Imidazopteridines. I. Synthesis of Imidazo[1,2-*c*]pteridine and Its Alkyl Derivatives

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The synthesis of imidazo[1,2-*c*]pteridine and its alkyl derivatives is described. The reaction of 4-aminopteridine with chloroacetaldehyde gave the ring-opened 2-formamido-3-(2-imidazolyl)pyrazine and the isomeric 2-amino-3-(1-formyl-2-imidazolyl)pyrazine but no imidazopteridine. 4-Amino-2-methylpteridine and chloroacetaldehyde similarly gave 2-acetamino-3-(2-imidazolyl)pyrazine in high yield. Hydrolysis of these compounds gave 2-amino-3-(2-imidazolyl)pyrazine, which was used as the key intermediate for the synthesis of the title compounds. Thus it reacted with triethyl orthoformate and homologues to give respectively the parent imidazo-[1,2-*c*]pteridine and its 6-methyl and 6-ethyl homologues. Their 2,3-dimethyl derivatives were prepared likewise from 2-amino-3-(2-imidazolyl)-5,6-dimethylpyrazine, which in turn was prepared from 4-amino-6,7-dimethyl- or 4-amino-2,6,7-trimethylpteridine.

Interest in tricyclic imidazoazines with a bridgehead nitrogen atom has been enhanced by the isolation and structural elucidation of the fluorescent imidazo[1,2-*a*]-purines from baker's yeast ^{Phe}t-RNA[1] and *T. utilis* ^{Phe}t-RNA.[2] Also, imidazo[2,1-*i*]purines[3-8] and analogous systems[9,10] have been studied extensively; several phosphate derivatives of ribofuranosyl imidazo[2,1-*i*]-purine have been found to be active in several enzymatic systems.[4,5]

In continuing our research programs on tricyclic imidazoazines,[2,10,11] we became interested in the chemistry and possible biological activities of hitherto unknown imidazopteridines, since several hydrogenated derivatives of imidazo[1,2-*c*]quinazoline, the 1,4-deaza analogues of imidazo[1,2-*c*]pteridine, have interesting pharmacological activities on the central nervous system.[12,13] In this paper we describe the synthesis of the parent imidazo[1,2-*c*]pteridine (**6a**) and some of its alkyl derivatives (**6b**—**f**).

We first attempted to prepare the unsubstituted imidazo[1,2-*c*]pteridine (**6a**) by condensation of 4-aminopteridine (**1a**) with chloroacetaldehyde. The condensation in water gave several fluorescent compounds, but not the desired imidazopteridine (**6a**). From the mixture, three compounds (**A**, **B**, and **C**) were isolated; the remaining were too little to be isolated Compound **A** with the molecular formula $C_8H_7N_5O$ exhibited weak sky blue fluorescence. Acid hydrolysis of **A** in hot dilute hydrochloric acid afforded the intensely blue fluorescent 2-amino-3-(2-imidazolyl)pyrazine (**5a**). The ^{1}H NMR spectrum of **5a** in trifluoroacetic acid showed a singlet at δ 7.41 for both protons of the imidazole ring and a pair of doublets at δ 7.87 and 8.12 (J=3 Hz) for the protons of the pyrazine ring. The results suggest that compound **A** is a formyl derivative of **5a**, either 2-formamido-3-(2-imidazolyl)pyrazine (**2a**) or 2-amino-3-(1-formyl-2-imidazolyl)pyrazine (**3**). We assigned the structure **2a** to this compound, since its ^{1}HNMR spectrum showed a sharp singlet at δ 7.70 for the imidazole ring protons indicating that the two protons are chemically equivalent, a pair of doublets at δ 8.77 and 8.84 (J=3 Hz) for the pyrazine ring protons, and a singlet at δ 9.12 for the formyl group. The second product (**B**) was found to be the isomer of **A** from elemental analysis and gave **5a** on hydrolysis in dilute hydrochloric acid. The ^{1}H NMR spectrum of **B** showed two pairs of AB doublets at δ 7.27 and 7.42 (J=2 Hz) representing the imidazole ring protons and at δ 8.22 and 8.33 (J=3 Hz) representing the pyrazine ring protons, and a singlet at δ 9.54 for the formyl group. This indicates that the protons of the imidazole ring are no longer equivalent, and hence, compound **B** was assigned as 2-amino-3-(1-formyl-2-imidazolyl)pyrazine (**3**).

The third compound (**C**) was yellow, showing λ_{max} at a wavelength longer than **2a**: the neutral molecule absorbed at 371 nm and the cation at 380 nm (see Table 1). The mass spectrum of **C** exhibited the molecular ion(M) peak at *m/e* 221 and M+2 peak with an intensity about one third of the M peak, suggesting that **C** contains a chlorine atom. From these data and the fact that **C** yielded **5a** on heating in 1 M sodium hydroxide at 70 °C, we determined the compound **C** to be 2-(2-chloroethylideneamino)-3-(2-imidazolyl)pyrazine (**4**), a Schiff base formed by the condensation of **5a** with chloroacetaldehyde. This conclusion was supported by the ^{1}H NMR spectrum, in which the 2-chloroethylidene group appears as a set of a doublet at δ 4.00 (J=2 Hz) and a triplet at δ 6.70 (J=2 Hz), the imidazole ring protons as a sharp singlet at δ 7.55, and the pyrazine ring protons as a pair of doublets at δ 7.91 and 8.03 (J=3 Hz).

The relative yield of the three compounds depends a great deal on the acidity of the reaction solution. In general, when the reaction was carried out in a neutral solution at pH 6—7, **2a** was formed as the main product; in contrast, **4** became predominant in an acidic solution at pH 3—4. In either case, **3** was formed only in a small amount.

4-Amino-6,7-dimethylpteridine (**1c**) reacted similarly with chloroacetaldehyde, yielding 2-formamido-3-(2-imidazolyl)-5,6-dimethylpyrazine (**2c**) in a low yield.

It is obvious that these imidazolylpyrazines (**2a**, **3**, and **2c**) were produced by a ring-opening reaction of the initially formed **6a** or **6d** from 4-aminopteridine (**1a**) or the 6,7-dimethyl homologue (**1c**) with chloroacetaldehyde, respectively. This reaction took place most probably *via* a nucleophilic addition of water to the 6,5-double bond of **6a** or **6d**. We therefore expected that introduction of a blocking methyl group[14] at the

site of the nucleophilic addition would impede ring-opening, and accordingly investigated the reaction of of 4-amino-2-methylpteridine (**1b**) with chloroacetaldehyde in order to obtain 6-methylimidazo[1,2-*c*]-pteridine (**6b**). However, although the reaction was carried out under various conditions, no imidazopter-

Table 1. The pK_a values and UV spectra of 2-amino-3-(2-imidazolyl)pyrazines and imidazo[1,2-*c*]pteridines

Compound	pK_a	pH and ionic species[a]	λ_{max} (log ε)[b]
2a	3.13±0.01	1.0 (+)	264(4.04), 311(3.94)
		5.5 (0)	226(4.04), 283(4.10), 339(4.05)
2b	3.84±0.02	1.5 (+)	215(3.79), 265(3.80), 303(4.14)
		6.0 (0)	225(3.85), 283(3.97), 335(3.90)
2c	3.94±0.01	2.0 (+)	266(4.06), 315(4.02)
		6.0 (0)	225(4.03), 284(4.16), 341(4.12)
2d	4.57±0.01	2.0 (+)	214(4.04) ,268(4.01), 311(4.06)
		7.5 (0)	223(4.01), 283(4.16), 333(4.10)
3	3.10±0.01	1.0 (+)	265(4.03), 312(3.92)
		5.5 (0)	226(4.05), 283(4.11), 338(4.06)
4	4.06±0.02	2.0 (+)	256(3.93), 270(3.84), 380(4.03)
		6.0 (0)	216(4.17), 268(3.74), 371(4.12)
5a	0.10±0.05	−2.5 (++)	212(4.00), 254(3.88), 361(4.03)
	3.82±0.02	2.0 (+)	213(3.91), 259(3.95), 353(3.99)
		6.0 (0)	212(3.92), *254(3.91)*, 270(3.90), 359(4.11)
5b	0.53±0.03	−2.5 (++)	213(4.03), 269(4.03), 377(4.16)
	4.33±0.02	2.5 (+)	215(4.01), 264(3.99), 356(4.06)
		6.5 (0)	213(4.01), 270(4.02), 363(4.16)
6a[c]		MeOH	218(4.25), 261(3.96), 304(3.66), 345(3.90)
6b	2.21±0.01	0.0 (+)	215(4.27), 266(3.65), 318(3.96)
		4.5 (0)	220(4.31), 262(3.92), *304(3.58)*, 343(3.94)
6c	2.49±0.01	0.5 (+)	214(4.32), *265(3.71)*, 321(4.00)
		4.5 (0)	219(4.32), 262(3.93), *303(3.61)*, 344(3.94)
6d	2.98±0.04	0.5 (+)	214(4.20), 277(3.88), 317(4.00)
		5.0 (0)	225(4.37), 264(3.88), 304(3.72), 343(3.96)
6e	2.84±0.01	0.5 (+)	220(4.48), 272(3.72), *281(3.70)*, 326(4.11), *341(4.09)*
		5.0 (0)	225(4.43), 262(3.86), *301(3.69)*, 344(4.05)
6f	3.02±0.01	1.0 (+)	220(4.45), 271(3.71), *280(3.70)*, 326(4.10), *340(4.00)*
		5.0 (0)	224(4.42), 261(3.85), *300(3.68)*, 344(4.04)

a) Negative figures are H_0 values; ionic species are shown by 0 (neutral molecule), + (monocation), and ++ (dication). b) Wavelength in nm and inflexions or shoulders in italics. c) Accurate pK_a value could not be obtained. The observed pK_a value was 2.65±0.13 and the UV spectra at pH 1.0 (+) : 220(4.48), 272 (3.72), *281(3.70)*, 317(4.00); at pH 5.0 (0) : 225(4.43), 262(3.86), *301(3.69)*, 344(4.05) were recorded.

Table 2. The ^{1}H NMR spectra of 2-amino-3-(2-imidazolyl)pyrazines and imidazo[1,2-*c*]pteridines

Compound	Solvent	δ[a]
2a	TFA-*d*	7.70(s, 2), 8.77(d, J=3, 1), 8.84(d, J=3, 1), 9.12(s, 1)
2b	TFA-*d*	2.39(s, 3), 7.50(s, 2), 8.62(d, J=3, 1), 8.76(d, J=3, 1)
2c	TFA-*d*	2.74(s, 3), 2.96(s, 3), 7.53(s, 2) 8.07(d, J=3, 1), 8.37(d, J=3, 1), 9.58(s, 1)
2d	TFA-*d*	2.39(s, 3), 2.72(s, 3), 2.77(s, 3), 7.51(s, 2)
3[b]	Acetone-d_6	7.27(d, J=2, 1), 7.42(d, J=2, 1), 8.22(d, J=3, 1), 8.33(d, J=3, 1), 9.54(s, 1)
4	TFA-*d*	4.00(d, J=2, 2), 6.70(t, J=2, 1), 7.55(s, 2), 7.91(d, J=3, 1), 8.03(d, J=3, 1)
5a	TFA-*d*	7.41(s, 2), 7.87(d, J=3, 1), 8.12(d, J=3, 1)
5b	TFA-*d*	2.53(s, 3), 2.64(s, 3), 7.44(s, 2)
6a[b]	DMSO-d_6	7.79(d, J=2, 1), 8.24(d, J=2, 1), 8.97(s, 2), 9.54(s, 1)
6b[b]	DMSO-d_6	2.95(s, 3), 7.81(d, J=2, 1), 8.25(d, J=2, 1), 8.94(s, 2)
6c[b]	DMSO-d_6	1.46(t, J=7, 3), 3.30(q, J=7, 2), 7.82(d, J=2, 1), 8.31(d, J=2, 1), 8.94(s, 2)
6d[b]	DMSO-d_6	2.69(s, 3), 2.72(s, 3), 7.71(d, J=2, 1), 8.17(d, J=2, 1), 9.45(s, 1)
6e[b]	DMSO-d_6	2.68(s, 3), 2.52(s, 3), 2.91 (s, 3), 7.75(d, J=2, 1), 8.17(d, J=2, 1)
6f[b]	DMSO-d_6	1.43(t, J=7, 3), 3.25(q, J=7, 2), 2.68(s, 3), 2.72(s, 3), 7.74(d, J=2, 1), 8.21 (d, J=2, 1)

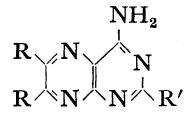
a) Relative to TMS; coupling constants(J) in Hz. Suffixes: s, singlet; d, doublet; t, triplet; q, quartet.
b) Measured on a Varian HA-100 NMR spectrometer.

idine was obtained. Instead, only the ring-opened 2-acetamido-3-(2-imidazolyl)pyrazine (**2b**) was obtained in a high yield from **1b** and chloroacetaldehyde. The location of the acetyl group on the amino group, as in **2a**, was confirmed by the ^{1}H NMR spectrum which exhibits a sharp singlet at δ 7.50 for both protons of the imidazole ring (see Table 2).

4-Amino-2,6,7-trimethylpteridine (**1d**) and chloroacetaldehyde similarly gave 2-acetamido-3-(2-imidazolyl)-5,6-dimethylpyrazine (**2d**). Both **2b** and **2d** were converted in high yield into their 2-amino analogues (**5a** and **5b**), respectively, by boiling in dilute hydrochloric acid.

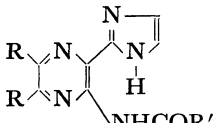
We then used the aminoimidazolylpyrazines (**5a** and **5b**) for the synthesis of imidazo[1,2-*c*]pteridine (**6a**) and its alkyl homologues and found that they are excellent precursors. Heating **5a** in a mixture of triethyl orthoformate and toluene under reflux gave the parent compound (**6a**) in a high yield. The compound was unstable in an aqueous solution, undergoing the ring-opening reaction. The change could be easily monitored by TLC on a Merck silica gel G plate developed by ethyl acetate.

Synthesis of 6-methylimidazo[1,2-*c*]pteridine (**6b**) from **5a** and triethyl orthoacetate required more severe conditions: **5a** was boiled in the ortho ester in the presence of trifluoroacetic acid as a catalyst. In the absence of the catalyst, **5a** was converted only to a small extent into **6b** after prolonged refluxing. Triethyl orthopropionate and **5a** similarly gave 6-ethylimidazo-[1,2-*c*]pteridine (**6c**). Likewise, their 2,3-dimethyl derivatives (**6d**, **6e**, and **6f**) were synthesized by the reaction of **5b** with an appropriate ortho ester. The structures of these imidazo[1,2-*c*]pteridines (**6a**—**f**) were confirmed by elemental analyses, pK_a values (Table 1), UV spectra (Table 1), and ^{1}HNMR spectra (Table 2).



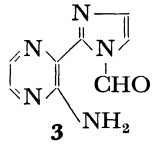
1

	R	R′
a:	H	H
b:	H	CH_3
c:	CH_3	H
d:	CH_3	CH_3



2

	R	R′
a:	H	H
b:	H	CH_3
c:	CH_3	H
d:	CH_3	CH_3



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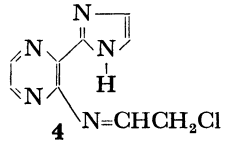

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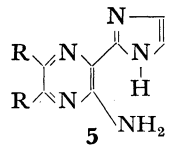
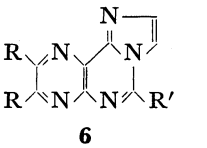


5

a: R=H
b: R=CH_3



6

	R	R′
a:	H	H
b:	H	CH_3
c:	H	CH_2CH_3
d:	CH_3	H
e:	CH_3	CH_3
f:	CH_3	CH_2CH_3

Experimental

The elemental analyses were carried out at the Analytical Section, Faculty of Agriculture, Nagoya University, and at the Analytical Section, Meijo University, Nagoya. The pK_a values were determined by a spectroscopic method and the UV spectra on a JASCO UVIDEC-1 spectrophotometer. The ^{1}H NMR spectra were determined on a JEOL JNM-MH-60 or Varian HA-100 NMR spectrometer with TMS as an internal standard.

*2-Formamido-3-(2-imidazolyl)pyrazine (**2a**) and 2-Amino-3-(1-formyl-2-imidazolyl)pyrazine(**3**).* A solution of 4-aminopteridine[15] (0.50 g) and chloroacetaldehyde (50% aqueous solution, 5 g) in water (150 ml) was kept at 60 °C for 5 h; during this time the solution was maintained at pH 6—7 with sodium acetate. After being chilled in a refrigerator overnight, the solid (0.25 g) was collected by filtration. The solid was extracted with hot ethyl acetate to remove a little insoluble material and then chromatographed on five Merck silica gel 60 PLC plates (20×20 cm) using ethyl acetate as a solvent to give **2a** (150 mg) and **3** (15 mg). The main product (**2a**) melted at 214—215 °C (from ethyl acetate) (Found: C, 50.95; H, 3.57; N, 37.03%. Calcd for $C_8H_7N_5O$: C, 50.77; H, 3.74; N, 37.03%). The isomer (**3**) melted at 228—228.5 °C (from ethyl acetate) (Found: C, 50.62; H, 3.56; N, 36.99%).

*2-(2-Chloroethylideneamino)-3-(2-imidazolyl)pyrazine (**4**).* A solution of 4-aminopteridine (0.50 g) and chloroacetaldehyde (50%, 2 g) in water (150 ml) was kept at 60 °C for 24 h without the addition of alkali for neutralization; the pH of the solution reached *ca.* 3 at the end of the reaction. After neutralization with sodium acetate, the solution was concentrated to *ca.* 30 ml under reduced pressure and chilled to give a solid. Crystallization of the solid from methanol (about 50 ml) gave crude **2a**. The mother liquor was concentrated to *ca.* 10 ml and chilled to give yellow needles (0.18 g) of **4**, mp 173—173.5 °C (from ethyl acetate) (Found: C, 48.78; H, 3.71; N, 31.48%. Calcd for $C_9H_8ClN_5$: C, 48.76; H, 3.64; N, 31.61%).

*2-Formamido-3-(2-imidazolyl)-5,6-dimethylpyrazine (**2c**).* A solution 4-amino-6,7-dimethylpteridine[16] (0.40 g) and chloroacetaldehyde (50%, 20 g) in water (300 ml) was maintained at 60 °C for 10 h. The pH of the solution was adjusted at 6—7 with sodium acetate and then the solution was concentrated to *ca.* 50 ml under reduced pressure. A small amount of solid was removed by filtration and the filtrate was chilled in a refrigerator overnight to give a solid. The solid was purified by preparative layer chromatography (PLC) as above to give almost colorless needles (80 mg) of **2c**, mp 218.5—220 °C (from ethyl acetate) (Found: C, 55.29; H, 4.98; N, 32.22%. Calcd for $C_{10}H_{11}N_5O$: C, 55.29; H, 5.10; N, 32.24%).

*2-Acetamido-3-(2-imidazolyl)pyrazine (**2b**).* A solution of 4-amino-2-methylpteridine[17] (1.0 g) and chloroacetaldehyde (50%, 10 g) in water (200 ml) was heated at 60 °C for 5 h. The solution was neutralized with sodium acetate, concentrated to *ca.* 60 ml under reduced pressure, and chilled to give colorless needles (0.75 g) of **2b**, mp 227—228 °C (from methanol) (Found: C, 53.57; H, 4.48; N, 34.39%. Calcd for $C_9H_9N_5O$: C, 53.19; H, 4.47; N, 34.47%).

*2-Acetamido-3-(2-imidazolyl)-5,6-dimethylpyrazine (**2d**).* Replacement of 4-amino-2-methylpteridine by 4-amino-2,6,7-trimethylpteridine[18] (1.0 g) in the foregoing reaction gave colorless needles (0.76 g) of **2d**, mp 218—219 °C (from methanol) (Found: C, 57.33; H, 5.64; N, 30.08%. Calcd for $C_{11}H_{13}N_5O$: C, 57.12; H, 5.68; N, 30.29%).

*2-Amino-3-(2-imidazolyl)pyrazine (**5a**).* A solution of **2b** (200 mg) in 0.1 M hydrochloric acid (20 ml) was heated under reflux for 4 h. The solution was made alkaline with ammonia and chilled to give slightly yellow leaflets (160 mg) of **5a**. The analytical sample was prepared by sublimation at 140 °C/2 mmHg, mp 203—203.5 °C(Found: C, 52.25; H, 4.41; N, 43.64%. Calcd for $C_7H_7N_5$: C, 52.16; H, 4.39; N, 43.46%).

The same compound was obtained in a similar way from **2a** in 92% yield and from **3**. Heating of **4** in 1 M sodium hydroxide at 70 °C for 20 h and subsequent extraction with ether afforded **5a** in 80% yield.

*2-Amino-3-(2-imidazolyl)-5,6-dimethylpyrazine (**5b**).* A solution of **2d** (200 mg) in 1 M hydrochloric acid (40 ml) was heated at 80 °C for 4 h. The solution was evaporated to dryness under reduced pressure at *ca.* 40 °C. The residue, dissolved in water (10 ml) and made alkaline with ammonia, gave slightly yellow leaflets (130 mg) of **5b**, mp 226—226.5 °C (sublimed at 140 °C/2 mmHg)(Found: C, 57.23; H, 6.01; N, 37.04%. Calcd for $C_9H_{11}N_5$: C, 57.11; H, 5.87; N, 37.01%).

The same compound was obtained in 93% yield by boiling **2C** (90 mg) in 0.1 M hydrochloric acid (5 ml) under reflux for 4 h, followed by neutralization with ammonia and chilling in a refrigerator.

*Imidazo[1,2-c]pteridine (**6a**).* 2-Amino-3-(2-imidazolyl)-pyrazine (80 mg) was dissolved in triethyl orthoformate (60 ml) by gentle heating. After addition of toluene (30 ml), the solution was heated under reflux for 24 h. The solution was evaporated to dryness under reduced pressure and the residue triturated with a small amount of ethyl acetate and filtered. Sublimation of the solid at 180 °C/2 mmHg gave a colorless solid (60 mg), analytically pure **6a**, mp 303—304 °C (dec) (Found: C, 56.25; H, 2.90; N, 40.93%. Calcd for $C_8H_5N_5$: C, 56.13; H. 2.95; N, 40.92%).

*6-Methylimidazo[1,2-c]pteridine (**6b**).* To a solution of **5a** (65 mg) in triethyl orthoacetate (20 ml) was added trifluoroacetic acid (30 μl). The solution was heated under reflux for 2.5 h. After cooling, the solution was diluted with acetone (60 ml), treated with Dowex 1X2 anion exchange resin(OH form) for neutralization, and then evaporated to dryness under reduced pressure. The residue was triturated with cold ethanol (2 ml) and filtered to give colorless needles (45 mg) of **6b**, mp 278—279 °C (dec)(sublimed at 180 °C/2 mmHg)(Found: C, 58.42; H, 3.87; N, 37.72%. Calcd for $C_9H_7N_5$: C, 58.36; H, 3.82; N, 37.82%).

*6-Ethylimidazo[1,2-c]pteridine (**6c**).* Aminoimidazolyl-pyrazine(**5a**)(160 mg), trifluoroacetic acid (160 μl), and triethyl orthopropionate (30 ml) were heated under reflux for 7 h. After dilution with acetone (100 ml) and neutralization with Dowex 1X2 resin as above, the solution was evaporated to dryness under reduced pressure. The residue was crystallized from ethyl acetate to give colorless prisms (155 mg) of **6c**, mp 184—184.5 °C (sublimed at 155 °C/2 mmHg)(Found: C, 60.58; H, 4.52; N, 35.16%. Calcd for $C_{10}H_9N_5$: C, 60.28; H, 4.52; N, 35.16%).

*2,3-Dimethylimidazo[1,2-c]pteridine (**6d**).* A solution of **5b** (100 mg) in triethyl orthoformate (10 ml) and toluene (30 ml) was heated under reflux for 9 h. Evaporation to dryness under reduced pressure and subsequent crystallization from toluene gave colorless needles (99 mg) of **6d**, mp 304—305 °C (dec)(sublimed at 200 °C/2 mmHg)(Found: C, 59.90; H, 4.56; N, 35.38%. Calcd for $C_{10}H_9N_5$: C, 60.28; H, 4.52; N, 35.16%).

*2,3,6-Trimethylimidazo[1,2-c]pteridine (**6e**).* A solution of **5b** (65 mg) in a mixture of triethyl orthoacetate (30 ml) and trifluoroacetic acid (50 μl) was heated under reflux for 6 h. Dilution with acetone (50 ml), neutralization with Dowex 1X2 resin, and evaporation to dryness under reduced pressure gave a solid. The solid was crystallized from ethanol to give colorless needles (47 mg) of **6e**, mp 308—309 °C (dec)(sublimed at 195 °C/2 mmHg)(Found: C, 62.01; H, 5.28; N, 32.61%. Calcd for $C_{11}H_{11}N_5$: C, 61.94; H, 5.21; N, 32.84%).

*6-Ethyl-2,3-dimethylimidazo[1,2-c]pteridine (**6f**).* A solution of **5b** (320 mg) and trifluoroacetic acid (300 μl) in triethyl orthopropionate (30 ml) was heated under reflux for 5 h. The solution was chilled to give slightly brown prisms (280 mg) which were collected by filtration and washed with ether. The prisms were then dissolved in cold ethanol and treated with Dowex 1X2 anion exchange resin (OH form) till the solution became neutral. After removal of the resin by filtration, the filtrate was evaporated to dryness under reduced pressure and the residue was triturated with a little ether. The solid was collected by filtration and sublimed at 160 °C/2 mmHg to give colorless needles (250 mg) of **6f**, mp 235—235.5 °C(Found: C, 63.50; H, 5.84; N, 30.96%. Calcd for $C_{12}H_{13}N_5$: C, 63.41; H, 5.78; N, 30.82%).

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