Direct Arylation of 5-Iodouracil and 5-Iodouridine with Heteroarenes and Benzene *via* Photochemical Reaction

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A method for the direct arylation of 5-iodouracil and 5-iodouridine was found to proceed in moderate yields. By irradiating mixtures of 5-iodouracil or 5-iodouridine and a series of five-membered heterocycles such as 1*H*-pyrrole, furan, 2-methylfuran, 1-methyl-1*H*-pyrrole, thiophene, as well as benzene in MeCN/H_2O with a Hg lamp, 5-aryluracils and 5-aryluridines were synthesized. The reaction proceeded smoothly without the requirement of adding any transition metals or ligands.

Introduction. – As important nucleoside derivatives, the 5-substituted pyrimidine nucleosides show a broad spectrum of biological activity, such as antibacterial [1], antifungal [2], anti-inflammatory [3], anticancer [4], and antiviral [5][6]. Bromovinyldeoxyuridine (=5-[(*E*)-2-bromoethenyl]-2′-deoxyuridine; BVDU) and derivatives are highly selective inhibitors of varicella-zoster virus (VZV), (dideoxy)nucleoside reverse transcriptase inhibitors (NRTIs), and non-nucleoside reverse transcriptase inhibitors (NNRTIs) [7]. The 5-aryl substituted uracil analog cambinol also exhibits antitumor activity as sirtuin inhibitor [8]. Moreover, 5-(furan-2-yl)-2′-deoxyuridine was incorporated into DNA as the fluorescent probe to investigate nucleic acid structure, dynamics, and recognition [9][10].

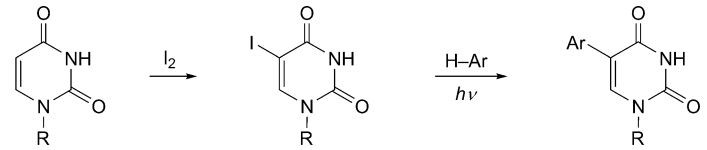
The arylation and heteroarylation of uracil and uracil nucleoside at the 5-position have been accomplished efficiently using cross-coupling reactions [11]. In 1993, various 5-alkynyl derivatives were obtained in high yields (70–97%) by the cross-coupling reactions of acetylated uridine triflate with several terminal alkynes [11a], and in 1991, 5-iodouridine was coupled with esters of acrylic acid in the Pd-catalyzed *Heck* reaction to generate a series of esters of 5-[(*E*)-2-carboxyethenyl]uridine [11b]. In 2002, *Amann et al.* reported the synthesis of 5-(pyren-1-yl)-2′-deoxyuridine and 8-(pyren-1-yl)-2′-deoxyguanosine *via* Pd-catalyzed *Suzuki–Miyaura* cross-coupling reactions [11c]. Furthermore, in 2005, *Peyron et al.* synthesized 5-substituted 2′-deoxyuridine nucleosides by the *Stille* reaction [11d], and in 2012, the *Stille* procedure was also successful on a polyuridine RNA strand bearing 5-iodouridine base, although 60 equiv. of 2-(tributylstannyl)furan reagent and 15 equiv. of $Pd_2(dba)_3$ catalyst along with 30 equiv. of tri(furan-2-yl)phosphine ligand were required [12]. These reactions require

the preliminary preparation of organometallic reagents, which might be tricky in several cases. Moreover, these couplings provide an organic metal salt as byproduct.

Recently, direct arylation of pyrimidine rings with Pd-activated aryl halides have been established. *Čerňová et al.* developed regioselective Pd-catalyzed direct C–H arylation of 1,3-diprotected uracil derivatives at the 5- or 6-position, controlled by the presence or absence of CuI [13]. Pd-Catalyzed arylation of 1,3-dimethyluracil with aryl bromides or aryl iodides were also reported to give aryluracil in recent years [14][15]. In 2014, *Liang et al.* synthesized 5-arylated uracils and uracil nucleosides by the Pd-catalyzed direct arylation of 5-halouracils with arenes and electron-excessive heterocycles promoted by bases [16].

Photochemistry has shown intrinsically advantageous, because activation is achieved by the absorption of a photon, which leaves no residue, whereas most catalytic methods involve the use of toxic/polluting reagents [17]. Furthermore, the reactions occur under unparalleled mild conditions and, in many cases, deep-seated chemical transformations occurring in high yields and with high selectivity. To investigate whether pyrimidyne was an intermediate, *Youssefyeh* and *Lichtenberg* reported the photolysis of 5,6-diiodo-1,3-dimethyluracil in benzene and in furan, which gives products derived from a radical intermediate [18]. Herein, we would like to report the synthesis of 5-arylated uracil and uracil nucleoside by the photo-induced cross coupling of 5-iodouracil and 5-iodouridine with heteroaromatics and benzene under the Hg light, which did not cause the cleavage of the nucleoside-glycosidic bond and was suitable for the natural (N(3) and OH unprotected) uridines and uracils (*Scheme 1*).

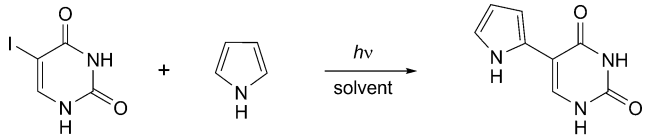
Scheme 1. *Steps for the Photochemical Synthesis of Heteroaryluracils and Heteroaryluridines*



R = H, β-D-Ribofuranosyl

Results and Discussion. – Initially, 5-iodouracil (**1a**; 0.2 mmol) and 1*H*-pyrrole (**2a**; 6 mmol) were dissloved in MeOH (40 ml) and irradiated with a Hg lamp (500 W) at 20°. After 7 h, the solution appeared yellow, indicating release of I_2 from 5-iodouracil to the solution, and **1a** disappeared as judged by TLC. The arylated product **3a** (yield 10%) was isolated, and its structure was confirmed by means of NMR and HR-MS (*Table 1*, *Entry 1*). Then, a systematic investigation, with different solvents and concentrations of **2a**, was carried out, and the results are listed in *Table 1*. In DMF and AcOEt, only a trace of **3a** was obtained (*Entries 2* and *3*), and in CH_2Cl_2 and ^{i}PrOH, the yield of product **3a** was lower than that in MeOH (*Entries 4* and *5*). Eventually, the yield of **3a** obtained in MeCN was 28% (*Entry 6*). Then, H_2O was added as a co-solvent to improve the solubility of **1a** and to reduce the amount of organic solvents. When a mixture of MeCN/H_2O (1:1) was used, the yield of **3a** was increased to 37% with no

Table 1. *Optimization of Photochemical Synthesis of 5-(1*H*-Pyrrol-2-yl)uracil*[a])



1a **2a** **3a**

Entry	Solvent	Concentration of **2a** [M]	Base	Yield [b]) [%]
1	MeOH	1.5×10^{-1}	–	10
2	DMF	1.5×10^{-1}	–	Trace
3	AcOEt	1.5×10^{-1}	–	Trace
4	CH_2Cl_2	1.5×10^{-1}	–	6
5	^{i}PrOH	1.5×10^{-1}	–	8
6	MeCN	1.5×10^{-1}	–	28
7	MeCN/H_2O 1:1	1.5×10^{-1}	–	37
8	MeCN/H_2O 1:1	4×10^{-2}	–	20
9	MeCN/H_2O 1:1	2×10^{-1}	–	43
10	MeCN/H_2O 1:1	2.5×10^{-1}	–	51
11	MeCN/H_2O 1:1	3.5×10^{-1}	–	40
12	MeCN/H_2O 1:1	2.5×10^{-1}	NaOH	45
13	MeCN/H_2O 1:1	2.5×10^{-1}	K_2CO_3	41
14	MeCN/H_2O 1:1	2.5×10^{-1}	$NaHCO_3$	43
15	MeCN/H_2O 1:1	2.5×10^{-1}	Et_3N	53
16	MeCN/H_2O 1:1	2.5×10^{-1}	AcONa[c])	60

[a]) Couplings were performed by irradiating 0.2 mmol of 5-iodouracil (**1a**; 5×10^{-3} M), 6–14 mmol of 1*H*-pyrrole (**2a**; $1.5 \times 10^{-1} - 3.5 \times 10^{-1}$ M), and 0.2 mmol of base in 40 ml of solvent with a Hg lamp at 20° for 7 h under Ar. [b]) Yield of isolated material after column chromatography on silica gel. [c]) In the cases of 0.1 and 0.3 mmol of AcONa, the yields of **3a** were 55 and 58%, respectively.

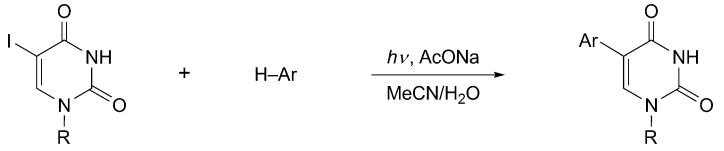
significant byproduct (*Entry 7*). Therefore, a mixture of MeCN/H_2O (1:1) was chosen as the reaction medium for all further reactions.

Changing the concentration of 1*H*-pyrrole (**2a**) is another possibility for increasing the yield of product **3a**. When increasing the amount of the starting **2a** up to 2.5×10^{-1} M, a good yield of **3a** (51%) was obtained (*Entry 10*). However, the yield of **3a** decreased significantly when the concentration of **2a** was increased up to 3.5×10^{-1} M (*Entry 11*).

In the presence of base, the yield of 6-aryl/alkyl BINOLs were improved by the photochemistry reaction [19]. Next, we investigated the arylation of 5-iodouracils **1a** in the presence of an organic or inorganic base. The result indicated that an equimolar amount of organic base can increase the yields of **3a** significantly (*Entry 12–16*), and the best yield is 60% with AcONa as the base (*Entry 16*).

With the optimized reaction conditions in hand, the coupling of a variety of heteroaromatics, benzene (**2**) and 5-iodouracil or 5-iodouridine **1** has been studied to illustrate the photochemical synthesis of aryluracil and aryluridine. When the five-membered heterocycles **2** were reacted with 5-iodouracil (**1a**), the yields of **3** were generally higher than those with 5-iodouridine (**1b**; *Table 2*, *Entries 1–8*). The

Table 2. *Synthesis of Heteroaryluracils and Heteroaryluridines by Photochemical Reaction*[a])



1a R = H
1b R = β-D-Ribofuranosyl

2

3

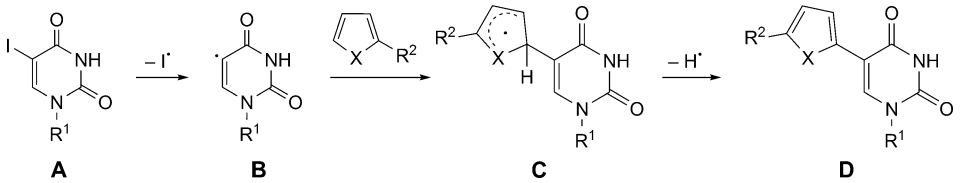
Entry	**1**	**2**	**3**	Yield[b]) [%]
1	**1a**	1*H*-Pyrrole	**3a**	60
2	**1a**	Furan	**3b**	55
3	**1a**	1-Methyl-1*H*-pyrrole	**3c**	64
4	**1b**	Furan	**3d**	28
5	**1b**	1*H*-Pyrrole	**3e**	35
6	**1b**	Thiophene	**3f**	23
7	**1b**	2-Methylfuran	**3g**	32
8	**1b**	1-Methyl-1*H*-pyrrole	**3h**	41
9	**1a**	Benzene	**3i**	10
10	**1a**	Benzene	**3i**	79[c])
11	**1b**	Benzene	**3j**	7
12	**1b**	Benzene	**3j**	46[c])

[a]) Irradiating 0.2 mmol of **1** (5×10^{-3} M), 6 mmol of **2** (2.5×10^{-1} M), and 0.2 mmol of AcONa (5×10^{-3} M) in MeCN/H_2O (40 ml) with a Hg lamp at 20° for 7 h under Ar. [b]) Yield of isolated product after column chromatography on silica gel. [c]) 0.2 mmol of **1** (5×10^{-3} M), 110 mmol of benzene (3M), and 0.2 mmol of AcONa (5×10^{-3} M) in MeCN/H_2O 5 : 1 (30 ml).

electron-donating heterocycles **2** were efficient to give the product **3** in good yield. For 2-methylfuran and furan coupling with the same substrate **1b** by the photochemical reaction, the yield of **3g** was higher than that of **3d** (*Entries 4* and *7*). Meanwhile, for 1*H*-pyrrole and 1-methyl-1*H*-pyrrole, the yield of **3h** was higher than that of **3e** (*Entries 5* and *8*). Because the electron density of benzene is lower than that of five-membered heterocycles, the yield of 5-phenyluracil and 5-phenyluridine decreased to 10 and 7%, respectively (*Entries 9* and *11*). Increasing the concentration of benzene to 3M, the best yields of 5-phenyluracil (79%) and 5-phenyluridine (46%) were obtained (*Entries 10* and *12*).

A plausible mechanism for the formation of **3** is proposed in *Scheme 2*. First, under the radiation of UV light, the photoinduced homocleavage of the C–I bond of **A** gave

Scheme 2. *Mechanism for the Synthesis of Heteroaryluracils and Heteroaryluridines*



A **B** **C** **D**

the uracil radical **B**. Then, **B** was coupled with heteroaromatics or benzene to afford an intermediate **C**, and elimination of H· provided the desired coupled product **D**.

Conclusions. – In summary, we have demonstrated that the radical arylation of 5-iodouracil and 5-iodouridine with heteroaromatics and benzene in MeCN/H_2O gave 5-arylated uracil and uracil nucleoside in good yield. The radical arylation protocol developed here avoids the usage of organometallic precursors which are necessary for *Suzuki* or *Stille* coupling. It proceeded smoothly without the requirement of adding any transition metals or ligands. Compared with the photoreaction reported by *Youssefyeh* and *Lichtenberg* [18], we not only optimized the solvent of photoreaction and improved the yield of 5-arylated uracil, but also the uracil nucleosides 5-arylated with 1*H*-pyrrole and thiophene were synthesized. The presented reaction was also compatible with natural nucleoside, as no glycosidic bond cleavage was observed, and no protecting group was required.

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Experimental Part

General. All the irradiation experiments were performed in a *BL-GHX-V* photochemical reactor equipped with a 500-W high-pressure Hg lamp. TLC: Silica gel *60 GF_{254}* (SiO_2; *Qingdao Haiyang Chemistry Plant*, Qingdao, P. R. China). Column chromatography (CC): SiO_2 (200 mesh; *Qingdao Haiyang Chemistry Plant*); CH_2Cl_2/MeOH 20 : 1 as eluent. M.p.: *X-5 micro* melting point apparatus; uncorrected. IR Spectra: *Nicolet 170SX* FT-IR spectrophotometer with KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker AM-400 Advance* spectrometer at 400 (^1H) and 100 (^{13}C) MHz, resp.; in (D_6)DMSO; δ in ppm rel. to (D_6)DMSO solvent peaks, *J* in Hz. HR-MS: *Bruker MALDI-TOF-MS* using ESI technique; in *m*/*z*.

Procedure for Synthesis of 5-Iodouracil (**1a**) [20]. Uracil (0.33 g, 3 mmol), I_2 (1.52 g, 6 mmol), and $(NH_4)_2Se(NO_3)_6$ (0.82 g, 1.5 mmol) were added into an oven-dried round-bottom flask with 100 ml of MeCN, and the resulting mixture was stirred at r.t. for 3 d until a white precipitation appeared. Then, the residue was filtered and washed with Et_2O (20 ml) to afford **1a** (0.67 g, 95%) as white powder. 5-Iodouridine (**1b**) was obtained by the same method as **1a**.

*Synthesis of 5-(1*H*-Pyrrol-2-yl)uracil* (**3a**). A soln. of **1a** (0.05 g, 0.2 mmol), 1*H*-pyrrole (**2a**; 0.67 g, 10 mmol), and AcONa (0.02 g, 0.2 mmol) in MeCN/H_2O 1 : 1 (40 ml) in a 50-ml quartz tube was deaerated by bubbling Ar for 30 min and irradiated for 7 h with a high-pressure Hg lamp (500 W), which was cooled to *ca.* 20° with tap water by means of an internal cold finger. The progress of reaction was monitored by TLC at regular intervals. Then, the solvent was removed under reduced pressure, and the residue was separated by CC (SiO_2) to give the corresponding product **3a** (0.02 g, 60%). Compounds **3b** – **3h** were obtained by the same method as **3a**.

Synthesis of 5-Phenyluracil (**3i**). A soln. of **1a** (0.05 g, 0.2 mmol), benzene (8.7 g, 0.11 mol), and AcONa (0.02 g, 0.2 mmol) in MeCN/H_2O 5 : 1 (30 ml) in a 50-ml quartz tube was deaerated by bubbling Ar for 30 min and irradiated for 7 h with a high-pressure Hg lamp (500 W) at 20°. The reaction was stopped until lots of white precipitation appeared in aq. phase. Then, the resulting suspension was filtered. The residue was dissolved in DMSO and precipitated in H_2O again. The process was repeated until the product **3i** was obtained (0.03 g, 79%).

Synthesis of 5-Phenyluridine (**3j**). Benzene (8.7 g, 0.11 mol) and AcONa (0.02 g, 0.2 mmol) were added to a stirring soln. of **1b** (0.07 g, 0.2 mmol) in MeCN/H_2O 5 : 1 (30 ml) in a 50-ml quartz tube at r.t., followed by degasing with Ar for 30 min. The resulting soln. was irradiated by a high-pressure Hg

lamp (500 W) for 7 h. After being cooled down to r.t., the volatiles were removed under the reduced pressure, and the residue was separated by CC (SiO_2; CH_2Cl_2/MeOH 20:1) to give **3j** (30 mg, 46%) as white solid.

*5-(1*H*-Pyrrol-2-yl)uracil* (**3a**) [21]. Grey powder. M.p. 276.7–280.0°. IR (KBr): 3401, 2815, 1746, 1661, 1405, 1239, 1103, 842, 720, 657, 555, 450. ^{1}H-NMR: 11.25 (*s*, H–N(1′), 11.04 (*d*, *J* = 4.7, H–N(1)); 10.84 (*s*, H–N(3)), 7.70 (*d*, *J* = 5.9, H–C(6)); 6.73 (*dd*, *J* = 4.1, 2.5, H–C(5′)); 6.49 (*t*, *J* = 3.6, H–C(4′)); 6.01 (*dd*, *J* = 5.8, 2.6, H–C(3′)). ^{13}C-NMR: 162.8; 150.4; 134.7; 123.9; 117.7; 107.8; 106.1; 105.9. HR-ESI-MS: 200.0425 ($[M+Na]^+$, $C_8H_7N_3NaO_2^+$; calc. 200.0436).

5-(Furan-2-yl)uracil (**3b**) [22]. White powder. M.p. 291.0–295.7°. IR (KBr): 3211, 2829, 1738, 1681, 1638, 1440, 1348, 1237, 999, 765, 728, 654, 556, 453. ^{1}H-NMR: 11.39 (*s*, H–N(1)), 11.19 (*s*, H–N(3)), 7.71 (*s*, H–C(6)); 7.63 (*s*, H–C(5′)); 6.83 (*s*, H–C(4′)); 6.51 (*s*, H–C(3′)). ^{13}C-NMR: 161.1; 150.3; 146.7; 141.2; 136.2; 111.5; 107.3; 104.4. HR-ESI-MS: 201.0263 ($[M+Na]^+$, $C_8H_6N_2NaO_3^+$; calc. 201.0276).

*5-(1-Methyl-1*H*-Pyrrol-2-yl)uracil* (**3c**) [22a][23]. Grey powder. M.p. 257.3–261.3°. IR (KBr): 3043, 2827, 1749, 1679, 1638, 1495, 1447, 1420, 1314, 1226, 1210, 767, 711, 642, 549, 437, 421. ^{1}H-NMR: 11.24 (*s*, H–N(1)); 11.06 (*s*, H–N(3)); 7.38 (*s*, H–C(6)); 6.77 (*s*, H–C(5′)); 5.96 (*s*, H–C(3′,4′)); 3.35 (*s*, MeN). ^{13}C-NMR (151 MHz, (D_6)DMSO): 163.2; 151.2; 141.2; 125.6; 123.2; 109.4; 106.6; 105.8; 34.2. HR-ESI-MS: 214.0581 ($[M+Na]^+$, $C_9H_9N_3NaO_2^+$; calc. 214.0592).

5-(Furan-2-yl)uridine (**3d**) [16][24]. Yellow powder. M.p. 234.8–238.1°. IR (KBr): 3407, 3067, 1692, 1639, 1569, 1472, 1384, 1260, 1092, 1036, 990, 930, 747, 406. ^{1}H-NMR: 11.65 (*s*, H–N(3)); 8.42 (*s*, H–C(6)); 7.61 (*s*, H–C(5″)); 6.87 (*d*, *J* = 2.8, H–C(3″)); 6.59–6.48 (*m*, H–C(4″)); 5.87 (*d*, *J* = 4.9, H–C(2′)); 5.42 (*d*, *J* = 4.8, HO–C(3′)); 5.20 (*s*, HO–C(4′)); 5.11 (*d*, *J* = 2.5, HO–C(6′)); 4.12 (*d*, *J* = 4.1, H–C(3′)); 4.03 (*d*, *J* = 3.1, H–C(4′)); 3.91 (*d*, *J* = 1.9, H–C(5′)); 3.69 (*d*, *J* = 11.6, 1 H, CH_2(6′)); 3.60 (*d*, *J* = 11.6, 1 H, CH_2(6′)). ^{13}C-NMR: 160.1; 149.7; 146.4; 141.5; 134.9; 111.5; 107.9; 105.6; 88.2; 84.9; 74.0; 69.8; 60.6. HR-ESI-MS: 333.0683 ($[M+Na]^+$, $C_{13}H_{14}N_2NaO_7^+$; calc. 333.0699).

*5-(1*H*-Pyrrol-2-yl)uridine* (**3e**) [16]. Grey powder. M.p. 223.4–227.0°. IR (KBr): 3407, 3067, 2856, 1639, 1569, 1466, 1284, 1260, 1092, 990, 930, 747, 406. ^{1}H-NMR: 11.57 (*s*, H–N(1″)); 10.84 (*s*, H–N(3)); 8.22 (*s*, H–C(6)); 6.77 (*s*, H–C(5″)); 6.39 (*s*, H–C(3″)); 6.04 (*d*, *J* = 2.7, H–C(4″)); 5.84 (*d*, *J* = 5.0, H–C(2′)); 5.41 (*d*, *J* = 5.6, HO–C(3′)); 5.25 (*t*, *J* = 4.5, HO–C(4′)); 5.09 (*d*, *J* = 5.2, HO–C(6′)); 4.15 (*dd*, *J* = 10.3, 5.1, H–C(3′)); 4.04 (*dd*, *J* = 9.5, 4.8, H–C(4′)); 3.88 (*d*, *J* = 3.6, H–C(5′)); 3.75–3.67 (*m*, 1 H, CH_2(6′)); 3.64–3.57 (*m*, 1 H, CH_2(6′)). ^{13}C-NMR: 162.0; 149.7; 133.6; 124.0; 118.4; 108.1; 107.4; 105.6; 88.2; 84.8; 73.6; 69.8; 60.7. HR-ESI-MS: 332.0838 ($[M+Na]^+$, $C_{13}H_{15}N_3NaO_6^+$; calc. 332.0859).

5-(Thiophen-2-yl)uridine (**3f**) [16][25]. Grey-white powder. M.p. 208.0–212.7°. IR (KBr): 3337, 2922, 2829, 1719, 1688, 1645, 1471, 1340, 1262, 1243, 1046, 992. ^{1}H-NMR: 11.71 (*s*, H–N(3)), 8.67 (*s*, H–C(6)); 7.47 (*d*, *J* = 5.1, H–C(5″)); 7.41 (*d*, *J* = 3.1, H–C(3″)); 7.07–7.05 (*m*, H–C(4″)); 5.85 (*d*, *J* = 4.2, H–C(2′)); 5.49 (*d*, *J* = 5.3, HO–C(3′)); 5.45 (*t*, *J* = 4.6, HO–C(4′)); 5.11 (*d*, *J* = 5.5, HO–C(6′)); 4.14 (*dd*, *J* = 9.4, 4.7, H–C(3′)); 4.07 (*dd*, *J* = 10.0, 5.0, H–C(4′)); 3.94–3.91 (*m*, H–C(5′)); 3.79–3.74 (*m*, 1 H, CH_2(6′)); 3.68–3.63 (*m*, 1 H, CH_2(6′)). ^{13}C-NMR: 161.3; 149.6; 135.7; 133.9; 126.4; 125.7; 122.5; 108.3; 88.7; 84.6; 74.3; 69.4; 60.2. HR-ESI-MS: 349.0452 ($[M+Na]^+$, $C_{13}H_{14}N_2NaO_6S^+$; calc. 349.0470).

5-(5-Methylfuran-2-yl)uridine (**3g**). Yellow powder. M.p. 230.0–234.2°. IR (KBr): 3327, 2828, 1719, 1656, 1597, 1542, 1261, 1090, 1045, 1018, 790. ^{1}H-NMR: 11.60 (*s*, H–N(3)); 8.41 (*s*, H–C(6)); 6.72 (*d*, *J* = 2.9, H–C(3″)); 6.11 (*d*, *J* = 2.7, H–C(4″)); 5.86 (*d*, *J* = 4.8, H–C(2′)); 5.44 (*d*, *J* = 5.4, HO–C(3′)); 5.22 (*d*, *J* = 4.3, HO–C(4′)); 5.11 (*d*, *J* = 5.1, HO–C(6′)); 4.14–4.09 (*m*, H–C(3′)); 4.07–4.01 (*m*, H–C(4′)); 3.91 (*s*, H–C(5′)); 3.71 (*d*, *J* = 11.5, 1 H, CH_2(6′)); 3.62 (*d*, *J* = 11.8, 1 H, CH_2(6′)); 2.29 (*s*, Me(5″)). ^{13}C-NMR: 160.1; 150.4; 149.6; 144.7; 134.0; 108.9; 107.5; 105.8; 88.2; 84.7; 74.0; 69.7; 60.4; 18.50. HR-ESI-MS: 347.0836 ($[M+Na]^+$, $C_{14}H_{16}N_2NaO_7^+$; calc. 347.0855).

*5-(1-Methyl-1*H*-Pyrrol-2-yl)uridine* (**3h**). White powder. M.p. 115.3–118.9°. IR (KBr): 3399, 3067, 2829, 1680, 1541, 1490, 1456, 1412, 1310, 1248, 1056, 725, 406. ^{1}H-NMR: 11.53 (*s*, H–N(3)); 7.96 (*s*, H–C(6)); 6.79 (*t*, *J* = 2.0, H–C(5″)); 5.98 (*dd*, *J* = 5.7, 2.8, H–C(3″,4″)); 5.85 (*d*, *J* = 5.4, H–C(2′)); 5.41 (*d*, *J* = 5.7, HO–C(6′)); 5.09 (*t*, *J* = 4.7, HO–C(3′,4′)); 4.11 (*dd*, *J* = 10.6, 5.3, H–C(4′)); 3.99 (*dd*, *J* = 9.0, 4.6, H–C(3′)); 3.87 (*d*, *J* = 3.0, H–C(5′)); 3.61 (*dt*, *J* = 7.3, 4.1, 1 H, CH_2(6′)); 3.56–3.52 (*m*, 1 H, CH_2(6′)); 3.35 (*d*, *J* = 2.1, MeN′). ^{13}C-NMR: 169.5; 163.1; 152.6; 150.9; 139.6; 135.9; 133.3; 128.1; 128.0; 127.9; 127.6; 126.9; 112.1; 52.9. HR-ESI-MS: 346.0996 ($[M+Na]^+$, $C_{14}H_{17}N_3NaO_6^+$; calc. 346.1015).

5-Phenyluracil (**3i**) [26]. White powder. M.p. 238.6–239.2°. IR (KBr): 3033, 2822, 1764, 1675, 1504, 1448, 1424, 1235, 1279, 1170, 759, 687, 788, 594, 551, 506, 460, 432. ^{1}H-NMR: 11.20 (*d*, *J* = 60.0, H–N(1,3)); 7.62 (*s*, H–C(6)); 7.54 (*d*, *J* = 7.6, H–C(2′,6′)); 7.36 (*t*, *J* = 7.6, H–C(3′,5′)); 7.28 (*t*, *J* = 7.3, H–C(4′)). ^{13}C-NMR: 163.2; 151.2; 141.2; 125.6; 123.2; 109.5; 106.6; 105.9. HR-ESI-MS: 211.0467 ([*M* + Na]$^+$, $C_{10}H_8N_2NaO_2^+$; calc. 211.0483).

5-Phenyluridine (**3j**) [27]. Grey-white powder. M.p. 190.4–192.7°. IR (KBr): 3244, 2828, 1703, 1648, 1602, 1495, 1421, 1387, 1340, 1243, 1100, 1065, 1016, 989, 788, 750, 698,589. ^{1}H-NMR: 11.53 (*s*, H–N(3)); 8.29 (*s*, H–C(6)); 7.56 (*d*, *J* = 7.4, H–C(3″,5″)); 7.37 (*t*, *J* = 7.5, H–C(2″,6″)); 7.31 (*t*, *J* = 7.3, H–C(4″)); 5.86 (*d*, *J* = 4.6, H–C(2′)); 5.44 (*d*, *J* = 5.5, HO–C(3′)); 5.22 (*t*, *J* = 4.5, HO–C(4′)); 5.09 (*d*, *J* = 5.3, HO–C(6′)); 4.16 (*dd*, *J* = 9.8, 4.8, H–C(3′)); 4.05 (*dd*, *J* = 9.3, 4.6, H–C(4′)); 3.90 (*s*, H–C(5′)); 3.71–3.64 (*m*, 1 H, CH_2(6′)); 3.62–3.55 (*m*, 1 H, CH_2(6′)). ^{13}C-NMR: 162.1, 150.1, 138.1, 133.1, 128.1, 127.9, 127.1, 113.4, 88.3, 84.7, 73.9, 69.6, 60.4. HR-ESI-MS: 343.0891 ([*M* + Na]$^+$, $C_{15}H_{16}N_2NaO_6^+$; calc. 343.0906).

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