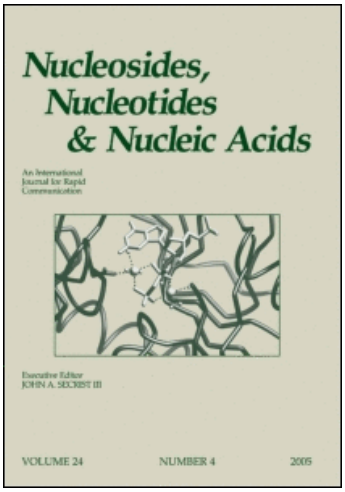

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Nucleic Acid Component Analogues: Synthesis of 2′-Deoxynucleosides from 5-Substituted-4-hydroxy-6(1H)-pyrimidinones

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ABSTRACT

Condensation of the silylated pyrimidines **5a–c** with methyl 2-deoxy-3,5-di-*O*-toluoyl-D-pentofuranoside 6, using trimethylsilyltriflate as catalyst gave anomeric mixtures of 2′-deoxynucleosides **7a–c**, the pure α- and β-anomers were separated and deprotected with sodium methoxide in methanol to give 1-(2′-deoxy-α-D-pentafuranosyl)-4-hydroxy-5-substituted-6(1H)-pyrimidinones **10a,b** and **13a** and their corresponding β-anomers **11a,b** and **13b**.

Key Words: 2′-Deoxynucleosides; 1-Chloromethyl naphalene; Pyrimidinones.

INTRODUCTION

Prystaš[1,2] reported on the synthesis of 1-glycosyl-4-alkoxy-5-(un)substituted-6(1H)-pyrimidinones by ribosylation or deoxyribosylation of 2,6-dialkoxypyrimidines. Transformation of these nucleosides to the corresponding 4-hydroxy

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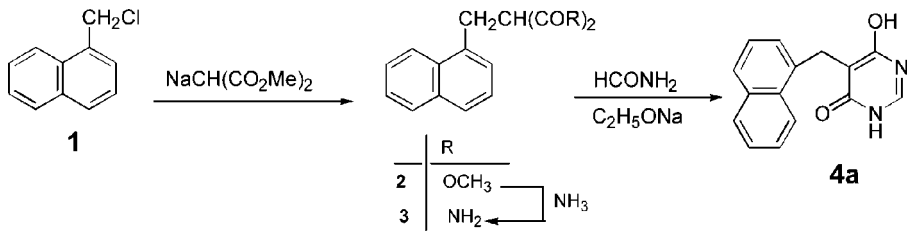
derivatives was accomplished only with difficulty by hydrogenolysis, which was accompanied by hydrogenation of the ring at position 2 and 3.[1,2] On the other hand, carcinogenic polycyclic aromatic hydrocarbons are known to undergo metabolic activation to reactive diol epoxide intermediates that bind covalently to DNA in vivo.[3] Thus, in this report, as a continuation of our interest in the synthesis of nucleosides and acyclonucleosides.[4–8] We describe a practical synthesis of 1-(2′-Deoxy-D-ribofuranosyl)-4-hydroxy-6(1H)-pyrimidinones, **10a,b; 11a,b** and **13a,b**, bearing an aromatic fragment at position 5.

RESULTS AND DISCUSSION

The commercial 1-chloromethyl naphthalene (**1**) reacts with sodium salt of dimethylmalonate to afford the new ester **2**, which has been shown to be a versatile synthon for further functionalizations and ring closure reactions to several heterocyclic compounds. The ester **2** was converted into the corresponding malondiamide **3**, that can be cyclised by reaction with formamide, in presence of sodium ethoxide, to give 4-hydroxy-5-(1-naphthylmethyl)-6(1H)-pyrimidinone **4a** (Sch. 1).

Similarly, condensation of benzyl malondiamide with fomamide afforded 4-hydroxy-5-benzyl-6(1H)-pyrimidinone **4b**, whereas, 4-hydroxy-5-phenyl-6(1H)-pyrimidinone **4c** was prepared, according to the procedure of Hull.[9] Silylation of **4a–c** with 1,1,1,3,3,3-hexamethyldisilizane (HMDS) in the presence of a catalytic amount of ammonium sulfate was performed according to Wittenburg[10] to give the silylated derivatives **5a–c** that were reacted with methyl 2-deoxy-3,5-di-*O*-toluoyl-D-pentofuranoside (**6**)[11] using trimethylsilyl trifluoromethanesulfonate (TMS triflate) as the catalyst according to the method of Vorbrügen et al.[12] in anhydrous acetonitrile to give anomeric mixtures of nucleosides **7a–c** in 60–86% yield with the α/β ratio 2:1. Stirring of the protected nucleosides **7a,b**, after their chromatographic purification, in dry diethylether at room temperature for 1 h followed by filtration resulted in complete separation of the anomeric mixture. The α anomers **8a,b** were obtained in 40–51% yields and the β anomers **9a,b** in 20–35% yield. Deprotection of the nucleosides with sodium methoxide in methanol afforded the deprotected α anomers **10a–b** (90–92%) and the β anomers **11a,b** (86–94%). The mixture of α and β anomers **7c** was deprotected using sodium methoxide in methanol to give the unprotected anomers **12** which could be separated by use of preparative HPLC to afford the α anomer **13a** in 38% yield and the β anomer **13b** in 48% yield (Sch. 2).



Scheme 1.

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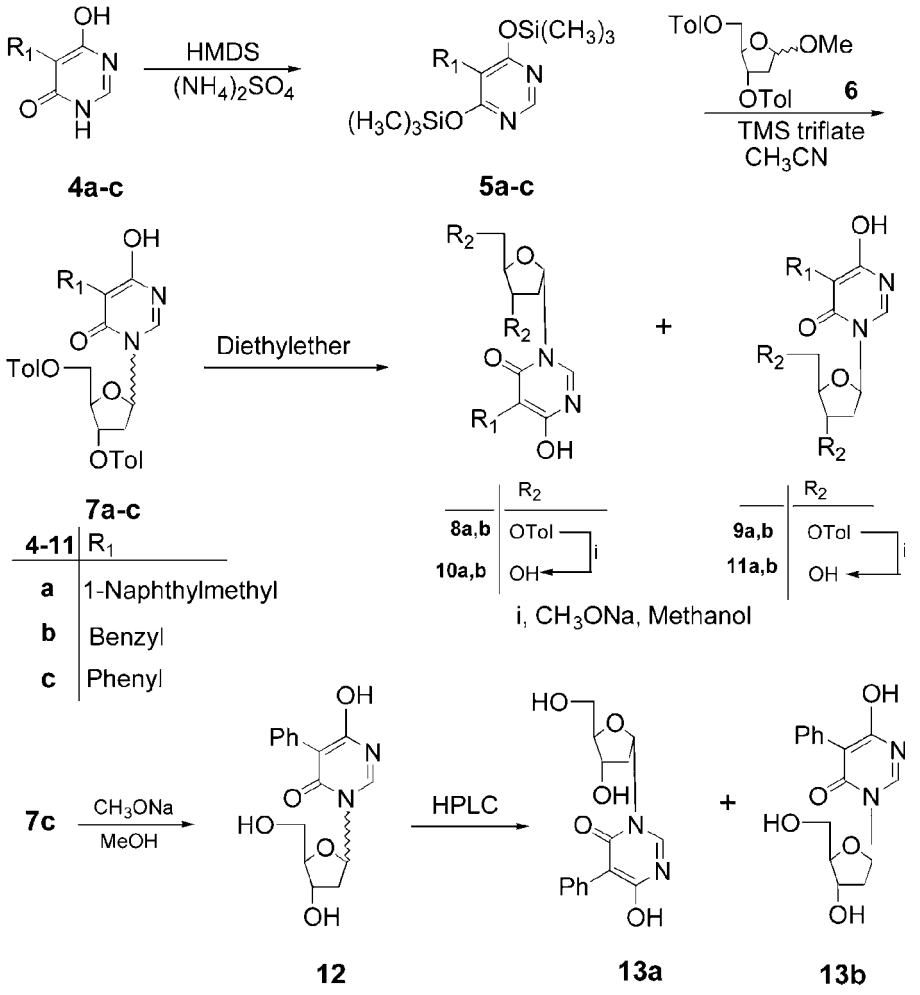

Scheme 2.

In agreement with the reported data,[4–6,13,14] the 4′-H protons of the α anomers **10a,b** and **13a** appear downfield from those observed for the β anomers **11a,b** and **13b**.

EXPERIMENTAL

Mps are uncorrected. Elemental analyses were carried out in the Microanalytical Laboratories of the Faculty of Science, Cairo University. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 250 FT-nmr spectrometer at 250 MHz for ^{1}H NMR and 62.9 MHz for ^{13}C NMR. Mass spectra (MS) were recorded using fast atom bombardment (FAB) on a Kratos MS 50-spectrometer. Analytical TLC plates

60 F_{254} and silica gel (0.040–0.063 mm) was purchased from Merck. Anhydrous CH_3CN was distilled from P_2O_5 followed by distillation from CaH. All other solvents were used after distillation and drying.

Dimethyl (1-naphthylmethyl) malonate (2). To methanol (300 mL) and sodium (19.3 g, 0.84 mol), dimethylmalonate (113 mL, 0.98 mol) was added dropwise with stirring then 1-chloromethylnaphthalene **1** (154 mL, 0.87 mol) was added. The reaction mixture was refluxed with stirring for 5 h. The excess alcohol was evaporated under reduced pressure and the residue dissolved in water, extracted with diethyl ether (3×100), dried (Na_2SO_4). Fractional distillation yielded **2** (62%; bp150–155°C, 20 mbar); ^{1}H-NMR (DMSO-d_6) δ 3.60 (m, 8H, CH_2 and $2 \times$ CH_3), 3.92 (t, 1H, $J = 7.6$ Hz, C*H*), 7.32–7.58 (m, 4H, arom.), 7.82 (d, 1H, $J = 8.0$ Hz, arom.), 7.94 (d, 1H, $J = 7.3$ Hz, arom.), 8.1 (d, 1H, $J = 7.7$ Hz, arom.). ^{13}C-NMR (DMSO-d_6) δ 31.03 (*C*H_2), 51.87 (*C*H), 52.1 ($2 \times$ *C*H_3), 123.10, 125.24, 125.62, 126.28, 126.63, 127.28, 128.59, 130.96, 133.25 and 133.31 (*C*-arom.), 168.66 (2 CO). MS FAB ($CHCl_3$ + 3-nitrobenzyl alcohol) m/z: 353 ($M^+ + 1$).

(1-Naphthylmethyl)-malondiamide (3). A solution of **2** (14 g, 48 mmol) in a 1:1 mixture (100 mL) of methanol and conc. ammonia (25%) was stirred at room temperature for 24 h. The solid product which formed was collected by filtration, dried and recrystallized from methanol to give **3** as white prisms (78%): mp. 268–70°C. ^{1}H-NMR (DMSO-d_6) δ 3.37–3.60 (m, 3H, *C*H and CH_2), 7.10 (s, 2H, NH_2), 7.28 (s, 2H, NH_2), 7.34–7.70 (m, 4H, arom.), 7.78 (d, 1H, $J = 7.3$ Hz, arom.), 7.92 (d, 1H, $J = 7.6$ Hz, arom.), 8.11 (d, 1H, $J = 8.0$ Hz, arom.). ^{13}C-NMR (DMSO-d_6) δ 31.98 (*C*H_2), 53.84 (*C*H), 123.53, 125.34, 125.47, 126.01, 126.47, 126.76, 128.55, 131.35, 133.34 and 135.19 (*C*-arom.), 170.84 ($2 \times$ *C*O). Anal. Calcd for $C_{14}H_{14}N_2O_2$ (242.37): C, 69.37; H, 5.82; N, 11.60. Found: C, 69.50; H, 5.70; N, 11.60.

4-Hydroxy-5-(1-naphthylmethyl)-6(1H)-pyrimidinone (4a). A mixture of 3 (7.2 g, 30 mmol), formamide (5 mL) and sodium ethoxide [prepared by dissolving (2.8 g, 120 mmol) of sodium metal in 100 mL ethanol] was refluxed for 12 h. The residue obtained after removal of ethanol *in vacuo* was dissolved in warm water (100 mL) and acidified with 4M HCl. The solid product, which formed, was filtered off, dried and recrystallized from water to afford **4a** (92%) as white prisms, mp 334–336 °C. ^{1}H-NMR (DMSO-d_6) δ 4.06 (s, 2H, CH_2), 7.25 (d, 1H, $J = 7.1$, arom.), 7.37 (t, 2H, $J = 7.5$ Hz, arom.), 7.51 (m, 2H, arom.), 7.73 (d, 1H, $J = 8.0$ Hz, arom.), 7.87 (d, 1H, $J = 8.3$ Hz, arom.), 8.03 (s, 1H, C_2-*H*), 8.37 (d, 1H, $J = 7.3$ Hz, arom.); 11.85 (s. br., 1H, N*H*). ^{13}C-NMR (DMSO-d_6) δ 25.26 (*C*H_2), 100.64 (*C*-5) 124.05, 125.34, 125.64, 126.04, 128.28, 131.83, 133.24, and 135.96 (*C*-arom.), 147.45 (*C*-2). 164.51 (*C*-4 and *C*O). Anal. Calcd for $C_{15}H_{12}N_2O_2$ (252.37): C, 71.38; H, 4.79; N, 11.14. Found: C, 71.60; H, 4.90; N, 11.30.

4-Hydroxy-5-benzyl-6(1H)-pyrimidinone (4b). This compound was obtained from benzyl malondiamide (5.37 g, 30 mmol), formamide (5 mL) and sodium ethoxide (2.8 g, sodium metal in 100 mL ethanol) according to the procedure described for **4a** to afford 4b as white prisms (86%), mp 326–326°C (DMF). ^{1}H-NMR (DMSO-d_6) δ 3.61 (s, 2H, CH_2), 7.09–7.26 (m, 5H, arom.), 7.97 (s, 1H, C_2-*H*), 11.78 (s. br, 1H,

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N*H*). ^{13}C-NMR (DMSO-d_6) δ 27.89 (*C*H_2), 102.02 (*C*-5), 125.45, 127.91 and 128.29 (*C*-arom.), 140.99 (*C*-2), 147.21 (*C*-4), 164.24 (*C*O). Anal. calcd for $C_{11}H_{10}N_2O_2$ (202.31): C, 65.30; H, 4.98; N, 13.89. Found: C, 65.20; H, 4.70; N, 13.60.

General Procedure for the Preparation of 7a–c. Pyrimidine derivatives **4a–c** (5 mmol) was treated with 1,1,1,3,3,3-hexamethyldisilazane (*HMDS*) (30 mL) and ammonium sulfate (30 mg) at reflux temperature for 6 h (clear solution after 2 h), and the solvent was removed in vacuo. The residue **5a–c** was dissolved in dry MeCN (20 mL), and the sugar **6** (3 mmol) in dry MeCN (50 mL) was added. The mixture was cooled to −35°C under magnetic stirring. A solution of $CF_3SO_3SiMe_3$ (1.1 mL, 6 mmol) in dry MeCN (5 mL) was then added dropwise with stirring over a period of 10 min. The reaction mixture was stirred at −25°C for 1 h and then at room temperature for 1 h. The reaction mixture was diluted with 200 mL of CH_2Cl_2 and washed ice-cold sat. aq. $NaHCO_3$ (3 × 100 mL). The organic phase was separated, washed with cold H_2O (3 × 100 mL), dried over Na_2SO_4, and evaporated to obtain the crude products which were chromatographed on a silica gel column using petroleum ether/diethyl ether (40–0%) as eluent.

Preparation of 8a,b and 9a,b. A suspension of anomeric mixtures **7a,b** (5 mmol) in dry diethyl ether (20 mL) was stirred at room temperature for 2 h, then filtered, washed with diethyl ether to afford the pure α anomer **8a,b** as a white solid. The mother liquor was evaporated to dryness to afford β anomer **9a,b** as white foam. Whereas, the anomeric mixtures **7c** fails to separate by this method or by using column chromatograph, using HPLC after deprotection separated these anomers.

1-[2′-Deoxy-3, 5-di-*O*-(4-methylbenzoyl)-α/β-D-pentofuranozyl]-5-phenyl-4-hydroxy-6(1H)-pyrimidinone (7c). Yield ((89%); (α/β mixture), ^{1}H-NMR($CDCl_3$) δ 2.19 (s, 3H, C*H*$_3$), 2.24–2.28 (m, 1H, *H*-2′), 2.32 (s, 3H, C*H*$_3$), 2.63–2.66 (m, 1H, *H*-2′), 2.97–3.12 (m, 2H, *H*-2′), 4.51–4.57 (m, 2H, *H*-5′), 4.64–4.66 (m, 1H, *H*-4′), 4.71–4.90 (m, 2H, *H*-5′), 4.95–4.98 (m, 1H, *H*-4′), 5.55 (d, 1H, *J* = 6.1 Hz, *H*-3′), 5.63 (d, 1H, *J* = 5.4 Hz, *H*-3′), 6.38 (t, 1H, *J* = 6.6 Hz, *H*-1′), 6.47 (d, 1H, *J* = 6.3 Hz, *H*-1′), 7.01 (d, 2H, *J* = 8.0 Hz, arom.), 7.10 (d, 2H, *J* = 8.1 Hz, arom.), 7.23–7.39 (m, 12H, arom.), 7.52–7.56 (m, 4H, arom.), 7.67 (d, 2H, *J* = 8.1 Hz, arom.), 7.81 (d, 2H, *J* = 8.1 Hz, arom.), 7.93 (d, 2H, *J* = 8.1 Hz, arom.), 8.37 (s, 1H, C_2-*H*), 8.40 (s, 1H, C_2-H). ^{13}C-NMR($CDCl_3$) δ 21.55 (*C*H_3), 21.64 (*C*H_3), 39.32 (*C*-2′), 39.81 (*C*-2′), 63.89 (2 *C*-5′), 74.83 (2 *C*-3′), 84.03 (*C*-4′), 85.82 (*C*-4′), 87.38 (*C*-1′), 89.02 (*C*-1′), 103.81 (*C*-5), 103.95 (*C*-5), 125.95–130.68 (*Carom.*), 144.29–145.15 (*Carom.*), 160.70 (*C*-2), 161.10 (*C*-2), 163.92 (*C*-4), 164.11 (*C*-4), 165.29, 165.93, 166.03 and 166.23 (4 *C*O).

1-[2′-Deoxy-3,5-di-*O*-(4-methybenzoyl)-α-D-pentofuranosyl]-4-hydroxy-5-(1-naphthylmethyl)-6(1H)-pyrimidinone (8a). (Yield (59%). ^{1}H-NMR (DMSO-d_6) δ 2.34 (s, 3H, C*H*$_3$), 2.39 (s, 3H, C*H*$_3$), 2.53 (d, 1H, *J* = 14.73 Hz, *H*-2′), 2.92–3.36 (m, 1H, *H*-2′), 4.08 (s, 2H, C*H*$_2$), 4.50–4.52 (m, 1H, *H*-5′), 5.10–5.13 (m, 1H, *H*-4′), 5.58 (d, 1H, *J* = 5.3 Hz, *H*-3′), 6.34 (d, 1H, *J* = 6.0 Hz, *H*-1′), 7.09–7.24 (m, 2H, arom.), 7.36 (d, 2H, *J* = 8.0 Hz, arom.), 7.46–7.48 (m, 2H, arom.), 7.62 (d, 2H, *J* = 8.2 Hz, arom.), 7.61 (d, 1H, *J* = 8.0 Hz, arom.), 7.70 (d, 1H, *J* = 7.9 Hz, arom.), 7.86

(d, 1H, $J = 7.3$ Hz, arom.), 7.94 (d, 1H, $J = 8.1$ Hz, arom), 8.43 (d, 1H, $J = 8.0$ Hz, arom.), 8.49 (s, C_2-H, arom.), 11.69 (s., br., 1H, O*H*). ^{1}H-NMR (DMSO-d_6) δ 21.07 ($2 \times C\text{H}_3$), 25.30 (*C*H$_2$), 38.27 (*C*-2′), 63.90 (*C*-5′), 74.72 (*C*-3′), 84.32 (*C*-4′), 88.01 (*C*-1′), 99.51 (*C*-5), 123.88–143.82 (*C*-arom.), 145.62 (*C*-2), 161.90 (*C*-4), 164.76, 165.38 and 165.66 ($3 \times C$O). MS FAB ($CHCl_3$ + 3-nitrobenzyl alcohol) *m/z*: 627 ($M + Na^+$).

1-[2′-Deoxy-3,5-di-*O*-(4-methylbenzoyl)-β-D-pentofuranosyl]-4-hydroxy-5-(1-naphthylmethyl)-6(1H)-pyrimidinone (9a). Yield (30%); ^{1}H-NMR (DMSO-d_6) δ, 2.33 (s, 3H, C*H*$_3$), 2.39 (s, 3H, C*H*$_3$), 2.61–2.65 (m, 1H, *H*-2′), 2.93–2.98 (m, 1H, *H*-2′), 4.11 (s, 2H, C*H*$_2$), 4.52–4.60 (m, 1H, *H*-4′), 4.65–4.68 (m, 2H, *H*-5′), 5.54–5.59 (m, 1H, *H*-3′), 6.38–6.43 (m, 1H, *H*-1′), 7.13–7.96 (m, 13H, arom.), 8.49 (m, 3H, C_2-*H* and arom.), 11.74 (s. br., 1H, O*H*). ^{13}C-NMR (DMSO-d_6) δ, 21.08 (2 *C*H$_3$), 25.33 (*C*H$_2$), 38.31 (*C*-2′), 63.95 (*C*-5′), 74.95 (*C*-3′), 82.10 (*C*-4′), 86.30 (*C*-1′), 99.70 (*C*-5), 123.89–135.71 (*C*-arom.), 143.76, 143.82 and 143.93 (*C*-arom.), 145.95 (*C*-2), 161.32 (*C*-4), 165.16, 165.39 and 165.66 ($3 \times C$O).

5-Benzyl-1-[2′-deoxy-3,5-di-*O*-(4-methylbenzoyl)-α-D-pentofuranosyl)-4-hydroxy-6(1H)pyrimidinone (8b). Yield (63%). ^{1}H-NMR (DMSO-d_6) δ 2.36 (s, 3H, C*H*$_3$), 2.39 (s, 3H, C*H*$_3$), 2.53 (d, 1H, $J = 14.73$ Hz, *H*-2′), 3.35 (m, 1H, *H*-2′), 3.65 (s, 2H, C*H*$_2$), 4.53–4.57 (m, 2H, *H*-5′), 5.15 (m, 1H, *H*-4′), 5.57 (d, $J = 5.2$ Hz, 1H, *H*-3′), 6.32 (d, $J = 6.0$ Hz, 1H, *H*-1′), 7.07–7.27 (m, 7H, arom.), 7.36 (d, 2H, $J = 7.8$ Hz, Hz, arom.), 7.63 (d, 2H, $J = 7.9$ Hz, arom), 7.93 (d, 2H, $J = 7.8$ Hz, arom.), 8.43 (s, 1H, C_2-H), 11.62 (s., br., 1H, O*H*). ^{13}C-NMR (DMSO-d_6) δ 21.08 ($2 \times C\text{H}_3$), 27.85 (*C*H$_2$), 38.18 (*C*-2′), 63.85 (*C*-5′), 74.76 (*C*-3′), 84.26 (*C*-4′), 87.79 (*C*-1′), 100.83 (*C*-5), 125.42–129.29, 140.67 and (*C*-arom.), 145.46 (*C*-2), 161.64 (*C*-4), 164.79 165.20 and 165.38 (3 *C*O). MS FAB ($CHCl_3$ + 3-nitrobenzyl alcohol) *m/z*: 577 ($M + Na^+$).

5-Benzyl-1-[2′-deoxy-3,5-di-*O*-(4-methybenzoyl)-β-D-pentofuranozyl]-4-hydroxy-6(1H)pyrimidinone (9b). Yield (31%). ^{1}H-NMR (DMSO-d_6) δ 2.36 (s, 3H, C*H*$_3$), 2.39 (s, 3H, C*H*$_3$), 2.70–2.75 (m, 1H, *H*-2′), 2.91–2.96 (m, 1H, *H*-2′), 3.65 (s, 2H, C*H*$_2$), 4.50–4.55 (m, 1H, *H*-4′), 4.61–4.65 (m, 2H, *H*-5′), 5.52–5.56 (m, 1H, *H*-3′), 6.32–6.36 (m, 1H, *H*-1′), 7.24–7.47 (m, 8H, arom.), 7.63 (d, 2H, $J = 7.9$ Hz, arom.), 7.81–7.83 (m, 3H, arom.), 8.34 (s, 1H, C_2-H), 11.63 (s. br., 1H, O*H*). ^{13}C-NMR (DMSO-d_6) δ 21.08 (2 *C*H$_3$), 27.85 (*C*H$_2$), 38.18 (*C*-2′), 63.55 (*C*-5′), 74.75 (*C*-3′), 83.01 (*C*-4′), 85.91 (*C*-1′), 100.92 (*C*-5), 125.42–129.29 (*C*-arom.), 140.66 and 143.83 (*C*-arom.), 145.83 (*C*-2), 161.84 (*C*-4), 164.79, 165.20 and 165.28 (3 *C*O).

General Procedure for the Preparation of 10–12. Compounds **8a,b, 9a,b** and **7c** (2.5 mmol) were dissolved in MeOH (25 mL) and then MeONa (0.81 g, 15 mmol) was added. The reaction mixture was stirred at room temperature for 1 h, NH_4Cl (0.8 g, 15 mmol) was added and the stirring was continued for 1 h. The reaction mixture was evaporated to dryness and purified on silica gel column using methanol/diethyl ether as eluentted **10a,b, 11a,b** and **12,** respectively.

1-(2′-Deoxy-α-D-pentofuranosyl)-4-hydroxy-5-(1-naphthylmethyl)-6(1H)-pyrimidinone (10a). Yield (91%). ^{1}H-NMR (DMSO-d_6) δ 2.00 (d, 1H, $J = 13.9$ Hz,

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H-2′), 2.50–2.61 (m, 1H, *H*-2′), 3.35–3.43 (m, 2H, *H*-5′), 4.05 (s, 2H, CH_2), 4.25–4.29 (m, 2H, *H*-3′ and *H*-4′), 5.22 (s. br., 1H, OH), 6.20–6.22 (m, 1H, *H*-1′), 7.29–7.88 (m, 6H, C_2-*H* and arom.) 8.34–8.41 (m, 2H, arom.). ^{13}C-NMR (DMSO-d_6) δ 25.77 (*C*H_2), 40.78 (*C*-2′), 60.67 (*C*-5′), 70, 76 (*C*-3′), 86.41 (*C*-4′), 89.89 (*C*-1′), 98.15 (*C*-5), 124.22, 125.22, 125.33, 125.44, 125.54, 125.87, 128.22, 131.90, 133.21 and 136.48 (*C*-arom.), 146.34 (*C*-2), 161.68 (*C*-4), 166.27 (*C*O). MS FAB ($CHCl_3$ + 3-nitrobenzyl alcohol) *m*/*z*: 391 ($M^+ + Na$).

1-(2′-Deoxy-β-D-pentofuranosyl)-4-hydroxy-5-(1-naphthylmethyl)-6(1H)-pyrimidinone (11a). Yield (86%); ^{1}H-NMR (DMSO-d_6) δ 2.29 (m, 1H, *H*-2′), 2.35 (m, 1H, *H*-2′), 3.63 (m, 2H, *H*-5′), 3.85–3.87 (m, 1H, *H*-4′), 4.06 (s, 2H, CH_2), 4.31 (m, 1H, *H*-3′), 6.25–6.28 (m, 1H, *H*-1′), 7.25–7.90 (m, 6H, C_2-*H* and arom.), 8.39 (d, 1H, $J = 5.3$ Hz, arom.), 8.53 (d, 1H, $J = 7.6$ Hz, arom.). ^{13}C-NMR (DMSO-d_6) δ 25.74 (*C*H_2), 41.07 (*C*-2′), 60.85 (*C*-5′), 69.94 (*C*-3′), 84.57 (*C*-4′), 87.67 (*C*-1′), 98.51 (*C*-5), 124.11, 125.24, 125.36, 125.57, 128.24, 131.84, 133.21 and 136.16 (*C*-arom.), 146.21 (*C*-2), 161.52 (*C*-4), 165.92 (*C*O). MS FAB ($CHCl_3$ + 3-nitrobenzyl alcohol) *m*/*z*: 391 ($M^+ + Na$).

5-Benzyl-1-(2′-deoxy-α-D-pentofuranosyl)-4-hydroxy-6(1H)-pyrimidinone (10b). Yield (91%). ^{1}H-NMR (DMSO-d_6) δ 1.96 (d, 1H, $J = 13$ Hz, *H*-2′), 2.54 (m, 1H, *H*-2′), 3.55–3.59 (m, 2H, *H*-5′), 3.60–3.64 (m, 2H, CH_2), 4.24–4.28 (m, 2H, *H*-3′ and *H*-4′), 5.35 (s. br., 2H, 2 O*H*), 6.23–6.27 (m, 1H, *H*-1′), 7.06–7.26 (m, 5H, arom.), 8.27 (s, 1H, C_2-H). ^{13}C-NMR (DMSO-d_6) δ 28.52 (*C*H_2), 41.11 (*C*-2′), 61.67 (*C*-5′), 70.76 (*C*-3′), 86.12 (*C*-4′), 89.70 (*C*-1′), 99.22 (*C*-5), 125.19, 127.74, 128.30, 129.22 and 141.81 (*C*-arom.), 146.11 (*C*-2), 161.62 (*C*-4), 166.62 (*C*O). MS FAB ($CHCl_3$ + 3-nitrobenzyl alcohol) *m*/*z*: 341 ($M^{++}Na$).

5-Benzyl-1-(2′-deoxy-β-D-pentofuranosyl)-4-hydroxy-6(1H)-pyrimidinone (11b). Yield (88%). ^{1}H-NMR (DMSO-d_6) δ 2.00–2.13 (m, 1H, *H*-2′), 2.21–2.25 (m, 1H, *H*-2′), 3.43–3.61 (m, 4H, CH_2 and *H*-5′), 3.85–3.91 (m, 1H, *H*-4′), 4.28–4.31 (m, 1H, *H*-3′), 5.26–5.36 (m, 2H, 2 O*H*), 6.23–6.28 (m, 1H, *H*-1′), 7.10–7.23 (m, 5H, arom.), 8.43 (s, 1H, 1H, C_2-*H*). ^{13}C-NMR (DMSO-d_6) δ 28.53 (*C*H_2), 41.04 (*C*-2′), 60.98, (*C*-5′), 70.10 (*C*-3′), 84.39 (*C*-4′), 87.63 (*C*-1′), 99.58 (*C*-5), 125.33, 127.83, 128.29 and 141.51 (*C*-arom.), 145.99 (*C*-2), 161.51 (*C*-4), 166.25 (*C*O). MS FAB ($CHCl_3$ + 3-nitrobenzyl alcohol) *m*/*z*: 341 ($M^+ + Na$).

1-(2′-Deoxy-α-D-pentofuranosyl)-4-hydroxy-5-phenyl-6(1H)-pyrimidinone (13a). Yield (54%). ^{1}H-NMR (DMSO-d_6) δ, 2.09 (d, 1H, $J = 14.2$ Hz, *H*-2′), 2.59 (m, 1H, *H*-2′), 3.38–3.54 (m, 2H, *H*-5′), 4.25–4.35 (m, 2H, *H*-3′ and *H*-4′), 6.19 (d, 1H, $J = 6.6$ Hz, *H*-1′), 7.15–7.51 (m, 5H, arom.), 8.37 (s, 1H, C_2-*H*). ^{13}C-NMR (DMSO-d_6) δ 40.72 (*C*-2′), 61.69 (*C*-5′), 70.76 (*C*-3′), 87.08 (*C*-4′), 90.18 (*C*-1′), 100.63 (*C*-5), 125.85, 127.05, 130.36 and 133.20 (*C*-arom.), 146.58 (*C*-2), 160.49 (*C*-4), 165.50 (*C*O). MS FAB ($CHCl_3$ + 3-nitrobenzyl alcohol) *m*/*z*: 327 ($M + Na^+$).

1-(2′-Deoxy-β-D-pentofuranosyl)-4-hydroxy-5-phenyl-6(1H)-pyrimidinone (13b). Yield (26%). ^{1}H-NMR (DMSO-d_6) δ, 2.15–2.28 (m, 1H, *H*-2′), 2.30–2.35 (m, 1H, *H*-2′), 3.55–3.70 (m, 2H, *H*-5′), 3.87–3.90 (m, 1H, *H*-4′), 4.28 (m, 1H, *H*-3′), 6.25

(t, 1H, $J = 6.2$ Hz, *H*-1′), 7.16–7.50 (m, 5H, arom.), 8.59 (s, 1H, C_2-*H*). ^{13}C-NMR (DMSO-d_6) δ 41.13 (*C*-2′), 60.77 (*C*-5′), 69.83 (*C*-3′), 85.04 (*C*-4′), 87.80 (*C*-1′), 100.85 (*C*-5), 125.99, 127.10, 130.01, 133.01 (*C*-arom.), 146.56 (*C*-2), 160.34 (*C*-4), 163.86 (*C*O). MS FAB ($CHCl_3$ + 3-nitrobenzyl alcohol) m/z: 305 ($M + H^+$).

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