Syntheses of 8-Aminoimidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidines: Linear Tricyclic Analogs of Adenine

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The syntheses of 8-aminoimidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidines (**7**), stretched-out versions of the naturally occuring nucleoside base adenine, are reported. Their preparation involves conversion of purine into 5-aminoimidazo[4,5-*b*]pyrimidine-6-carbonitrile (**1**) by reaction with malononitrile, followed by construction of the pyrimidine ring in two steps *via* the ethoxymethylene derivative **3**. 8-Azapurine can be converted to 8-amino-1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]pyrimidines **8** in a similar fashion.

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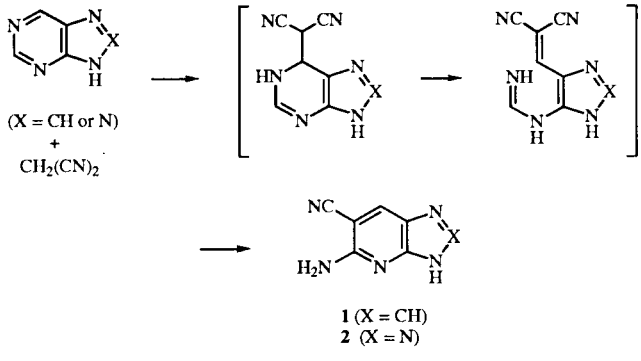
The use of elongated purine derivatives to investigate the dimensional restrictions of enzyme binding regions for purine-based substrates has been investigated by Leonard and coworkers [1]. Heterocycles with the pyrimidine and imidazole rings of purine separated by 2.4Å with a benzene ring were employed as probes to assess the size of lateral space available for substrates in the enzyme-coenzyme binding sites. Such linear benzoadenines do indeed exhibit biological activity with purine-utilizing enzyme systems such as adenosine deaminase [2].

As part of a program to develop novel anti-viral nucleosides, we were interested in preparing stretched-out purines employing a pyridine ring spacer, since this would maintain the dimensional spacing while including a nitrogen at the central ring to allow additional binding as a hydrogen bond acceptor site. Furthermore, the observation that 3-deazaadenosine is neither deaminated by adenosine deaminase [3] nor phosphorylated by adenosine kinase [4] indicates that the presence of a nitrogen at this position, or the central ring of a stretched adenosine, could play a key role in enzyme recognition. Such recognition is necessary for anti-viral activity since, for example, nucleosides which act by inhibiting DNA polymerase require enzymatic phosphorylation to allow incorporation into viral DNA.

Herein we report that 8-aminoimidazo[4',5':5,6]-pyrido[2,3-*d*]pyrimidines **7** can be efficiently prepared from purine. The initial step involves condensation with malononitrile in refluxing isopropanol to give 5-aminoimidazo[4,5-*b*]pyrimidine-6-carbonitrile (**1**) in high yield, as shown in Scheme 1. This represents an improved procedure for the ring transformation of pyrimidines and purines with Michael reagents first reported by Albert and Pendergast [5]. An earlier application of this reaction with 6,7-dimethylpteridine led to a series of linear tricyclic analogs of pteridines [6].

Reaction of the *o*-aminonitrile **1** with diethoxymethyl acetate gave the imino ether **3** which upon treatment with primary amines in refluxing ethanol resulted in cyclization

Scheme 1



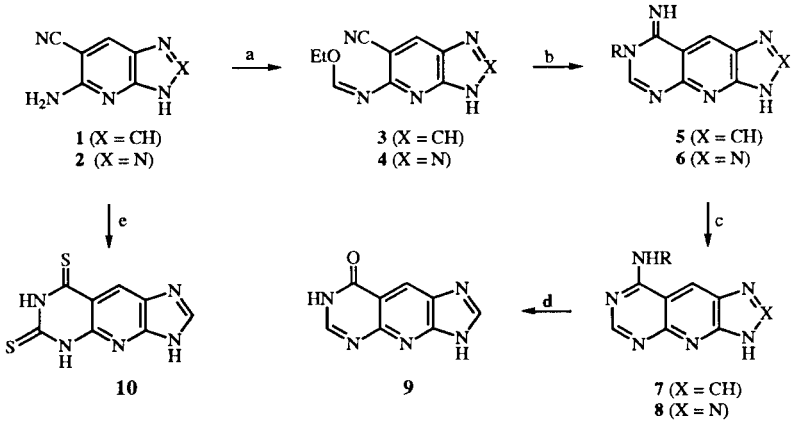
1 (X = CH)
2 (X = N)

to the 8-aminoimidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidines **7**, as shown in Scheme 2. The initial cyclized products, the 8-imino analogs **5**, were not isolated under these reaction conditions, but underwent Dimroth rearrangement to the more stable 8-amino isomers. The only previous example of this heterocyclic system was reported recently by Ramsden and co-workers *via* an analogous intermediate 5-amino-2,3-dimethyl[4,5-*b*]pyridine-6-carbonitrile, which was prepared in three steps from 1,2-dimethyl-5-nitroimidazole [7]. Hydrolysis of **7a** in refluxing sodium hydroxide solution gave the stretched-out hypoxanthine **9**. The *o*-aminonitrile **1** was converted directly to the imidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine-6,8-dithione (**10**) by treatment with carbon disulfide in pyridine.

Similarly, 8-azapurine (triazolo[4,5-*d*]pyrimidine) was converted to the *o*-aminonitrile **2** on reaction with malononitrile in 2-propanol [8]. Formation of the imino ether **4** and subsequent treatment with primary amines led to isolation of the 8-imino-1,2,3-triazolo[4',5':5,6]-pyrido[2,3-*d*]pyrimidines **6**, along with minor amounts of the 8-amino isomers **8**. The mixture could be fully converted to the 8-amino isomer **8** on additional refluxing in ethanol with a further portion of the appropriate amine added.

The 8-substituted imidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine heterocyclic system contains three aromatic C-H protons; one each at the imidazole, pyridine and pyrimidine

Scheme 2



rings. The proton and carbon resonances of 8-aminoimidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**7a**) were assigned on the basis of an HMQC spectrum. Carbon chemical shifts of **7a** were empirically predictable; C6 resonating furthest downfield at 156.4 ppm, and C9 resonating furthest upfield at 121.2 ppm. The imidazole C2 resonated at 148.1 ppm. Given the carbon resonance assignments, the protons were directly assignable at 8.46, 8.97 and 8.67 ppm for H6, H9 and H2, respectively.

In conclusion, we have developed a concise route to 8-aminoimidazo- and 8-aminotriazolo[4',5':5,6]pyrido-[2,3-*d*]pyrimidines. Evaluation of these heterocycles as substrates for enzymatic ribosylation and phosphorylation is in progress.

EXPERIMENTAL

The nmr spectra were recorded on Varian XL-200 and XL-300 spectrometers; chemical shifts (δ) are in parts per million downfield from tetramethylsilane. Mass spectra were determined by Oneida Research Services, Whitesboro, NY, on a Finnegan 4500 instrument. Methane was used as the reagent gas in determinations of desorption chemical ionization (CI) mass spectra. Samples were dissolved in methanol prior to deposition on the wire for CI. Analysis were performed by Atlantic Microlab, Inc., Norcross, Ga. The heterocycles were very tenacious of water of crystallization, and in cases where the elemental analysis indicated the presence of water, the ^{1}H nmr spectrum in rigorously dried dimethyl sulfoxide-d_6 reflected this.

5-Aminoimdazo[4,5-*b*]pyrimidine-6-carbonitrile (**1**).

Purine (2.5 g, 21 mmoles) and malononitrile (6.5 g, 100 mmoles) were dissolved in hot 2-propanol (150 ml) and the stirred solution refluxed for 66 hours. On cooling, yellow crystals were deposited from solution. The solution was cooled in ice-water and filtered. The filtrate was washed with 2-propanol and dried to give 3.0 g (90%) of **1** as a light green solid, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 6.56 (s, 2H), 8.19 (s, 2H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 81.4, 114.1, 121.0*, 128.7*, 139.1*, 153.6 (*broad signals).

Anal. Calcd. for $C_7H_5N_5$: C, 52.83; H, 3.17; N, 44.00. Found: C, 52.71; H, 3.18; N, 43.95.

5-Amino-1,2,3-triazolo[4,5-*b*]pyrimidine-6-carbonitrile (**2**).

8-Azapurine [9] (1.0 g, 8.3 mmoles) was dissolved in hot 2-propanol (150 ml) and malononitrile (0.6 g, 9.1 mmoles) in 2-propanol (50 ml) was added and the resulting yellow solution refluxed with stirring for 0.5 hour. During the course of the reaction a precipitate deposited from solution and the color darkened to an orange-red. The solution was cooled in ice-water and filtered. The filtrate was washed with 2-propanol and dried to give 0.89 g (67%) of **2** as a yellow solid, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 7.27 (s, 2H), 8.78 (s, 2H); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 91.7, 117.7, 129.7, 137.0, 150.1, 160.1.

Anal. Calcd. for $C_6H_4N_6$; C, 45.00; H, 2.52; N, 52.48. Found: C, 45,03; H, 2.57; N, 52.38.

Preparation of Ethyl *N*-(6-Cyanoimidazo[4,5-*b*]pyridin-5-yl)formimidate (**3**).

5-Amino-1*H*-imidazo[4,5-*b*]pyrimidine-6-carbonitrile (**1**) (1.6 g, 10.1 mmoles) was treated with diethoxymethyl acetate (5 ml) and the slurry heated to reflux while stirring for 0.5 hours. The resulting dark solution was allowed to cool and evaporated *in vacuo* to give an oily residue. This was redissolved in absolute ethanol (5 ml) and evaporation of this solution gave a brown solid. The solid was partially dissolved in hot benzene and filtered while hot. On cooling, light brown crystals formed which were filtered off and dried to give 0.75 g (35%) of **3**; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 1.37 (t, J = 7.0 Hz, 3H), 4.41 (q, J = 7.0 Hz, 2H), 8.55 (m, 3H); ms: (CI) m/z 216 (100%, M + 1).

Anal. Calcd. for $C_{10}H_9N_5O{\cdot}0.31H_2O$: C, 54.40; H, 4.39; N, 31.72. Found: C, 54.41; H, 4.41; N, 31.69.

Preparation of Ethyl *N*-(6-Cyano-1,2,3-triazolo[4,5-*b*]pyridin-5-yl)formimidate (**4**).

5-Amino-1,2,3-triazolo[4,5-*b*]pyrimidine-6-carbonitrile (**2**) (1.5 g, 9.4 mmoles) was treated with diethoxymethyl acetate (8 ml) and the solution heated to reflux while stirring for 5 minutes. The resulting dark solution was allowed to cool and evaporated *in vacuo* to give an oily residue. This was redissolved in absolute ethanol (5 ml) and evaporation of this solution gave a brown solid. The solid was partially dissolved in hot toluene and filtered while hot. On cooling, brown crystals formed which were filtered off and dried to give 0.55 g (27%) of **4**; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 1.38 (t, J = 7.1 Hz, 3H), 4.43 (q, J = 7.1 Hz, 2H), 8.56 (s, 1H), 9.19 (s, 1H).

Anal. Calcd. for $C_9H_8N_6O$: C, 50.00; H, 3.73; N, 38.87. Found: C, 50.00; H, 3.69; N, 38.73.

General Procedure for the Preparation of 8-Aminoimidazo-[4',5':5,6]pyrido[2,3-*d*]pyrimidines **7a-f**.

Ethyl *N*-(6-cyanoimidazo[4,5-*b*]pyridin-5-yl)formimidate (**3**) was dissolved into a 10% ethanolic solution of the appropriate amine (10 ml) and refluxed for 2 hours during which time precipitation from the solution occurred. The solution was allowed to cool, the precipitate filtered off, washed several times with with ethanol and dried to give the 8-aminoimidazo-[4',5':5,6]pyrido[2,3-*d*]pyrimidines **7a-f**.

8-Aminoimidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**7a**).

This compound was obtained as a light brown solid in 87% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 7.90 (bs, 2H), 8.46 (s, 1H), 8.67 (s, 1H), 8.97 (s, 1H), 13.10 (bs, 1H); ms: (CI) m/z 187 (100%, M + 1).

Anal. Calcd. for $C_8H_6N_6 \cdot 0.015H_2O$: C, 51.54; H, 3.26; N, 45.07. Found: C, 51.54; H, 3.26; N, 45.07.

8-(Methylamino)imidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**7b**).

This compound was obtained as a light brown solid in 82% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 3.07 (d, J = 4.3 Hz, 3H), 8.53 (bd, J = 4.5 Hz, 1H), 8.58 (s, 1H), 8.71 (s, 1H), 8.97 (s, 1H), 13.20 (bs, 1H).

Anal. Calcd. for $C_9H_8N_6$: C, 53.00; H, 4.12; N, 41.21. Found: C, 53.05; H, 4.08; N, 41.20.

8-(Butylamino)imidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**7c**).

This compound was obtained as a light brown solid in 63% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 0.93 (t, J = 7.2 Hz, 3H), 1.40 (sextet, J = 7.4 Hz, 2H), 1.65 (quintet, J = 7.3 Hz, 2H), 3.57 (q, J = 6.5 Hz, 2H), 8.42 (bt, J = 3.8 Hz, 1H), 8.53 (s, 1H), 8.67 (s, 1H), 9.04 (s, 1H), 13.20 (bs, 1H); ms: (CI) m/z 243 (100%, M + 1).

Anal. Calcd. for $C_{12}H_{14}N_6 \cdot 0.15H_2O$: C, 58.85; H, 5.86; N, 34.38. Found: C, 58.82; H, 5.85; N, 34.33.

8-(Hexylamino)imidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**7d**).

This compound was obtained as a light brown solid in 75% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 0.86 (t, J = 76.5 Hz, 3H), 1.30 (m, 6H), 1.66 (m, 2H), 3.56 (m, 2H), 8.44 (bt, J = 3.8 Hz, 1H), 8.52 (s, 1H), 8.64 (s, 1H), 9.03 (s, 1H), 13.15 (bs, 1H).

Anal. Calcd. for $C_{14}H_{18}N_6 \cdot 0.28H_2O$: C, 61.09; H, 6.75; N, 30.54. Found: C, 61.22; H, 6.70; N, 30.47.

8-(Cyclopropylamino)imidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**7e**).

This compound was obtained as a light brown solid in 40% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 0.69 (d, J = 2.9 Hz, 2H), 0.83 (d, J = 4.6 Hz, 2H), 3.08 (m, 1H), 8.42 (bd, J = 2.5 Hz, 1H), 8.60 (s, 1H), 8.69 (s, 1H), 9.01 (s, 1H), 13.15 (bs, 1H).

Anal. Calcd. for $C_{11}H_{10}N_6 \cdot 0.15H_2O$: C, 58.27; H, 4.43; N, 37.08. Found: C, 58.33; H, 4.50; N, 37.05.

8-(Allylamino)imidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**7f**).

This compound was obtained as a light brown solid in 64% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 4.24 (m, 2H), 5.11-5.26 (m, 2H), 5.97-6.06 (m, 1H), 8.54 (s, 1H), 8.68 (s, 1H), 8.68 (bt, 1H), 9.06 (s, 1H), 13.20 (bs, 1H).

Anal. Calcd. for $C_{11}H_{10}N_6 \cdot 0.16H_2O$: C, 57.67; H, 4.51; N, 36.70. Found: C, 57.77; H, 4.42; N, 36.52.

8-(Anilino)imidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**7g**).

This compound was obtained as a light brown solid in 61% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 7.15 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H), 8.68 (s, 1H), 8.78 (s, 1H), 9.38 (s, 1H), 9.97 (s, 1H), 13.35 (s, 1H).

Anal. Calcd. for $C_{14}H_{10}N_6 \cdot 0.35H_2O$: C, 62.62; H, 3.99; N, 31.35. Found: C, 62.55; H, 3.89; N, 31.38.

8-(Benzylamino)imidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**7h**).

This compound was obtained as a light brown solid in 73% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 4.86 (d, J = 5.6 Hz, 2H), 7.29-7.40 (m, 5H), 8.56 (s, 1H), 8.74 (s, 1H), 9.05 (bt, 1H), 9.11 (s, 1H), 13.20 (s, 1H).

Anal. Calcd. for $C_{15}H_{12}N_6 \cdot 0.07H_2O$: C, 64.92; H, 4.38; N, 30.30. Found: C, 64.95; H, 4.41; N, 30.24.

General Procedure for the Preparation of 8-Amino-1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]pyrimidines **8a-f**.

Ethyl *N*-(6-cyano-1,2,3-triazolo[4,5-*b*]pyridin-5-yl)formimidate (**4**) (0.15 g, 0.69 mmole) was dissolved in warm ethanol and the appropiate amine (0.74 mmole) was added. After standing the mixture for 2 hours at room temperature a precipitate formed. The reaction mixture was refluxed for 0.5 hour, cooled in ice-water and the solid filtered off. Analysis of the solid by ^{1}H nmr indicated formation of the 8-imino-1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]pyrimidine **6** with the 8-amino analog **8** as a minor component. The solid was partially dissolved in a mixture of ethanol (15 ml) and the amine (0.5 ml) and refluxed for 2 hours. The reaction solution was cooled, acidified with acetic acid and the solid filtered off to give the 8-amino-1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]pyrimidines **8a-f**.

8-Amino-1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**8a**).

This compound was obtained as a light brown solid in 46% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 8.50 (bs, 2H), 8.57 (s, 1H), 9.55 (s, 1H).

Anal. Calcd. for $C_7H_5N_7 \cdot 0.28H_2O$: C, 43.74; H, 2.92; N, 51.01. Found: C, 43.73; H, 2.72; N, 51.03.

8-(Methylamino)-1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**8b**).

This compound was obtained as a light green solid in 55% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 3.09 (d, J = 3.6 Hz, 3H), 8.65 (s, 1H), 9.10 (bs, 1H), 9.51 (s, 1H); ms: (CI) m/z 202 (100%, M + 1).

Anal. Calcd. for $C_8H_7N_7$: C, 47.76; H, 3.51; N, 48.73. Found: C, 47.86; H, 3.51; N, 48.61.

8-(Butylamino)-1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**8c**).

This compound was obtained as a light green solid in 67% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 0.94 (t, J = 7.2 Hz, 3H), 1.40 (sextet, J = 7.3 Hz, 2H), 1.67 (quintet, J = 7.5 Hz, 2H), 3.6 (m, 2H), 8.63 (s, 1H), 8.97 (bs, 1H), 9.61 (s, 1H); ms: (CI) m/z 244 (100%, M + 1).

Anal. Calcd. for $C_{11}H_{12}N_7$: C, 54.31; H, 5.39; N, 40.30. Found: C, 54.32; H, 5.34; N, 40.33.

8-(Hexylamino)-1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**8d**).

This compound was obtained as a light green solid in 48% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 0.87 (t, J = 6.3 Hz, 3H), 1.38 (m, 6H), 1.67 (m, 2H), 3.60 (m, 2H), 8.60 (s, 1H), 8.95 (bs, 1H), 9.60 (s, 1H); ms: (CI) m/z 272 (100%, M + 1).

Anal. Calcd. for $C_{13}H_{17}N_7$: C, 57.55; H, 6.32; N, 36.14. Found: C, 57.52; H, 6.35; N, 36.06.

8-(Cyclopropylamino)1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]-pyrimidine (**8e**).

This compound was obtained as a light green solid in 60% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 0.75 (d, J = 2.3 Hz, 2H), 0.88 (d, J = 5 Hz, 2H), 3.33 (m, 1H), 8.70 (s, 1H), 8.9 (bs, 1H), 9.59 (s, 1H).

Anal. Calcd. for $C_{10}H_9N_7$: C, 52.86; H, 3.99; N, 43.15. Found: C, 52.80; H, 3.94; N, 43.04.

8-(Allylamino)-1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**8f**).

This compound was obtained as a light green solid in 74% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 4.29 (s, 2H), 5.14-5.31 (m, 2H), 5.90-6.10 (m, 1H), 8.64 (s, 1H), 9.20 (bs, 1H), 9.64 (s, 1H).

Anal. Calcd. for $C_{10}H_9N_7$: C, 52.86; H, 3.99; N, 43.15. Found: C, 52.92; H, 3.94; N, 43.13.

8-(Anilino)-1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**8g**).

This compound was obtained as an orange solid in 35% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 7.23 (t, J = 7.0 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H), 8.78 (s, 1H), 9.97 (s, 1H), 13.40 (bs, 1H); ms: (CI) m/z 264 (100%, M + 1).

Anal. Calcd. for $C_{13}H_9N_7$: C, 59.31; H, 3.45; N, 37.24. Found: C, 59.36; H, 3.43; N, 37.21.

8-(Benzylamino)-1,2,3-triazolo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**8h**).

This compound was obtained as a light green solid in 84% yield, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 4.88 (d, J = 4.6 Hz, 2H), 7.26-7.43 (m, 5H), 8.64 (s, 1H), 9.67 (s, 1H), 9.5 (bs, 1H); ms: (CI) m/z 278 (100%, M + 1).

Anal. Calcd. for $C_{14}H_{11}N_7$: C, 60.64; H, 4.00; N, 35.36. Found: C, 60.69; H, 4.02; N, 35.25.

1,7-Dihydroimidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidin-8-one (**9**).

8-Aminoimidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine (**7a**) (0.27 g, 1.4 mmoles) was dissolved in hot 5% sodium hydroxide solution (10 ml) and this solution was refluxed for 16 hours. On cooling, the solution was acidified by addition of acetic acid resulting in precipitation of a light brown solid. This was filtered off, washed with water and dried to give 0.125 g (45%) of **9**, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 8.25 (s, 1H), 8.67 (s, 1H), 8.72 (s, 1H), 12.40 (bs, 1H), 13.3 (bs, 1H); ms: (CI) m/z 188 (100%, M + 1).

Anal. Calcd. for $C_8H_5N_5O{\cdot}0.29H_2O$: C, 49.95; H, 2.92; N, 36.40. Found: C, 49.94; H, 2.88; N, 36.44.

Imidazo[4',5':5,6]pyrido[2,3-*d*]pyrimidine-6,8(5*H*,7*H*)-dithione (**10**).

5-Aminoimdazo[4,5-*b*]pyrimidine-6-carbonitrile (**1**) (1.0 g, 53 mmoles) was dissolved in pyridine (25 ml) and the stirred solution heated to reflux. Carbon disulfide (25 ml) was added slowly over 10 minutes. The reaction was maintained at reflux for 16 hours during which time a precipitate steadily deposited from the solution. The solution was allowed to cool, the precipitate filtered off, washed several times with with hot ethanol and dried to give 1.05 g (77%) of **10** as a light green solid, mp >250°; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 8.6 (bs, 1H), 8.8 (s, 1H), 13.6 (bs, 1H), 13.7 (bs, 1H); ms: (CI) m/z 236 (67%, M + 1).

Anal. Calcd. for $C_8H_5N_5S_2$: C, 40.84; H, 2.14; N, 29.76; S, 27.25. Found: C, 40.90; H, 2.11; N, 29.66, S, 27.29.

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