Bioorganic Chemistry 37 (2009) 180–184

Contents lists available at ScienceDirect

Bioorganic Chemistry

journal homepage: www.elsevier.com/locate/bioorg

Synthesis and NMR properties of derivatives of 5,6-dihydroborauracil and 5,6-dihydroborathymine

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ARTICLE INFO

Article history:
Received 30 June 2009
Available online 18 July 2009

Keywords:
Borauracil
Dihydroborauracil
Dihydroborathymine
Hydroboration

ABSTRACT

Novel boron compounds, a series of 4-hydroxy-5,6-dihydroborauracil and 4-hydroxy-5,6-dihydroborathymine derivatives containing various substituents at 3-, 5- and 6-positions, is presented. The spectroscopic properties, along with analyses of NMR-controlled boron compound–alcohol and boron compound–amine interactions, proves the existence of sp^3-hybridized, stable B,B-bis-methoxy-5,6-dihydroborauracils and pyridine-/*n*-butylamine-5,6-dihydroborauracils ate-complexes in solution.

1. Introduction

There are only few boron analogues of nucleic acid bases known, including earlier described benzoborauracils and recently presented 5,6-dihydroborauracils [1,2]. It should be noted that borauracils, borathymines or boracytosines and their derivatives should be valuable compounds in search for new inhibitors of enzymes involved in nucleotide metabolism, as boron analogues of biologically active compounds show certain unique properties that may promote enzyme inhibition. In this context, of particular interest is capacity to form tetrahedral sp^3 hybridized boron "ate" complexes following the nucleophilic attack of an enzyme onto the boron atom. Importantly, in contrast to the corresponding complexes of carboxylic acids and in spite of similar pKa values and steric/electronic properties, the boronic acid "ate" complexes with enzymes are highly stable, resulting in effective inhibition [3–5]. Additionally, boron-containing compounds can be considered potentially active in boron-neutron capture therapy (BNCT) [6]. A series of novel boron analogues of uracil – 5,6-dihydroborauracil and 5,6-dihydroborathymine is presented here.

2. Results and discussion

2.1. Boron analogues of uracil and 5,6-dihydrouracil

There are only few known heterocyclic compounds containing covalently bound boron atom or atoms within ring structure. The first derivatives of boron analogues of uracil, containing boron at 4-position of heterocyclic ring, were presented by Zhuo et al. in 1990 (see Fig. 1) [1].

However, those benzoborauracils contain fused at 5,6-positions of the heterocyclic moiety benzene (Fig. 1A–D) or thiophene (Fig. 1E) ring, offering a synthetic advantage by forcing proper alignment, i.e. *cis* orientation, of 1,2-groups for the ring closing reaction. Unfortunately, compounds of this type have very limited applicability, as additional steric hindrance of aromatic ring makes them poor pyrimidine analogues.

In order to synthesize novel compounds of nucleoside and nucleotide type that contain boron in heterocyclic ring, we prepared a series of 5,6-saturated boron derivatives of uracil or 5,6-saturated borathymine (compounds **1**–**8**, Fig. 2), being currently the closest uracil or thymine analogues.

2.2. Synthesis of derivatives of 5,6-dihydroborauracil and 5,6-dihydroborathymine

Hydroboration of *N*-vinylurea with borane-dimethylsulfide complex (BMS) was shown to result in formation of various carbonyl group reduction products. Conditions were found under which dibromoborane–dimethylsulfide complex and dibromoborane–tetrahydrofurane complex, the latter being an *in situ* formed hydroboration-active reagent, would not react with carbonyl group as observed for BH_3:SMe_2 complex. The hydroboration product was then cyclized to 4-bromo-5,6-dihydroborauracil that could be converted to 4-hydroxy- or 4-methoxy-derivative after hydrolysis or methanolysis, respectively [2]. However, a drawback of the

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doi:10.1016/j.bioorg.2009.07.004

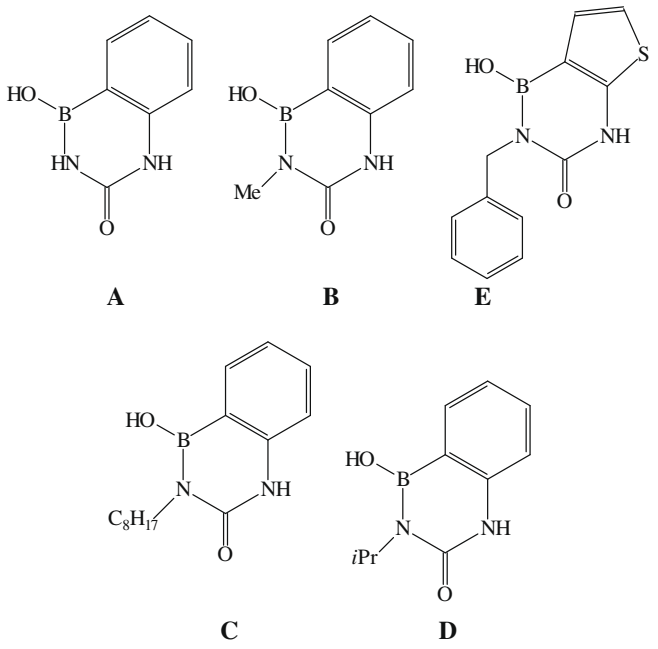

Fig. 1. Known boron analogues of borauracil–benzoborauracils (A–D) and thiopheneborauracil (E).

described synthetic route is poor commercial availability of *N*-vinylurea derivatives.

The synthetic route presented here differs from the one shown previously. The first step of preparation of 5,6-dihydroborauracils or 5,6-dihydroborathymines is the reaction of nitrile (Fig. 3A) with sodium hydride (R_2M = NaH, R_2 = H), providing the hydrogen atom at C(6) in the final cyclic product (Fig. 2, compounds **1**, **2**, **5**–**8**). Consequently, the first reaction step, performed with the use of phenyllithium (R_2M = PhLi, R_2 = Ph), resulted in heterocyclic products with phenyl group at C(6) (Fig. 2, compounds **3** and **4**). It should be noted that deprotonation of nitrile was not observed which would be noticeable by evolution of gaseous hydrogen and increase of internal pressure during reaction of nitrile with sodium hydride. The use of priopionitrile in the first reaction step yielded 5,6-dihydroborathymines or 5-methyl derivatives of 5,6-dihydroborauracil (**5** and **6**). Following the first addition reaction, the formal imino group formed was protected with trimethylchlorosilane (Fig. 3B). The *N*-trimethylsilylimino product underwent then reaction with trimethylsilyltriflate to give *N*,*N*-bis(trimethylsilyl)enamine (Fig. 3C), whose hydroboration, followed by hydrolysis, led to the formation of α- (Fig. 3E) and β- (Fig. 3D) boronic amino acids. The final cyclic product was obtained with the method presented by Zhuo et al. [1,2], with the use of two isocyanates: methyl isocyanate (R_3 = Me, compounds **2**, **4**, **6** and **8**) or isocyanic acid generated *in situ* from potassium cyanate under acidic conditions (R_3 = H, compounds **1**, **3**, **5** and **7**).

2.3. NMR properties of 5,6-dihydroborauracils

Boron compounds known to present very unique reactivity and coordination behavior due to relatively easy change of boron hybridization state. Boronic acids, and their derivatives of sp^2 hybridization, possess a unique property to form stable "ate" complexes upon coordination of an electron pair donor. The resulting formation of sp^3 anionic form may be taken advantage of in enzyme inhibition, with covalent binding of enzyme protein by borate demonstrated by the X-ray structure studies [7,8]. It has been already shown that the hybridization state of boron can be

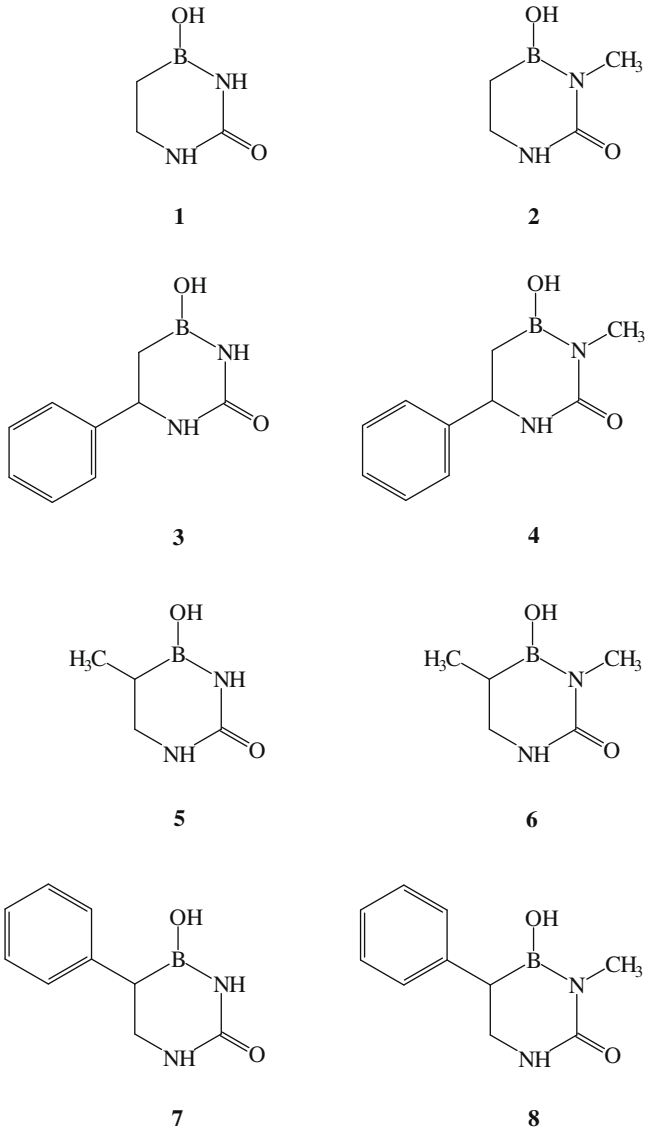

Fig. 2. Derivatives of 5,6-dihydroborauracil and 5,6-dihydroborathymine.

studied with the use of ^{11}B NMR [1,2]. NMR-controlled experiments of interactions of boron atom in 5,6-dihydroborauracil and 5,6-dihydroborathymine derivatives with electron pair donors (alcohols, amines, carboxylates) are of a great importance due to mimicking enzyme side chain interactions. We presented recently an interesting aspect of coordination equilibrium of 4-hydroxy-5,6-dihydrouracil in methanol solutions, the results suggesting the formation of tetrahedral bis-methanol adduct of **1** with two methoxy groups attached to boron atom [2]. The ^{11}B chemical shift of this product was *upfield* shifted to 1.6 ppm, similar to those described by Zhuo et al. [1].

A series of similar NMR experiments with compounds **2**–**8** is presented here. The titration of acetone-*d6* solution of compounds **2**–**8** with CD_3OD resulted in a large *upfield* shift of ^{11}B resonances.

The ^{11}B chemical shifts of acetone-*d6* solutions of compounds **1**–**8** are shown in Table 1. All of them are in 24–29 ppm range, typical for compounds of this type [1,2,9–17]. The ^{11}B chemical shifts of compounds **1**–**8** in methanol-*d4* are in 1.5–5.2 ppm range, confirming the formation of B,B-bis-methoxy derivatives of analyzed compounds (see Fig. 4, **1**·$(\mathbf{CD_3O})_2$). The solution of bis-methoxy adduct may contain the B–O (carbonyl oxygen coordinating to boron, Fig. 4, bottom) form in equilibrium with B–N form. The removal of

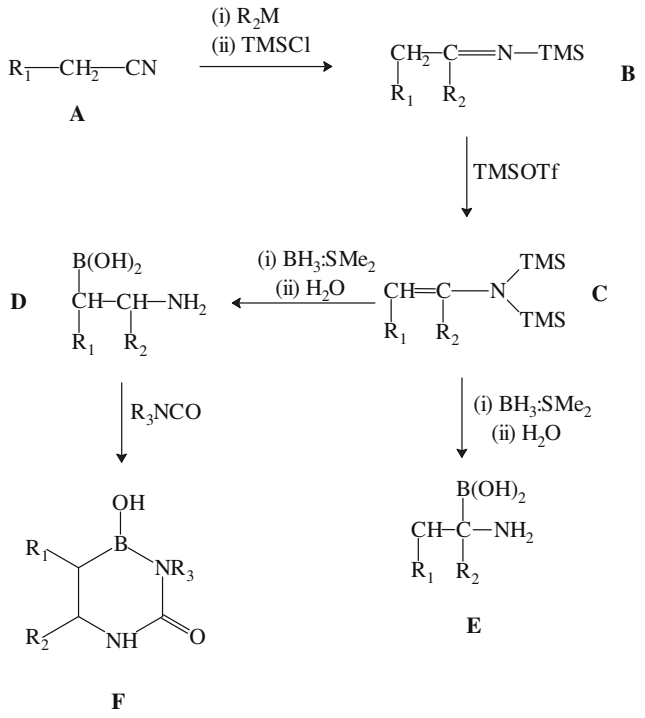

Fig. 3. Synthetic route for preparation of 5,6-dihydroborauracils. R_2M = PhLi or NaH.

methanol gives starting B–N form as judged from ^{11}B NMR spectra. Behavior of other compounds (**2**–**8**) was similar to that shown for **1**.

Differences between ^{11}B NMR chemical shifts of acetone-*d6* and methanol-*d4* solutions of compounds **1**–**8** are presented in the fourth column in Table 1. Interestingly, all of the above mentioned shift differences ($\Delta\delta$) are very similar, ranging from 23.0 to 24.4 ppm. This observation should be useful in prediction of ^{11}B chemical shifts of compounds similar to those presented here.

In order to select suitable reaction solvent, sets of experiments were done, using pyridine and *n*-butylamine as nitrogen electron pair donors, mimicking amino acids side chain nitrogen atom interactions with compounds **1**–**8**, with pyridine mimicking tryptophan or histidine, and *n*-butylamine mimicking lysine or proline side chains. The deuterated water or alcohols should be avoided due to strong interactions of theirs oxygen lone pairs with boron atom of 5,6-dihydroborauracils and 5,6-dihydroborathymines. The NMR results are presented in Table 1 (columns 2, 5 and 6). The presented ^{11}B chemical shifts concern compounds **1**–**8** in acetone-*d6* (column 2), and in approx. 35 mM solution of either pyridine (column 5) or *n*-butylamine (column 6) in acetone-*d6*. While with various 5,6-dihydroborauracil-py and 5,6-dihydroborathymine-py complexes the ^{11}B chemical shifts are in the 1.4 to −1.2 ppm range, and 2.5–3.8 ppm *upfield* shifted, compared to 5,6-dihydroborauracils- and 5,6-dihydroborathymine–CD_3OD complexes, with the corresponding 5,6-dihydroborauracil–butylamine and 5,6-dihydroborathymine–butylamine complexes the ^{11}B resonances are in the 0.0–0.7 ppm range (Table 1). The observed chemical shift differences are in accord with literature data [1,2,9–17]. The results of the foregoing experiments suggest the formation of the 'ate' complexes of 5,6-dihydroborauracil and 5,6-dihydroborathymine, containing additional nitrogen donors.

3. Conclusions

The synthesis, reactivity and spectroscopic properties of novel boron compounds, 4-hydroxy-5,6-dihydroborauracils and 4-hydroxy-5,6-dihydroborathymines, are presented. The synthetic route started with the reaction of nitrile with sodium hydride or phenyllithium, followed by the trimethylsilyl chloride protection step. *N*-trimethylsilylimino product formed underwent then reaction with trimethylsilyltriflate to yield the enamine product that was hydroborated with borane–dimethylsulfide complex and hydrolyzed. The cyclization of α- and β-boronic amino acids with the use of various isocyanates led to interesting cyclic products. The ^{11}B chemical shifts of compounds **1**–**8** in methanol-*d4* are in the 1.5–5.2 ppm range, pointing to the formation of B,B-bis-methoxy derivatives of analyzed compounds. The bis-methoxy adduct formed may contain the B–O (carbonyl oxygen coordinating to boron) form, in equilibrium with B–N form, in solution. Experiments with amine reagents were also conducted. Pyridine, mimicking interactions of tryptophan and histidine, and *n*-butylamine, mimicking interactions of lysine and proline side chains, were used in NMR-controlled experiments. The results suggest formation of the 'ate' complexes of 5,6-dihydroborauracil and 5,6-dihydroborathymine, containing additional nitrogen donors.

4. Experimental

4.1. Materials and methods

^1H NMR spectra were obtained with Bruker Avance II spectrometer, operating in the quadrature mode at 500 MHz. All ^{11}B spectra were performed using 5 mm pure quartz NMR tube. The residual peaks of deuterated solvents were used as internal standards. Elemental analysis was performed using Carlo Erba Elemental Analyser EA 1108. GC–MS analysis was carried out on Agilent Technologies 6890 N apparatus with 5973-Network mass detector. FTIR spectra were recorded on Perkin Elmer Paragon 1000 apparatus. All other reagents and deuterated solvents of the highest commercially available grade were purchased from Aldrich and used

Table 1
^{11}B NMR chemical shifts of compounds **1**–**8** in acetone-*d6*, methanol-*d4* and in amine solutions.

Compound	δ ^{11}B in CD_3COCD_3 (ppm)	δ ^{11}B in CD_3OD (ppm)	$\Delta\delta$ (ppm)[a]	δ ^{11}B in CD_3COCD_3/py (ppm)[b]	δ ^{11}B in CD_3COCD_3/$BuNH_2$ (ppm)[c]
1	24.9	1.6	23.3	−1.1	0.1
2	25.0	1.5	23.5	−1.0	0.2
3	26.1	1.7	24.4	−1.1	0.0
4	26.0	1.7	24.3	−1.2	0.1
5	24.6	1.5	23.1	−1.0	0.2
6	25.1	2.1	23.0	−0.6	0.3
7	29.2	5.1	24.1	1.3	0.7
8	29.5	5.2	24.3	1.4	0.7

[a] Difference of chemical shift between δ ^{11}B in CD_3COCD_3 and δ ^{11}B in CD_3OD (ppm).
[b] 1:1 5,6-Dihydroborauracils or 5,6-dihydroborathymines to pyridine molar ratios.
[c] 1:1 5,6-Dihydroborauracils or 5,6-dihydroborathymines to *n*-butylamine molar ratios.

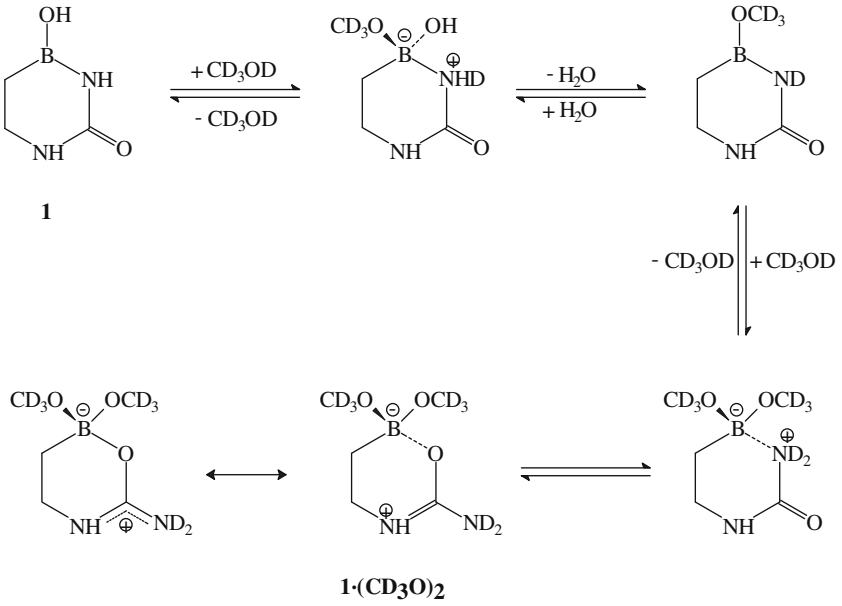

Fig. 4. Methanolysis equilibrium of 4-hydroxy-5,6-dihydrouracil (**1**).

without further purification (with exception for acetone-*d6* which was dried with anhydrous sodium sulfate). Rubber septa joints were purchased from Aldrich. All procedures, including preparation of samples for the NMR measurements, were carried out under nitrogen. The sodium hydride and phenyllithium reactions steps, as well as all operations performed with the reagents, were performed in airbag filled with dry nitrogen.

4.2. Preparation of compound **1** (4-hydroxy-5,6-dihydroborauracil)

To the solution (−10 °C) of anhydrous acetonitrile (0.2 ml, 3.83 mmol) in tetrahydrofurane (1.5 ml) in two-neck round bottom flask filled with dry nitrogen, the sodium hydride suspension (0.086 g, 3.58 mmol in 1.5 ml of dry THF) was added over the period of 1 h. The reaction mixture was a stirred for another 1 h, followed by addition of trimethylchlorosilane (0.45 ml; 3.58 mmol) and further 4 h stirring. The reaction mixture was then filtered under nitrogen atmosphere, filtrate dried under high vacuum and used in the next reaction step without further purification. Thus obtained imine derivative (0.392 g, 3.40 mmol) was inserted into a three-neck reaction flask containing triethylamine (0.95 ml, 6.82 mmol) and toluene (5 ml). Trimethylsilyltriflate (0.63 ml, 3.48 mmol) was then added to the reaction mixture over a period of 1 h, followed by 4 h stirring of the mixture at room temperature. The resulting enamine derivative was purified by vacuum distillation. Enamine (0.395 g, 2.11 mmol) was then dissolved in dichloromethane (1 ml) and added slowly with a syringe into a three-neck round bottom flask containing borane–dimethylsulfide complex dichloromethane solution (2.11 ml of 1 M BMS solution at 0 °C). After 24 h of stirring (final temperature ~20 °C), a solution of deoxygenated water (0.08 ml, 4.44 mmol) in THF (2 ml) was added and the mixture stirred for another 2 h. Solvents were then removed from the reaction mixture under high vacuum and the reaction product used in the next synthetic step. To the obtained isomeric boronic amino acids (93.3 mg, Fig. 2, products D and E), dissolved in 50% acetic acid (5 ml), a solution of potassium isocyanate (0.170 g, 2.1 mmol) in water (0.5 ml) was added and the resulting mixture stirred for 48 h at RT. The solvent were then removed from the reaction mixture under high vacuum, and acetone (2 × 0.8 ml) was used to wash out the cyclic product, 5,6-dihydroborauracil, with 48 mg yield. The analytical data for this compound was shown previously [2].

4.3. Preparation of compound **2** (4-hydroxy-3-methyl-5,6-dihydroborauracil)

Compound **2** was obtained by the reaction of boronic amino acids (93.5 mg, Fig. 2, products D and E, see Section 4.2) with methyl isocyanate (0.124 ml, 2.1 mmol) tetrahydrofurane solution (1 ml) at RT (24 h). The product was then vacuum dried. Yield – 35 mg. Analytical data for **2**: MS (electrospray ionization, *m/z*): 127–128 (100%). Elemental Anal. Calcd for $C_4H_9BN_2O_2$: C, 37.55%; H, 7.09%; N, 21.90%. Found: C, 37.51; H, 7.13; N, 21.85. ^{1}H NMR (acetone-*d6*, ppm): 8.51 (br, B–OH, 1H); 5.72 (br, NH, 1H); 3.45 (m, N–C$\underline{H}_2$, 2H); 2.81 (s, Me, 3H); 1.33 (m, B–C$\underline{H}_2$, 2H). ^{13}C NMR (acetone-*d6*, ppm): 156.5 (C=O); 35.8 (N–$\underline{C}H_2$); 27.2 (Me); 17.4 (B–$\underline{C}H_2$). ^{11}B NMR (acetone-*d6*, ppm): 25.0. ^{11}B NMR (methanol-*d4*, ppm): 1.5.

4.4. Preparation of **3** (4-hydroxy-6-phenyl-5,6-dihydroborauracil)

Preparation procedure for **3** is analogical to that presented for **1**, but for 1.8 M phenyllithium di-*n*-buthylether solution (2 ml, 3.6 mmol of PhLi) used in the first reaction step (0.2 ml of acetonitrile) instead of sodium hydride. Final yield was 101 mg of **3**. Analytical data for **3**: MS (electrospray ionization, *m/z*): 190 (100%). Elemental Anal. Calcd for $C_9H_{11}BN_2O_2$: C, 56.89%; H, 5.83%; N, 14.74%. Found: C, 56.87; H, 5.87; N, 14.70. ^{1}H NMR (acetone-*d6*, ppm): 8.45 (br, B–OH, 1H); 7.25–7.39 (m, Ph, 5H); 5.69, 5.92 (br, NH, 2H); 4.32 (m, N–C$\underline{H}$, 1H); 1.42 (m, B–C$\underline{H}_2$, 2H). ^{13}C NMR (acetone-*d6*, ppm): 159.1 (C=O); 127.2, 125.6, 124.5 (Ph); 41.9 (N–$\underline{C}H$); 19.2 (B–$\underline{C}H_2$). ^{11}B NMR (acetone-*d6*, ppm): 26.1. ^{11}B NMR (methanol-*d4*, ppm): 1.7.

4.5. Preparation of **4** (4-hydroxy-3-N-methyl-6-phenyl-5,6-dihydroborauracil)

Preparation procedure for **4** is analogical to that presented for **1**, but for 1.8 M phenyllithium di-*n*-buthylether solution (2 ml, 3.6 mmol of PhLi) used in the first reaction step (0.2 ml of acetonitrile) instead of sodium hydride. Additionally, methyl isocyanate (2:1 methyl isocyanate to boronic amino acid molar ratio) was

used in the last step of reaction procedure. Final yield was 121 mg of **4**. Analytical data for **4**: MS (electrospray ionization, *m/z*): 204 (100%). Elemental Anal. Calcd for $C_{10}H_{13}BN_2O_2$: C, 58.87%; H, 6.42%; N, 13.73%. Found: C, 58.81; H, 6.47; N, 13.70. ^{1}H NMR (acetone-*d6*, ppm): 8.52 (br, B–OH, 1H); 7.28–7.45 (m, Ph, 5H); 5.85 (br, NH, 1H); 4.30 (m, N–C<u>H</u>, 1H); 2.88 (s, Me, 3H); 1.45 (m, B–C<u>H</u>$_2$, 2H). ^{13}C NMR (acetone-*d6*, ppm): 156.0 (C=O); 127.1, 122.4, 123.2 (Ph); 42.2 (N–<u>C</u>H); 27.1 (Me); 19.3 (B–<u>C</u>H$_2$). ^{11}B NMR (acetone-*d6*, ppm): 26.0. ^{11}B NMR (methanol-*d4*, ppm): 1.7.

4.6. Preparation of **5** (4-hydroxy-5,6-dihydroborathymine)

Preparation procedure for **5** is analogical to that presented for **1**, but for priopionitrile (0.27 ml, 3.8 mmol) used in the first reaction step instead of acetonitrile. Final yield was 82 mg of **5**. Analytical data for **5**: MS (electrospray ionization, *m/z*): 127–128 (100%). Elemental Anal. Calcd for $C_4H_9BN_2O_2$: C, 37.55%; H, 7.09%; N, 21.90%. Found: C, 37.53; H, 7.11; N, 21.88. ^{1}H NMR (acetone-*d6*, ppm): 8.36 (br, B–OH, 1H); 5.92, 5.75 (br, NH, 2H); 3.38 (m, N–C<u>H</u>$_2$, 2H); 1.34 (m, B–C<u>H</u>, 1H); 1.24 (d, Me, 3H). ^{13}C NMR (acetone-*d6*, ppm): 153.4 (C=O); 34.7 (N–<u>C</u>H$_2$); 17.0 (B–<u>C</u>H); 12.1 (Me). ^{11}B NMR (acetone-*d6*, ppm): 24.6. ^{11}B NMR (methanol-*d4*, ppm): 1.5.

4.7. Preparation of **6** (4-hydroxy-3-N-methyl-5,6-dihydroborathymine)

Preparation procedure for **6** is analogical to that presented for **1**, but for priopionitrile (0.27 ml, 3.8 mmol) used in the first reaction step instead of acetonitrile. Additionally, methyl isocyanate (2:1 methyl isocyanate to boronic amino acid molar ratio) was used in the last step of the reaction procedure. Final yield was 65 mg of **6**. Analytical data for **6**: MS (electrospray ionization, *m/z*): 141–142 (100%). Elemental Anal. Calcd for $C_5H_{11}BN_2O_2$: C, 42.30%; H, 7.81%; N, 19.73%. Found: C, 42.27; H, 7.88; N, 19.68. ^{1}H NMR (acetone-*d6*, ppm): 8.47 (br, B–OH, 1H); 5.90 (br, NH, 1H); 3.41 (m, N–C<u>H</u>$_2$, 2H); 2.85 (s, 3-Me, 3H); 1.37 (m, B–C<u>H</u>, 1H); 1.22 (d, 5-Me, 3H). ^{13}C NMR (acetone-*d6*, ppm): 157.0 (C=O); 34.8 (N–<u>C</u>H$_2$); 26.1 (3-Me); 17.9 (B–<u>C</u>H); 12.3 (5-Me). ^{11}B NMR (acetone-*d6*, ppm): 25.1. ^{11}B NMR (methanol-*d4*, ppm): 2.1.

4.8. Preparation of **7** (4-hydroxy-5-phenyl-5,6-dihydroborauracil)

Preparation procedure for **7** is analogical to that presented for **1**, but for phenylacetonitrile (0.44 ml, 3.8 mmol) used in the first reaction step instead of acetonitrile. Yield was 55 mg of **7**. Analytical data for **7**: MS (electrospray ionization, *m/z*): 190 (100%). Elemental Anal. Calcd for $C_9H_{11}BN_2O_2$: C, 56.89%; H, 5.83%; N, 14.74%. Found: C, 56.84; H, 5.87; N, 14.69. ^{1}H NMR (acetone-*d6*, ppm): 8.63 (br, B–OH, 1H); 7.31–7.46 (m, Ph, 5H); 5.79, 5.71 (br, NH, 2H); 3.57 (m, N–C<u>H</u>$_2$, 2H); 2.81 (m, B–C<u>H</u>, 1H). ^{13}C NMR (acetone-*d6*, ppm): 155.9 (C=O); 126.3, 125.0 121.2 (Ph); 39.2 (N–<u>C</u>H$_2$); 27.4 (B–<u>C</u>H). ^{11}B NMR (acetone-*d6*, ppm): 29.2. ^{11}B NMR (methanol-*d4*, ppm): 5.1.

4.9. Preparation of **8** (4-hydroxy-3-N-methyl-5-phenyl-5,6-dihydroborauracil)

Preparation procedure for **8** is analogical to that presented for **1**, but for phenylacetonitrile (0.44 ml, 3.8 mmol) used in the first reaction step instead of acetonitrile. Additionally, methyl isocyanate (2:1 methyl isocyanate to boronic amino acid molar ratio) was used in the last step of the reaction procedure. Yield was 69 mg of **8**. Analytical data for **8**: MS (electrospray ionization, *m/z*): 204 (100%). Elemental Anal. Calcd for $C_4H_9BN_2O_2$: C, 58.87%; H, 6.42%; N, 13.73%. Found: C, 58.80; H, 6.45; N, 13.71. ^{1}H NMR (acetone-*d6*, ppm): 8.75 (br, B–OH, 1H); 7.33–7.52 (m, Ph, 5H); 5.84 (br, NH, 1H); 3.59 (m, N–C<u>H</u>$_2$, 2H); 2.90 (s, Me, 3H); 2.83 (m, B–C<u>H</u>, 1H). ^{13}C NMR (acetone-*d6*, ppm): 154.8 (C=O); 126.2, 125.7, 124.1 (Ph); 39.6 (N–<u>C</u>H$_2$); 27.1 (Me); 27.9 (B–<u>C</u>H). ^{11}B NMR (acetone-*d6*, ppm): 29.5. ^{11}B NMR (methanol-*d4*, ppm): 5.2.

4.10. Interactions of **1**–**8** with pyridine and n-butylamine

Approx. 2 mg of a given cyclic compound was dissolved in 0.5 ml of acetone-*d6*, containing pyridine or *n*-butylamine (1:1 pyridine or *n*-butylamine to 5,6-dihydroborauracil molar ratios). The NMR results are presented in Table 1.

Acknowledgment

This work was supported by the Ministry of Education and Science, Poland, Grant No. N204 088 31/2052 2006–2009.

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