, 0.15 mol) and EtI (53 ml, 0.66 mol) in $AcNMe_2$ (500 ml) was stirred at room temperature for 5.5 h and then at 30 °C for 163 h. The reaction mixture was concentrated *in vacuo* to leave a yellowish brown oil, which was washed with ether and then dissolved in 0.5 N aqueous HCl (450 ml). The resulting solution was heated at 95—100 °C (bath temperature) for 45 min, concentrated *in vacuo* to a volume of *ca.* 150 ml, brought to pH 8.5 by addition of concentrated aqueous NH_3, and kept in a refrigerator overnight. The yellowish brown precipitate that resulted was filtered off and dried to give **3b**·1/2H_2O (20.5 g, 80%). Recrystallization from MeOH and drying over P_2O_5 at 2 mmHg and 55 °C for 16 h yielded a pure sample as colorless prisms, mp 252—253 °C (dec.). This sample was identical [by comparison of the thin-layer chromatographic (TLC) mobility] with the one prepared by method (i).

1-Ethyladenine Hydrochloride (3b·HCl) The free base **3b**·1/2H_2O (1.53 g, 8.89 mmol) was dissolved in 5% aqueous HCl (26 ml), and the resulting solution was concentrated to dryness *in vacuo*. The residue was then recrystallized from EtOH to furnish **3b**·HCl·1/5H_2O (1.45 g, 80%) as colorless needles, mp 259.5—261 °C (dec.). Further recrystallization from EtOH and drying over P_2O_5 at 2 mmHg and 75 °C for 14 h provided an analytical sample as colorless needles, mp 260—261 °C (dec.). *Anal.* Calcd for $C_7H_9N_5$·HCl·1/5H_2O: C, 41.37; H, 5.16; N, 34.46. Found: C, 41.61; H, 5.22; N, 34.54.

1-Ethyladenine Perchlorate (3b·$HClO_4$) i) The hydrochloride **3b**·HCl·1/5H_2O (201 mg, 0.98 mmol) was dissolved in a small amount of H_2O, and a solution of $NaClO_4$ (185 mg, 1.51 mmol) in H_2O (0.2 ml) was added. The resulting mixture was concentrated *in vacuo* to a volume of *ca.* 1 ml and then kept in a refrigerator overnight. The colorless precipitate that deposited was filtered off, washed with a little H_2O, and dried to afford **3b**·$HClO_4$ (195 mg, 75%). Recrystallization from H_2O yielded an analytical sample as colorless prisms, mp 277.5—278.5 °C (dec.); pK_a 7.08 ± 0.06 and 11.40 ± 0.06 (at 40 °C and ionic strength 1.0)[11] (lit.[3a] pK_a 6.9 and 11.4); UV $\lambda_{max}^{95\%\ EtOH}$ 225 nm (sh) (ε 8700), 265 (11500); $\lambda_{max}^{H_2O}$ (pH 1) 259 (12900); $\lambda_{max}^{H_2O}$ (pH 7) 265 (12000); $\lambda_{max}^{H_2O}$ (pH 13) 271 (16100); ^{1}H-NMR (Me_2SO-d_6) δ: 1.34 (3H, t, *J* = 7 Hz, CH_2Me), 4.30 (2H, q, *J* = 7 Hz, CH_2Me), 8.48 and 8.65 (1H each, s, purine protons), 8.8—10.0 (2H, br, NH_2), 13.7—14.3 (1H, br, NH). *Anal.* Calcd for $C_7H_9N_5$·$HClO_4$: C, 31.89; H, 3.82; N, 26.56. Found: C, 31.77; H, 3.79; N, 26.55.

ii) A mixture of adenosine (**1**) (10.0 g, 37.4 mmol) and EtI (58.3 g, 374 mmol) in $AcNMe_2$ (125 ml) was stirred at 35 °C for 98 h. The reaction mixture was worked up as described above for **3b** under item (ii), giving crude **3b** as a colorless solid. The total amount of the solid was dissolved

in aqueous $HClO_4$, which had been prepared by diluting 70% aqueous $HClO_4$ (6.44 g, 44.9 mmol) with H_2O (30 ml). The resulting solution was kept in a refrigerator for 2 h, and the colorless prisms that resulted were filtered off and dried to provide **3b**·$HClO_4$ (4.49 g, 46% overall yield from **1**). Recrystallization from H_2O yielded a pure sample as colorless prisms, mp 277.5—278.5 °C (dec.). This sample was identical [by comparison of the infrared (IR) spectrum] with the one obtained by method (i).

iii) A mixture of **2b**·$HClO_4$ (158 mg, 0.4 mmol) and AcOH (1.2 ml) was heated under reflux for 60 min. After cooling, the reaction mixture deposited a colorless precipitate, which was collected by filtration, washed successively with a little AcOH and ether, and dried to give **3b**·$HClO_4$ (75 mg, 71%), mp 275—276 °C (dec.). This sample was identical (by comparison of the IR spectrum and TLC mobility) with the one prepared by method (i). Recrystallization from H_2O formed colorless prisms, mp 277.5—278.5 °C (dec.).

Determination of 1-Ethyladenine (3b) in Glycosidic Cleavage Study The glycosidic cleavage reactions of **2b**, **2b**·HI, and **2b**·$HClO_4$ were carried out as specified in Table I. After cooling, an aliquot (0.2 ml) of each reaction mixture was applied along a 13-cm line on Toyo Roshi No. 51A filter paper. Paper electrophoresis was then conducted with a Toyo Kagaku EP-2 apparatus at 500 V for 3 h using 0.01 M KH_2PO_4–Na_2HPO_4 buffer (pH 8.09 at 18 °C). A zone whose mobility corresponded to that of authentic **3b** was detected on the filter paper under UV light (254 nm), excised, and extracted with 0.01 N aqueous HCl (5 ml). The optical density of the extract at 258 nm was then read against a blank extract, and the concentration of **3b** in the extract was estimated from a calibration curve which had been obtained by applying a similar process to AcOH solutions containing known amounts of pure samples of **3b** and **2b**. The results are listed in Table I.

References and Notes

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8) For the ^{13}C-NMR spectral data for **2b**·HI, see ref. 6*d*.
9) For the ^{13}C-NMR spectral data for **2b**, see refs. 6*c* and 6*d*.
10) For the anodic peak potential (E_{pa}) data for **3b**, see T. Sato, K. Fukuzaki, and T. Fujii, *Bull. Chem. Soc. Jpn.*, **59**, 1599 (1986).
11) Determined by UV spectrophotometry in a manner similar to that described previously.[2b]