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A Versatile Synthesis of Dihydropyrimidinone *C*-Nucleosides

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ABSTRACT

A versatile synthesis of *N*-substituted dihydropyrimidinone *C*-nucleosides (**20–29**) is described. Glycosyl amino esters (**3–9**), obtained by reductive alkylation of glycosyl amino esters **1** and **2**, on condensation with different isocyanates afforded respective ureido derivatives (**10–19**) in good to quantitative yields. The latter on cyclative amidation with a combination of DBU/TBAB (tetrabutylammonium bromide)/4Å molecular sieve gave the corresponding nucleosides (**20–29**) in good yields.

Key Words: Glycosyl amino esters; Isocyanates; DBU; TBAB (tetrabutylammonium bromide); *C*-nucleosides.

INTRODUCTION

Dihydropyrimidinones have been used as reagents and chiral auxiliaries in asymmetric synthesis of β-amino acids and many other biologically important compounds.[1,2] *C*-Nucleosides, having a *C–C* linkage instead of a *C–N* linkage between the aglycon and sugar moiety are more stable towards the enzymatic degradation and

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therefore the half-life of these compounds is far greater than that of nucleosides. Further, these nucleosides are associated with anticancer,[3] antibacterial,[4–6] antiviral[7] and antileukemic activities.[8–10] In spite of so much importance, no serious attempt has been made for the last two decades to synthesize dihydropyrimidinone *C*-nucleosides. Several reports exist for the synthesis of *C*-nucleosides.[11–13] Prominent among these are reactions of suitably protected sugars or tetrahydrofurancarbaldehydes with metalated bases and to build heterocycles on preformed sugar derivatives.[14–17] Reports on the synthesis of tetrahydropyrimidinone heterocycles by cyclisation of D-or L-asparginine and other β-amino acids with aldehydes also exist.[18] Reported methods for the synthesis of *C*-nucleosides are difficult to perform and unsuitable for large-scale synthesis because of low yields and high cost.

In continuation of our recent work on the development of biologically active nucleosides[19–23] the present work describes the synthesis of different dihydropyrimidinone *C*-nucleosides having N^1 and N^3 substituents.

RESULTS AND DISCUSSION

The synthetic strategy (Scheme 1) begins with glycosylated amino esters **1** and **2** prepared by our earlier method.[19,20] Thus, ethyl 5-amino-5,6-dideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-β-L-*ido*-hepto-1,4-furanuronate (**1**) on reaction with benzaldehyde in a mixture of dichloromethane and trimethyl orthoformate followed by in situ reduction with sodium cyanoborohydride, gave corresponding N-benzyl derivative **3** in very good yield. Similarly, glycosyl amino esters **4–9** were prepared by reductive alkylation of **1** and **2** in fair to good yields. Addition of 4-chlorophenyl isocyanate to compound **3** gave the corresponding 5-ureido-heptofuranuronate **10** in 95% yield.

Similarly, ureidoheptofuranuronates **11–19** were prepared by addition of substituted phenyl isocyanates to the glycosyl amino esters **4–9** in almost quantitative yields. The structures of ureido derivatives were determined on the basis of their spectroscopic data and elemental analysis. The ureido derivative **10** on heating with a combination of DBU/TBAB/4Å molecular sieve in refluxing toluene afforded 6-glycosyl dihydrouracil (**20**) in 90 % yield. Similarly dihydrouracil *C*-nucleosides (**21–29**) were obtained on reaction of ureidoheptofuranuronates (**11–19**) with the above cycloamidative reagent in refluxing toluene in respectable yields.

Configuration at C-5 in the ureidosugars and that of C-6 in the nucleosides is always that of the starting amino esters used. The relative configuration at C-5 in the furanosylated amino esters **1** and **2** has already been established[19,20,24] to be '*S*' based on Felkin-Anh transition state models and ^{1}H NMR spectrum. Since urea formation is simple addition of isocyanates to the amines, the configuration at the carbon linked to nitrogen does not change in this reaction. Further nucleoside formation does not involve C-5 and therefore the configuration at that centre is also unchanged.

In conclusion, we have developed an efficient and stereo-controlled synthesis of dihydropyrimidinone *C*-nucleosides. The method involves addition of isocyanates to the glycosyl amino esters followed by cyclization of glycosyl β-ureido esters with DBU/4Å molecular sieve and TBAB in refluxing toluene. The method is simple and applicable to synthesize a variety of *C*-nucleosides with well-defined stereochemistry.

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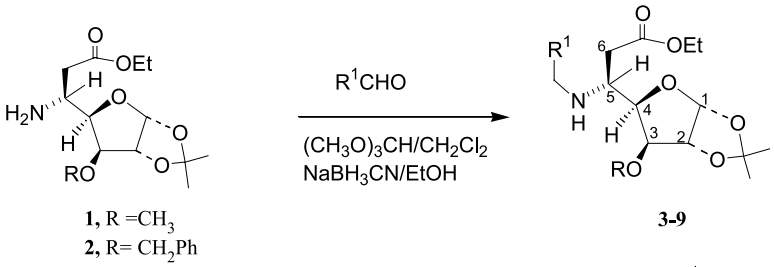

Comp.No.	R	R^1
3	CH_3	Ph
4	CH_3	4-OMe-Ph
5	CH_3	2-Cl-Ph
6	CH_3	3,4-di-OMe-Ph
7	CH_2Ph	4-OMe-Ph
8	CH_2Ph	2-Cl-Ph
9	CH_2Ph	3,4-di-OMe-Ph

Comp.No.	R	R^1	R^2
10, 20	CH_3	Ph	4-Cl-Ph
11, 21	CH_3	2-Cl-Ph	Ph
12, 22	CH_3	2-Cl-Ph	4-Cl-Ph
13, 23	CH_3	4-OMe-Ph	CH2Ph
14, 24	CH_3	3,4-di-OMe-Ph	Ph
15, 25	CH_3	3,4-di-OMe-Ph	CH2Ph
16, 26	CH_2Ph	2-Cl-Ph	Ph
17, 27	CH_2Ph	4-OMe-Ph	4-Cl-Ph
18, 28	CH_2Ph	3,4-di-OMe-Ph	Ph
19, 29	CH_2Ph	3,4-diOmePh	3-CH_3COPh

Scheme 1. Synthesis of C-glycosyl dihydropyrimidinones.

EXPERIMENTAL

General Methods. Thin-layer chromatographies were carried out on silica gel (Kiesel 60-F254, Merck), spots were visualized in iodine vapours and also by spraying with 5% sulfuric acid in alcohol followed by heating at 100°C. Column chromatographies were carried out on silica gel (silica gel 60, 70–230 mesh, Merck) using the indicated eluent. IR spectra of liquids were recorded as thin films on KBr plates with a Perkin Elmer 881 spectrophotometer. NMR spectra were recorded on 200 MHz or 300 MHz Bruker spectrometers and $CDCl_3$ was used as the reference. Chemical shifts are given as δ values and '*J*' values are given in Hertz (Hz). Elemental analyses were performed on a Perkin–Elmer 2400 II elemental analyzer. The optical rotations were measured in a 1.0 dm tube with a Jasco dip-140 polarimeter in chloroform, methanol or

ethyl acetate. Excess of the reagents or solvents were evaporated under reduced pressure at a bath temperature between 45–55°C.

Ethyl[5-Benzylamino-5, 6-dideoxy]-1, 2-*O*-isopropylidene-3-*O*-methyl-β-L-*ido*-heptofuranuronate (3): Ethyl 5-amino-5, 6-dideoxy-1, 2-*O*-isopropylidene-3-*O*-methyl-β-L-*ido*-heptofuranuronate (**1**) (1.5 g, 4.10 mmol) was dissolved in a mixture of trimethyl orthoformate and dichloromethane (2:5) and stirred magnetically at 0°C. Benzaldehyde (0.7 mL, 6.15 mmol) was added and stirring continued for another 4h at the same temperature. $NaCNBH_3$ (0.25g, 4.1 mmol) was added to the stirring reaction mixture and stirring continued for 12h at 30°C. Solvent was evaporated under reduced pressure and the residue was dissolved in ethyl acetate and washed with aqueous NH_4Cl (2 × 25 mL) followed by water (2 × 20 mL). The organic layer was separated and dried (Na_2SO_4) and was evaporated under reduced pressure to give the crude mass, which was all chromatographed over SiO_2 using hexane: ethyl acetate (4:1) to give compound **3**, as colourless oil, yield 2.16g (85%): R_f 0.38 (5:1 hexane/ethyl acetate); $[\alpha]^{20}_D$ −41.28 (*c*, 0.014, $CH_3COOC_2H_5$). MS (FAB): *m/z* 380 $(M + H)^+$. IR (KBr), ν_{max} cm^{-1}: 3355, 3048, 2978, 2923, 2845, 1721. ^1H NMR ($CDCl_3$): δ 7.34–7.31 (m, 5H, ArH), 5.90 (d, *J* = 3.7 Hz, 1H, H-1), 4.57 (d, *J* = 3.7 Hz, 1H, H-2.), 4.23 (dd, *J* = 8.6 Hz and 3.1 Hz, 1H, H-4), 4.14 (q, *J* = 7.1 Hz, 2H, $-OCH_2CH_3$), 3.90 (d, *J* = 12 Hz, 1H, $-NHCH_APh$), 3.85 (d, *J* = 12 Hz, 1H, $-NHCH_BPh$), 3.73 (d, *J* = 3.1 Hz, 1H, H-3), 3.42–3.39 (m, 1H, H-5), 3.36 (s, 3H, $-OCH_3$), 2.55 (dd, *J* = 15.6 Hz and 4.7 Hz, 1H, $H\text{-}6_A$), 2.43 (dd, *J* = 15.6 Hz and 6.6 Hz, 1H, $H\text{-}6_B$), 2.02 (br s, 1H, $-NHCH_2Ph$), 1.47 and 1.30 [2 s, each 3H, $C(CH_3)_2$], 1.25 (t, *J* = 7.1 Hz, 3H, $-OCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 172.1 (C = O), 140.9, 128.7, 127.2 (Ar-C) 111.9 [$C(CH_3)_2$] 105.2 (C-1), 84.6 (C-2) 82.8 (C-4), 81.6 (C-3), 60.8 ($-OCH_2CH_3$), 57.6 ($-OCH_3$), 54.3 (C-5), 51.9 ($-NCH_2$), 36.9 (C-6), 27.1 and 26.9 [$C(CH_3)_2$], 14.62 (CH_3) Anal. Calcd for $C_{20}H_{29}NO_6$: C, 63.32; H, 7. 65; N, 3.69. Found: C, 63.57; H, 7.83; N, 3.60.

Ethyl[5,6-Dideoxy-5-(4-methoxybenzyl amino)]-1,2-*O*-isopropylidene-3-*O*-methyl-β-L-*ido*-heptofuranuronate (4): Colourless oil, Yield 2.4 g (85 %), R_f 0.60 (3:2 hexane/ethyl acetate). $[\alpha]^{20}_D$ −25.90 (*c* 0.2625, $CHCl_3$). MS (FAB): *m/z* 410 $(M + H)^+$. IR (KBr), ν_{max}: 3341, 2983, 1730, 1247, 1177, 1028, 757 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.23 and 6.83 (2 d, *J* = 8.6 Hz, each 2H, ArH), 5.86 (d, *J* = 3.8 Hz 1H, H-1), 4.56 (d, *J* = 3.8 Hz, 1H, H-2), 4.18–4.07 (m, 4H, H-4, NCH_A and $-OCH_2$), 3.83–3.74 (m, 6H, $-NCH_B$, H-3, Ar–OCH_3 and H-5), 3.40 (s, 3H, OCH_3), 2.77–2.52 (m, 2 H, H-6) 1.67 (br s, 1H, –NH) 1.47 and 1.31 [2 s, each 3H, $C(CH_3)_2$], 1.24 (t, *J* = 7.1 Hz, 3H, $-OCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 172.8 (C = O) 159.0, 133.3, 129.6 114.1, (Ar-C) 111.9 [$C(CH_3)_2$], 105.1 (C-1), 84.2 (C-2), 82.2 (C-4), 81.8 (C-3), 60.6 ($-OCH_2CH_3$), 58.0 (Ar–OCH_3), 55.6 ($-OCH_3$), 52.5 (C-5), 51.3 ($-NCH_2$), 36.6 (C-6), 27.1 and 26.7 [$C(CH_3)_2$]and 14.64 (CH_3). Anal. Calcd for $C_{21}H_{31}NO_7$: C, 61.61; H, 7.58; N, 3.42. Found: C, 61.84; H, 7.72; N, 3.31.

Ethyl[5-(2-Chlorobenzylamino)-5,6-dideoxy]-1,2-*O*-isopropylidene-3-*O*-methyl-β-L-*ido*-heptofuranuronate (5): Colourless oil, Yield 3.0 g (70 %), R_f 0.70 (3:2 hexane/ethyl acetate). $[\alpha]^{20}_D$ −40.00 (*c* 0.225,$CHCl_3$). MS (FAB): *m/z* 415 $(M + H)^+$, IR(KBr), ν_{max}: 3355, 3048, 2978, 2923, 2845,1721 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.44 (d, *J* = 6.7 Hz, 1H, ArH), 7.33–7.16 (m, 3H, ArH), 5.91 (d, *J* = 3.6 Hz, 1H, H-1), 4.58 (d,

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J = 3.6 Hz, 1H, H-2), 4.24 (dd, *J* = 8.2 Hz and 2.8 Hz, 1H, H-4), 4.13 (q, *J* = 7.1 Hz, 2H, $-OCH_2CH_3$), 3.96 (s, 2H, $-NCH_2$), 3.74 (d, *J* = 2.8 Hz, 1H, H-3), 3.45–3.43 (m, 1H, H-5), 3.36 (s, 3H, $-OCH_3$), 2.61–2.50 (m 2H, H-6), 1.86 (br s, 1H, –NH) 1.48 and 1.32 [2 s, each 3H, $C(CH_3)_2$], 1.25 (t, *J* = 7.1 Hz, 3H, $-OCH_2CH_3$). Anal. Calcd for $C_{20}H_{28}NO_6Cl$: C, 58.04; H, 6.77; N, 3.38. Found: C, 58.32; H, 6.94; N, 3.11.

Ethyl[5,6-Dideoxy-5-(3,4-dimethoxybenzylamino)]-1,2-*O*-isopropylidene-3-*O*-methyl-β-L-*ido*-heptofuranuronate (6): Colourless oil, Yield 2.58 g (85 %), R_f 0.45 (3:2 hexane/ethyl acetate). $[\alpha]^{20}_D$ −40.21 (*c* 0.4625, $CH_3COOC_2H_5$). MS (FAB): *m/z* 440 $(M + H)^+$. IR (KBr), ν_{max}: 3343, 2985, 2368, 1731,1514, 1261, 857, 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.89–6.73 (m, 3H, ArH), 5.88 (d, *J* = 3.8 Hz, 1H, H-1), 4.56 (d, *J* = 3.8 Hz, 1H, H-2), 4.23–4.07 (m, 3H, H-4 and $-OCH_2$), 3.87–3.77 (m, 8H, $ArOCH_3$ and $NHCH_2$), 3.70 (d, *J* = 2.7 Hz, 1H, H-3), 3.38–3.36 (m, 1H, H-5), 3.34 (s, 3H, $-OCH_3$), 2.52 (dd, *J* = 16.8Hz and 5.2 Hz, 1H, $H\text{-}6_A$), 2.39 (dd, *J* = 16.8Hz and 5.6 Hz, 1H, $H\text{-}6_B$), 1.97 (br s, 1H, –NH) 1.45 and 1.29 [2 s, each 3H, $C(CH_3)_2$], 1.23 (t, *J* = 7.1 Hz, 3H, $-OCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 172.1 (C = O), 149, 148.3, 133.0, 120.6, 111.4, 112.7 (Ar-C), 111.9 [$C(CH_3)_2$], 105.1 (C-1), 84.5 (C-2), 82.8 (C-4), 81.5 (C-3), 60.7 ($-OCH_2CH_3$), 57.7 ($-OCH_3$), 56.3, 56.2 ($Ar-OCH_3$), 54.2 (C-5), 51.6 ($-NCH_2$), 36.8 (C-6), 27.1 and 26.6 [$C(CH_3)_2$], 14.6 (CH_3). Anal. Calcd for $C_{22}H_{33}NO_8$: C, 60.13; H, 7.51; N, 3.19. Found: C, 60.31; H, 7.68; N, 3.05.

Ethyl[3-*O*-Benzyl-5,6-dideoxy-1,2-*O*-isopropylidene]-5-(4-methoxybenzylamino)-β-L-*ido*-heptofuranuronate (7): Colourless oil, Yield 2.25 g (86 %), R_f 0.38 (5:1 hexane/ethyl acetate). $[\alpha]^{20}_D$ −15.46 (*c* 0.37, $CHCl_3$). MS (FAB): *m/z* 486 $(M + H)^+$. IR (KBr), ν_{max}: 3339, 2987, 2431, 1729, 1612, 1513, 1378, 1248, 1078, 758 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.31–7.25 (m, 5H, ArH), 7.21 and 6.81 (2 d, *J* = 8.4 Hz, each 2H, ArH), 5.94 (d, *J* = 3.8 Hz, 1H, H-1), 4.69 and 4.44 (2 d, *J* = 11.7 Hz, each 1H, $-OCH_A$ and OCH_B), 4.63 (d, *J* = 3.8 Hz, 1H, H-2), 4.23 (dd, *J* = 9.6 and 3.0 Hz, 1H, H-4), 4.10 (q, *J* = 7.1 Hz, 2H, OCH_2), 3.99 (d, *J* = 3.0 Hz, 1H, H-3) 3.80–3.77 (m, 5H, $-NHCH_2$ and $Ar-OCH_3$), 3.52–3.48 (m, 1H, H-5), 2.42–2.31 (m, 2H, H-6), 1.95 (br s, 1H, –NH), 1.47 and 1.32 [2 s, each 3H, $C(CH_3)_2$], 1.22 (t, *J* = 7.1 Hz, 3H, $-OCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 172.1 (C = O), 137.4, 133.0, 131.9, 131.7, 129.8, 129.0, 128.8, 128.5, 128.4, 128.2, 127.3, 114.1 (Ar-C), 112.0 [$C(CH_3)_2$], 105.2 (C-1), 82.6 (C-2), 82.2 (C-4), 82.1 (C-3), 71.9 ($-OCH_2Ph$), 60.8 ($-OCH_2CH_3$), 55.6 ($Ar-OCH_3$), 54.1(C-5), 51.4 ($-NCH_2$), 36.8 (C-6), 27.1 and 26.7 [$C(CH_3)_2$], 14.6 (CH_3). Anal. Calcd for $C_{27}H_{35}NO_7$: C, 66.80; H, 7.21; N, 2.88. Found: C, 66.97; H, 7.37; N, 2.82.

Ethyl[3-*O*-Benzyl-5-(2-chlorobenzylamino)]-5,6-dideoxy-1,2-*O*-isopropylidene-β-L-*ido*-heptofuranuronate (8): Colourless oil, Yield 2.1 g (74 %), R_f 0.65 (3:2 hexane/ethyl acetate). $[\alpha]^{20}_D$ −20.32 (*c* 0.7625,$CHCl_3$). MS (FAB): *m/z* 491 $(M + H)^+$. IR (KBr), ν_{max}: 2984, 1731, 1454, 1377, 1216, 1078, 754 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.42 − 7.22 (m, 7H, ArH), 7.18 − 7.14 (m, 2H, ArH), 5.95 (d, *J* = 3.7 Hz 1H, H-1), 4.68 and 4.44 (2 d, *J* = 11.8 Hz, each 1H, $-OCH_A$ and OCH_B), 4.63 (d, *J* = 3.7 Hz, 1H, H-2), 4.25 (dd, *J* = 8.6 and 2.7 Hz, 1H, H-4), 4.07 (q, *J* = 7.1 Hz, 2H, OCH_2), 3.94 (s, 3H, $NHCH_2$ and H-3), 3.54–3.49 (m, 1H, H-5), 2.56 (dd, *J* = 10.7 Hz and 4.5 Hz, each 1H, $H\text{-}6_A$), 2.39 (dd, *J* = 10.7 Hz and 4.5 Hz, each 1H, $H\text{-}6_B$), 1.96 (br s, 1H, –NH) 1.48 and 1.31 [2 s, each 3H, $C(CH_3)_2$], 1.20 (t, *J* = 7.1 Hz, 3H, $-OCH_2CH_3$). ^{13}C NMR

($CDCl_3$): δ 172.1 (C = O), 138.5, 137.5, 134.1, 130.5, 129.7, 128.9, 128.4, 127.1 (Ar-C), 112.0 [$C(CH_3)_2$], 105.3 (C-1), 82.7 (C-2), 82.2 (C-4), 74.9 (C-3), 71.9 ($-OCH_2Ph$), 60.8 ($-OCH_2CH_3$), 54.1 (C-5), 49.2 ($-NCH_2$), 36.8 (C-6), 27.2 and 26.7 [$C(CH_3)_2$], 14.6 (CH_3). Anal. Calcd for $C_{26}H_{32}NO_6Cl$: C, 63.73; H, 6.53; N, 2.86. Found: C, 63.91; H, 6.72; N, 2.78.

Ethyl[3-*O*-Benzyl-5,6-dideoxy-5-(3,4-dimethoxybenzylamino)]-1,2-*O*-isopropylidene-β-L-*ido*-heptofuranuronate (9): Colourless oil; yield 2.64 g (85 %), R_f 0.65 (3:2 hexane/ethyl acetate), $[\alpha]^{20}_D$ −32.0 (*c* 0.225,$CHCl_3$), MS (FAB): *m/z* 517 $(M + H)^+$, IR (KBr), ν_{max} : 3355, 3048, 2978, 2923, 2845, 1721, 1207, 1078, 752 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.31–7.28 (m, 5H, ArH), 6.81–6.75 (m, 3H, ArH), 5.90 (d, *J* = 3.8 Hz 1H, H-1), 4.68 and 4.53 (2 d, *J* = 11.7 Hz, each 1H, $-OCH_A$ and OCH_B), 4.60 (d, *J* = 3.8 Hz, 1H, H-2), 4.21–4.07 (m, 4H, $-NHCH_A$, H-4 and $-OCH_2$), 3.84 and 3.82 (2 s, each 3 H, $ArOCH_3$), 3.75–3.64 (m, 2H, $-NHCH_B$ and H-3), 3.64–3.61 (m, 1H, H-5), 2.82 (dd, *J* = 16.8 Hz and 4.2 Hz, 1H, H-6_A), 2.56 (dd, *J* = 16.8Hz and 6.70 Hz, 1H, H-6_B), 1.61 (br s, 1H, −NH) 1.47 and1.31 [2 s, each 3H, $C(CH_3)_2$], 1.24 (t, *J* = 7.1 Hz, 3H, $-OCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 173.0 (C = O), 150.2,149.2, 138.4, 134.6, 129.8,129.3, 128.9, 121.6, 113.1 (Ar-C), 112.7 [$C(CH_3)_2$], 106.2 (C-1), 83.6 (C-2), 83.1 (C-4), 83.0 (C-3), 72.8 ($-OCH_2Ph$), 61.6 ($-OCH_2CH_3$), 57.2, 57.1 ($Ar-OCH_3$), 54.9 ($-NCH_2$) 52.6 (C-5), 37.7 (C-6), 28.0 and 27.6 [$C(CH_3)_2$], 15.5 (CH_3). Anal. Calcd for $C_{28}H_{37}NO_8$: C, 65.24; H, 7.18; N, 2.71. Found: C, 64.89; H, 7.35; N, 2.69.

Ethyl 5-[*N*-Benzyl-*N′*-(4-chlorophenyl)ureido]5,6-dideoxy-1,2,-*O*-isopropylidene-3-*O*-methyl-β-L-*ido*-heptofuranuronate (10) General Procedure: The above amino ester **3** (1.0 g, 2.64 mmol) and 4-chlorophenyl isocyanate (0.407g, 2.65 mmol) in anhydrous dichloromethane (15.0 ml) were magnetically stirred at 25°C temperature for 2 h. Solvent was evaporated and the reaction mixture was chromatographed over a SiO_2 column using a gradient of hexane: ethyl acetate (3:2) as eluent to give compound **10** as colourless foam; 1.48 g (95 %). R_f 0.40 (3:2 hexane/ethyl acetate), $[\alpha]_D^{20}$ −44.0 (*c* 0.2,$CHCl_3$). MS (FAB): *m/z* 534 $(M + H)^+$. IR (Neat) ν_{max}: 3370, 3306, 2926, 2372, 1712, 1665, 1602, 1546, 1212, 1078, 717 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.42–7.34 (m, 9H, ArH), 5.97 (d, *J* = 3.8 Hz, 1H, H-1), 4.86 and 4.24 (2 d, *J* = 15.3 Hz, each 1H, NCH_A and $-NCH_B$), 4.66 (d, *J* = 3.8 Hz, 1H, H-2), 4.44–4.40 (m, 2H, H-4, H-5), 4.08 (q, *J* = 7.1 Hz, 2H, $-OCH_2$), 3.63(d, *J* = 2.8 Hz, 1H, H-3), 3.39 (s, 3H, $-OCH_3$), 2.82–2.76 (m, 1H, H-6_A), 2.47 (dd, *J* = 15.7 and 3.6 Hz, 1H, H-6_B), 1.47 and 1.31 [2 s, each 3H, $C(CH_3)_2$] 1.24 (t, *J* = 7.1 Hz, 3H, $-OCH_2CH_3$). $^{13}CNMR$ ($CDCl_3$): δ 172.3 (C = O), 157.8 (NHCO), 129.2, 129.1, 122.3 (Ar-C), 112.2 [$C(CH_3)_2$], 105.0 (C-1), 84.3 (C-2), 81.3 (C-4), 79.7 (C-3), 61.4 ($-OCH_2CH_3$), 57.1 ($-OCH_3$), 34.9 (C-6), 27.1 and 26.5 [$C(CH_3)_2$], 14.4 (CH_3). Anal. Calcd for $C_{27}H_{33}N_2O_7Cl$: C, 60.84; H, 6.19; N, 5.25 Found: C, 60.72; H, 6.43; N, 5.14.

Ethyl 5-[*N*-(2-Chlorobenzyl)-*N′*-phenylureido]-5,6-dideoxy-1,2,-*O*-isopropylidene-3-*O*-methyl-β-L-*ido*-heptofuranuronate (11): Colourless foam; yield 0.48g (95 %), R_f 0.55 (3:2 hexane/ethyl acetate), $[\alpha]_D^{20}$ −92.0 (*c* 0.05,$CHCl_3$).MS (FAB) *m/z* = 436. IR (Neat) ν_{max}: 3342, 1717, 1670, 1543, 1079, 1022, 889, 755 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.41 (bs, 1H, NH), 7.47–6.98 (m, 9 H, ArH), 5.85 (d, *J* = 3.7 Hz, 1H, H-1), 4.97 and 4.47 (2 d, *J* = 16.3 Hz, each 1H, $-NCH_APh$ and $-NCH_BPh$), 4.73–4.65 (m, 1H,

H-5), 4.52 (d, J = 3.7 Hz, 1H, H-2), 4.24 (dd, J = 6.34 and 2.8 Hz, 1H, H-4), 4.10 (q, J = 7.1 Hz, 2H, $-OCH_2$), 3.45 (d, J = 2.8 Hz, 1H, H-3), 3.31(s, 3H, OCH_3), 2.91 (dd, J = 17.4 and 3.2 Hz, 1H, H-6_A), 2.70 (dd, J = 17.4 and 11.5 Hz, 1H, H-6_B), 1.44 and 1.29 [2 s, each 3H, $C(CH_3)_2$], 1.17 (t, J = 7.1 Hz, 3H, $-OCH_2CH_3$). Anal. Calcd for $C_{27}H_{33}N_2O_7Cl$: C, 60.84; H, 6.19; N, 5.25. Found: C, 61.03; H, 6.04; N, 5.39.

Ethyl 5-[*N*-(2-Chlorobenzyl)-*N*′-(4-chlorophenyl)ureido]-5,6-dideoxy-1,2,-*O*-isopropylidene-3-*O*-methyl-β-L-*ido*-heptofuranuronate (12): Colourless foam; yield 1.04 g (96 %), R_f 0.50 (3:2 hexane/ethyl acetate), $[\alpha]_D^{20}$ −50.0 (c 0.150,$CHCl_3$). MS (FAB): m/z 568 $(M + H)^+$. IR (Neat) ν_{max}: 2996, 2405, 1723, 1668, 1529, 1384, 1222, 1084, 1052, 759, 688 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.80 (br s, 1H, NH), 7.45(d, J = 6.7 Hz, 1H, ArH), 7.34 − 7.13 (m, 7H, ArH), 5.91 (d, J = 3.7 Hz, 1H, H-1), 4.83–4.62 (m, 3H, $-NCH_APh$, $-NCH_BPh$ and H-5), 4.61 (d, J = 3.7 Hz, 1H, H-2), 4.35–4.32 (m, 1H, H-4), 4.11 (q, J = 7.1 Hz, 2H, $-OCH_2$), 3.60 (d, J = 2.9Hz, 1H, H-3), 3.39 (s, 3H, OCH_3), 2.67 (dd, J = 16.4 and 9.8 Hz, 1H, H-6_A), 2.70 (dd, J = 16.4 and 3.7 Hz, 1H, H-6_B), 1.36 and 1.30 [2 s, each 3H, $C(CH_3)_2$], 1.20 (t, J = 7.1 Hz, 3H, $-OCH_2CH_3$). Anal. Calcd for $C_{27}H_{32}N_2O_7$: C, 57.14; H, 5.64; N, 4.93. Found: C, 57.22; H, 5.69; N, 4.76.

Ethyl 5-[*N*-(4-Methoxybenzyl)-*N*′-benzylureido]-5,6-dideoxy-1,2,-*O*-isopropylidene-3-*O*-methyl-β-L-*ido*-heptofuranuronate (13): Colourless foam; Yield 1.25 g (95 %), R_f 0.40 (3:2 hexane/ethyl acetate), $[\alpha]_D^{20}$ −54.66 (c 0.150, $CHCl_3$). MS (FAB): m/z 543 $(M + H)^+$. IR (Neat) ν_{max}: 3428, 2989, 2386, 1730, 1646, 1517, 1246, 1081, 759 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.29–7.13 (m, 7H, ArH), 6.81(d, J = 8.6 Hz, 2H, ArH), 5.88 (d, J = 3.8 Hz, 1H, H-1), 5.10 (br s, 1H, NH), 4.58 (d, J = 3.8 Hz, 1H, H-2), 4.52–4.44 (m, 4H, NCH_2, H-5 and H-4), 4.36 (d, J = 5.3 Hz, 2H, $-NHCH_2$), 4.08 (q, J = 7.1 Hz, 2H, $-OCH_2$), 3.77 (s, 3H, Ar$-OCH_3$), 3.58 (d, J = 2.2Hz, 1H, H-3), 3.34 (s, 3H, OCH_3), 2.80 (m, 1H, H-6_A), 2.42 (dd, J = 15.5 and 3.7 Hz, 1H, H-6_B), 1.39 and 1.30 [2 s, each 3H, $C(CH_3)_2$], 1.19 (t, J = 7.1 Hz, 3H, $-OCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 171.6 (C = O), 159.5 (NHC = O), 159.2, 140.2, 131.3, 128.6, 128.6, 127.6, 127.2, 114.5 (Ar-C), 112.1 [$C(CH_3)_2$], 105.0 (C-1), 84.2 (C-2), 81.2 (C-4), 80.1 (C-3), 61.2 ($-OCH_2CH_3$), 57.6 (Ar$-OCH_3$), 55.6 ($-OCH_3$), 45.1 ($-NCH_2$), 36.1 (C-6), 27.1 and 26.8 [$C(CH_3)_2$], 14.5 (CH_3). Anal. Calcd for $C_{29}H_{38}N_2O_8$: C, 64.20; H, 7.01; N, 5.16. Found: C, 64.48; H, 7.33; N, 4.97.

Ethyl 5,6-Dideoxy-5-[*N*-(3,4-dimethoxybenzyl)-*N*′-phenylureido]-1,2,-*O*-isopropyli-dene-3-*O*-methyl-β-L-*ido*-heptofuranuronate (14): Colourless foam; yield 1.20 g (95 %), R_f 0.35 (3:2 hexane/ethyl acetate), $[\alpha]_D^{20}$ −11.5 (c 0.40,$CHCl_3$). MS (FAB): m/z 559 $(M + H)^+$. IR (Neat) ν_{max}: 3343, 2938, 2838, 1720, 1667, 1601, 1518, 1450, 1254, 1080, 1023, 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.10 (br s, 1H, NH), 7.43–7.39, 7.29–7.21, 6.97–6.87, 6.81–6.78 (4 m, each 2 H, ArH), 5.86 (d, J = 3.8 Hz, 1H, H-1), 4.75 and 4.37 (2 d, J = 15.0 Hz, each 1H, NCH_A and NCH_B), 4.50 (d, J = 3.8 Hz, 1H, H-2), 4.24 (dd, J = 7.9 and 3.1 Hz, 1H, H-4), 4.18–4.04 (m, 3H, $-OCH_2$ and H-5), 3.84 and 3.83 (2 s, each 3H, Ar$-OCH_3$), 3.50 (d, J = 3.1Hz, 1H, H-3), 3.31 (s, 3H, OCH_3), 2.85 (dd, J = 16.8 and 3.2 Hz, 1H, H-6_A), 2.81 (dd, J = 16.8 and 10.0 Hz, 1H, H-6_B), 1.43 and 1.29 [2 s, each 3H, $C(CH_3)_2$], 1.19 (t, J = 7.1 Hz, 3H, $-CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 173.3 (C = O), 157.2 (NHC = O), 149.6, 148.7, 140.3, 132.4, 129.2,

122.6, 120.2, 119.4 (Ar-C), 112.2 [$C(CH_3)_2$], 111.6, 111.4 (Ar-C), 105.3 (C-1), 84.3 (C-2), 81.5 (C-4), 80.7 (C-3), 61.5 ($-OCH_2CH_3$), 58.10 ($-OCH_3$), 56.3, 56.3 (Ar$-OCH_3$), 53.80 (C-5), 35.9 (C-6), 27.1 and 26.5 [$C(CH_3)_2$], 14.6 (CH_3). Anal. Calcd for $C_{29}H_{38}N_2O_9$: C, 62.36; H, 6.81; N, 5.01. Found: C, 62.48; H, 6.44; N, 4.81.

Ethyl 5[*N*′-Benzyl-*N*-(3,4-dimethoxybenzyl)ureido]-5,6-dideoxy-1,2,-*O*-isopropyli-dene-3-*O*-methyl-β-L-*ido*-heptofuranuronate (15): Colourless foam, yield 1.23 g (96 %), R_f 0.40 (3:2 hexane/ethyl acetate), $[\alpha]_D^{20}$ −23.29 (*c* 0.85,$CHCl_3$). MS (FAB): *m/z* 573 $(M + H)^+$. IR (Neat) ν_{max}: 3404, 2989, 2368, 1730, 1646, 1519, 1259, 856, 755, 599 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.27−7.16 (m, 3H, ArH), 7.11−7.09 (m, 2H, ArH), 6.77−6.74 (m, 3H, ArH), 5.86 (d, *J* = 3.7 Hz, 1H, H-1), 5.13 (br s, 1H, NH), 4.58 (d, *J* = 3.7 Hz, 1H, H-2), 4.49−4.28 (m, 5H, $-NCH_2$, $-NHCH_2$ and H-5), 4.14−4.04 (m, 3H, H-4, and $-OCH_2$), 3.83 and 3.81 (2 s, each 3H, $ArOCH_3$), 3.58 (s, 1H, H-3), 3.35 (s, 3H, OCH_3), 2.94-2.86 (m, 1H, H-6_A), 2.44 (dd, *J* = 15.3 and 3.1 Hz, 1H, H-6_B), 1.35 and 1.29 [2 s, each 3H, $C(CH_3)_2$], 1.24 (t, *J* = 7.3 Hz, 3H, OCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 171.7 (C = O), 159.3 (NHC = O), 149.9, 148.6, 140.10, 131.8 128.9, 128.7, 127.9, 127.8 127.5, 127.4, 127.1, 118.9, 112.2 (Ar-C), 112.0 [$C(CH_3)_2$], 111.4, 111.2, 110.8 (Ar-C), 105.1 (C-1), 84.1 (C-2), 81.5 (C-4), 80.1 (C-3), 61.2 ($-OCH_2CH_3$), 57.7 ($-OCH_3$), 56.3, 56.2 (Ar$-OCH_3$), 45.4 ($-NCH_2$), 36.7 (C-1), 27.1 and 26.8 [$C(CH_3)_2$] 14.6 (CH_3). Anal. Calcd for $C_{30}H_{40}N_2O_9$: C, 62.93; H, 6.99; N, 4.89. Found: C, 61.8; H, 7.08; N, 4.63.

Ethyl 3-*O*-Benzyl-5-[*N*-(2-chlorobenzyl)-*N*′-phenylureido]-5,6-dideoxy-1,2,-*O*-isopropylidene-β-L-*ido*-heptofuranuronate (16): Colourless foam, yield 1.1 g (90 %), R_f 0.45 (3:2 hexane/ethyl acetate), $[\alpha]_D^{20}$ −12.5 (*c* 0.2,$CHCl_3$). MS (FAB): *m/z* 610 $(M + H)^+$. IR (Neat) ν_{max}: 3343, 2995, 2934, 2363, 1729, 1834, 1524, 1450, 1378, 1174, 1081, 1023, 853, 758 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.7 (br s, 1H, NH), 7.46−7.43 (m, 2H, ArH), 7.34−7.15 (m, 10H, ArH), 7.00−6.95 (m, 2H, ArH), 5.95 (d, *J* = 3.6 Hz, 1H, H-1), 4.86−4.54 (m, 5H, $-OCH_APh$, H-2, -NCH_2 and H-5), 4.40 (d, *J* = 11.9 Hz, 1H, $-OCH_B$), 4.34−4.30 (m, 1H, H-4), 4.05 (q, *J* = 7.1 Hz, 2H, $-OCH_2$), 3.77 (s, 1H, H-3), 2.56−2.43 (m, 1H, H-6_A), 2.00 (dd, *J* = 16.5 and 2.4 Hz, 1H, H-6_B), 1.55 and 1.37 [2 s, each 3H, $C(CH_3)_2$], 1.25 (t, *J* = 7.14 Hz, 3H, $-OCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 171.8 (C = O), 157.7 (NHC = O), 140.1, 137.0, 136.7, 132.6, 129.7, 129.6, 129.3, 129.1, 128.8 128.6, 127.5, 123.6, 120.2 (Ar-C), 111.9 [$C(CH_3)_2$], 105.2 (C-1), 82.2 (C-2), 80.9 (C-4), 79.5 (C-3), 71.8 ($-OCH_2Ph$), 61.5 ($-OCH_2CH_3$), 52.5 ($-NCH_2$), 34.8 (C-6), 27.2 and 26.8 [$C(CH_3)_2$], 14.5 (CH_3). Anal. Calcd for $C_{33}H_{37}N_2O_7Cl$: C, 65.07; H, 6.08; N,4.60. Found: C, 65.36; H, 6.32; N, 4.34.

Ethyl 3-*O*-Benzyl-5-[*N*′-(4-chlorophenyl)-*N*-(4-methoxybenzyl)ureido]-5,6-dideoxy-1,2-*O*-isopropylidene-β-L-*ido*-heptofuranuronate (17): Colourless foam, yield 1.25g (%), R_f 0.40 (3:2 hexane/ethyl acetate) $[\alpha]_D^{20}$ −13.81 (*c* 0.1375,$CHCl_3$). MS (FAB): *m/z* 640 $(M + H)^+$. IR (Neat) ν_{max}: 2992, 2312, 1729, 1682, 1597, 1426, 1211, 870, 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.59 (bs, 1H, NH), 7.30−7.23 (m, 8H, ArH), 7.16 (s, 3H, ArH), 6.82(d, *J* = 8.54 Hz, 2H, ArH), 5.96 (d, *J* = 3.7 Hz, 1H, H-1), 4.72 and 4.40 (2 d, *J* = 11.7 Hz, each 1H, OCH_A and OCH_B), 4.66 (d, *J* = 3.7 Hz, 1H, H-2), 4.56-4.37 (m, 4H, N-CH_2, H-4 and H-5), 4.08 (q, *J* = 7.1 Hz, 2H,-OCH_2), 3.76 (s, 4H, $-OCH_3$ and H-3), 2.84−2.77 (m, 1H, H-6_A), 2.03 (dd, *J* = 16.7 and 2.2 Hz, 1H, H-6_B), 1.40, 1.31 [2 s, each 3H, $C(CH_3)_2$], 1.23 (t, *J* = 7.14 Hz, 3H, $-OCH_2CH_3$). ^{13}C

NMR ($CDCl_3$): δ 171.9 (C = O), 159.2 (NHC = O), 139.1, 137.0, 128.2, 128.8, 128.7, 128.6, 121.1, 114.6 (Ar-C), 112.0 [$C(CH_3)_2$], 105.1 (C-1), 82.2 (C-2), 81.0 (C-4), 79.6 (C-3), 71.9 ($-OCH_2Ph$), 61.4 ($-OCH_2CH_3$), 55.6 ($-NCH_2$), 35.1 (C-6), 27.1 and 26.7 [$C(CH_3)_2$], 14.5 (CH_3). Anal. Calcd for $C_{34}H_{39}N_2O_8Cl$: C, 63.89; H, 6.10; N, 4.38. Found: C, 63.67; H, 6.35; N, 4.10.

Ethyl 3-*O*-Benzyl-5,6-dideoxy-5-[*N*-(3,4-dimethoxybenzyl)-*N*′-phenylureido]-1,2,-*O*-isopropylidene-β-L-*ido*-heptofuranuronate (18): Colourless foam, yield 0.66 g (90 %), R_f 0.40 (3:2 hexane/ethyl acetate). $[\alpha]_D^{20}$ −14.0 (*c* 0.05, $CHCl_3$). MS (FAB): *m/z* 658 $(M + Na)^+$. IR (Neat) ν_{max}: 3408, 1718, 1658, 1516, 1232, 1077, 1025, 857, 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.31–6.98 (m, 10H, ArH), 6.84–6.76 (m, 3H, ArH), 5.96 (d, *J* = 3.8 Hz, 1H, H-1), 4.72 and 4.41 (2 d, *J* = 11.7 Hz, each 1H, OCH_APh and OCH_BPh), 4.68 (d, *J* = 3.8 Hz, 1H, H-2), 4.56–4.38 (m, 3H, NCH_2 and H-4), 4.12 (q, *J* = 7.1 Hz, 2H, OCH_2), 3.86 and 3.85 (2 s, each 3H, $Ar-OCH_3$), 3.78 (d, *J* = 2.3 Hz, 1H, H-3), 3.58-3.42 (m, 1H, H-5), 2.78–2.62 (m, 1H, H-6_A), 2.11 (d, *J* = 14.7 Hz, 1H, H-6_B), 1.39 and 1.27 [2 s, each 3H, $C(CH_3)_2$], 1.25 (t, *J* = 7.1 Hz, 3H, $-OCH_2CH_3$). Anal. Calcd for $C_{35}H_{42}N_2O_9$: C, 66.24; H, 6.62; N, 4.41. Found: C, 66.85; H, 7.01; N, 4.02.

Ethyl x5-[*N*′-(3-Acetylphenyl)-*N*-(3,4-dimethoxybenzyl)ureido]-3-*O*-benzyl-5,6-dideoxy-1,2,-*O*-isopropylidene-β-L-*ido*-heptofuranuronate (19): Colourless foam, yield 0.70 g (89 %), R_f 0.35 (3:2 hexane/ethyl acetate), $[\alpha]_D^{20}$ −29.77 (*c* 0.225, $CHCl_3$). MS (FAB): *m/z* 677 $(M + H)^+$. IR (Neat) ν_{max}: 3012, 2369, 1729, 1677, 1594, 1518, 1263, 1077, 898, 755 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.8 (bs, 1H, NH), 7.63–7.57 (m, 1H, ArH), 7.52–7.26 (m, 8H, ArH), 6.83–6.80 (m, 2H, ArH), 5.98 (d, *J* = 3.8 Hz, 1H, H-1), 4.74 and 4.40 (2 d, *J* = 11.9 Hz, each 1H, $-OCH_APh$ and OCH_BPh), 4.68 (d, *J* = 3.8 Hz, 1H, H-2), 4.55 (s, 2H, NCH_2), 4.17–4.06 (m, 4H, H-4, H-5 and $-OCH_2$), 3.84 (s, 6H, $Ar-OCH_3$), 3.77 (d, *J* = 2.4 Hz, 1H, H-3), 2.57–2.55 (m, 5H, $ArCOCH_3$ and H-6), 1.37 and 1.31 [2 s, each 3H, $C(CH_3)_2$], 1.25 (t, *J* = 7.4 Hz, 3H, $-OCH_2CH_3$). Anal. Calcd for $C_{37}H_{44}N_2O_{10}$: C, 65.68; H, 6.50; N, 4.14. Found: C, 66.12; H, 7.08; N, 3.95.

General Procedure for the synthesis of compounds 20–29: (6*S*)-1-Benzyl-3-(4-chlorophenyl)-5,6-dihydro-6-(1,2-*O*-isopropylidene-3-*O*-methyl-α-D-*xylo*-tetrofuranos-4-yl)uracil (20): A mixture of compound **10** (0.3 g, 0.564 mmol), 4Å MS (0.03 g), TBAB (0.03 g, 0.093 mmol) and DBU (0.086 mL, 0.564 mmol) in anhydrous toluene (15 mL) was heated at reflux for 2 h. The solvent was evaporated and the residue was chromatographed over a SiO_2 column using a gradient of hexane: ethyl acetate (3:1) as eluent to give **20** as a colourless foam, yield 0.260 g (95 %). R_f 0.45 (3:2 Hexane/ethyl acetate), $[\alpha]_D^{25}$ −17.77 (*c* 0.1125,$CHCl_3$). MS (FAB): *m/z* 488. IR (Neat) ν_{max}: 3450, 2937, 2376, 1678 1599, 1450, 1372, 1203, 1082, 1018, 704 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.41 (d, *J* = 8.4 Hz, 2 H, ArH), 7.34–7.30 (m, 5H, ArH), 7.11 (d, *J* = 8.4 Hz, 2 H, ArH), 5.98 (d, *J* = 3.6 Hz, 1H, H-1′), 5.40 and 4.28 (2 d, *J* = 15.3 Hz, each 1H, NCH_A and NCH_B), 4.61 (d, *J* = 3.6 Hz, 1H, H-2′), 4.44 (d, *J* = 9.3 Hz, 1H, H-4′), 3.87–3.82 (m, 1H, H-6), 3.70 (s, 1H, H-3′), 3.36 (s, 3H, OCH_3), 2.87 (dd, *J* = 16.8 and 6.6 Hz, 1H, H-5_A), 2.56 (d, *J* = 16.8 Hz, 1H, H-5_B), 1.49 and 1.34 [2 s, each 3H, $C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 168.1 (C = O), 157.6 (NC = ON), 157.1, 134.1, 133.8, 129.9, 129.2, 128.7, 128.2, 127.6 (Ar-C), 111.8 [$C(CH_3)_2$], 105.0 (C-1), 83.6 (C-2), 80.7 (C-4), 80.3(C-3), 57.3

($-OCH_3$), 51.4 (C-6), 49.7 ($-NCH_2$), 34.6 (C-5), 26.6 and 26.0 [$C(CH_3)_2$]. Anal. Calcd for $C_{25}H_{27}N_2O_6Cl$: C, 61.66; H, 5.54; N, 5.75. Found: C, 61.97; H, 5.76; N, 5.62. Similarly, compounds **21–29** were synthesized from the corresponding ureido derivatives.

(6*S*)-1-(2-Chlorobenzyl-3-phenyl-5,6-dihydro-6-(1,2-*O*-isopropylidene-3-*O*-methyl-α-D-*xylo*-tetrofuranos-4-yl)uracil (21): Colourless foam, yield 0.24 g (90 %), R_f 0.45 (3:2 hexane/ethyl acetate). $[\alpha]_D^{25}$ −39.04 (*c* 0.3125, $CHCl_3$). MS (FAB): *m/z* 488 $(M + H)^+$. IR (Neat) ν_{max}: 3434, 2981, 2244, 1673, 1456, 1374, 1210, 1070, 1012, 858, 758 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.47–7.17 (m, 9H, ArH), 5.88 (d, *J* = 3.7 Hz, 1H, H-1′), 5.13 and 4.52 (2 d, *J* = 15.1 Hz, each 1H, NCH_A and NCH_B), 4.59 (d, *J* = 3.7 Hz, 1H, H-2′), 4.37–4.33 (m, 1H, H-4′), 4.00–3.96 (m, 1H, H-6), 3.76 (d, *J* = 3.4 Hz, 1H, H-3′), 3.75 (s, 3H, OCH_3), 3.18 (d, *J* = 16.8 Hz, 1H, H-5_A), 2.85 (dd, *J* = 16.9 and 6.5 Hz, 1H, H-5_B), 1.44 and 1.32 [2 s, each 3H, $C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 169.30 (C = O), 154.0 (NC = ON), 136.1, 134.8, 133.9, 131.2, 130.2, 129.7, 129.4, 129.2, 128.6, 127.8 (Ar-C), 112.4 [$C(CH_3)_2$], 105.4 (C-1), 84.9 (C-2), 81.2 (C-4), 80.1 (C-3), 57.6 ($-OCH_3$), 51.1 (C-6), 48.7 ($-NCH_2$), 34.6 (C-5), 27.3 and [$C(CH_3)_2$] 26.6. Anal. Calcd for $C_{25}H_{27}N_2O_6Cl$: C, 61.66; H, 5.55; N, 5.75. Found: C, 61.89; H, 5.84; N, 5.32.

(6*S*)-1-(2-Chlorobenzyl)-3-(4-chlorophenyl)-5,6-dihydro-6-(1,2-*O*-isopropylidene-3-*O*-methyl-α-D-*xylo*-tetrofuranos-4-yl)uracil (22): Colourless foam, yield 0.61 g (95 %), R_f 0.40 (3:2 hexane/ethyl acetate). $[\alpha]_D^{25}$ −2.66 (*c* 0.1875, $CHCl_3$). MS (FAB): *m/z* 522 $(M + H)^+$. IR (Neat) ν_{max}: 3403, 2986, 2939, 2377, 1688, 1592, 1458, 1368, 1194, 1077, 1023, 853, 754 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.44–7.37 (m, 4H, ArH), 7.25–7.22 (m, 2H, ArH), 7.07 (d, *J* = 8.6 Hz, 2H, ArH), 5.98 (d, *J* = 3.8 Hz, 1H, H-1′), 5.26 and 4.51 (2 d, *J* = 14.2 Hz, each 1H, NCH_A and NCH_B), 4.61 (d, *J* = 3.8 Hz, 1H, H-2′), 4.45 (dd, *J* = 9.9 and 2.7Hz, 1H, H-4′), 4.02–3.97 (m, 1H, H-6), 3.72 (d, *J* = 2.7 Hz, 1H, H-3′), 3.38 (s, 3H, OCH_3), 3.05 (dd, *J* = 16.9 and 6.5 Hz, 1H, H-5_A), 2.59 (d, *J* = 16.8 Hz, 1H, H-5_B), 1.49 and 1.34 [2 s, each 3H, $C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 166.4 (C = O), 150.7 (NC = ON), 132.7, 132.4, 131.9, 129.6, 128.1, 127.9, 127.4, 127.2, 125.0 (Ar-C), 110.1 [$C(CH_3)_2$], 103.3 (C-1), 81.8 (C-2), 78.9 (C-4), 78.8 (C-3), 55.6 ($-OCH_3$), 49.2 (C-6), 48.8 ($-NCH_2$), 35.0 (C-5), 27.2 and 26.5 [$C(CH_3)_2$]. Anal. Calcd for $C_{25}H_{26}N_2O_6Cl_2$: C, 57.6; H, 4.99; N, 5.37. Found: C, 57.95; H, 5.03; N, 5.01.

(6*S*)-3-Benzyl-5,6-dihydro-6-(1,2-*O*-isopropylidene)-3-*O*-methyl-α-D-*xylo*-tetrofuranos-4-yl)-1-(4-methoxybenzyl)-uracil (23): Colourless foam, yield 0.6 g (96 %), R_f 0.40 (3:2 hexane/ethyl acetate). $[\alpha]_D^{25}$ −25.0 (*c* 0.2, $CHCl_3$), MS (FAB): *m/z* 497 $(M + H)^+$. IR (Neat) ν_{max} : 3373, 2936, 2366, 1671, 1611, 1382, 1248, 1080, 850, 756 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.40–7.30 (m, 3H, ArH), 7.29–7.20 (m, 3H, ArH), 6.88–6.83 (m, 2H, ArH), 5.90 (d, *J* = 3.8 Hz, 1H, H-1′), 5.35 (d, *J* = 15.02 Hz, 1H, N^1CH_A), 5.02 (s, 2H, N^3CH_2Ph) 4.53 (d, *J* = 3.8 Hz, 1H, H-2′), 4.14–4.06 (m, 2H, H-4′ and N^1CH_B), 3.79 (s, 3H, Ar–OCH_3), 3.76–3.72 (m, 1H, H-6), 3.61(d, *J* = 3.2 Hz, 1H, H-3′), 3.31 (s, 3H, OCH_3), 2.66 (dd, *J* = 16.8 and 6.78 Hz, 1H, H-5_A), 2.42 (dd, *J* = 16.8 and 1.4 Hz, 1H, H-5_B), 1.27 [s, 6H, $-C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): 168.6 (C = O), 159.5 (NC = ON), 153.2, 138.2, 130.1, 129.9, 128.9, 128.9, 127.7, 114.5 (Ar-C), 112.4 [$C(CH_3)_2$], 105.5 (C-1), 84.2 (C-2), 81.4 (C-4), 80.9 (C-3), 57.8

($-OCH_3$), 55.7 ($Ar-OCH_3$), 51.0 (C-6), 49.8, 44.2 ($-NCH_2$) 34.7 (C-5), 27.1 and 26.6 [$C(CH_3)_2$]. Anal. Calcd for $C_{27}H_{32}N_2O_7$: C, 65.32; H, 6.45; N, 5.64. Found: C, 66.10; H, 7.01; N, 5.50.

(6*S*)-1-(3,4-Dimethoxybenzyl)-3-phenyl-5,6-dihydro-6-(1,2-*O*-isopropylidene-3-*O*-methyl-α-D-*xylo*-tetrofuranos-4-yl)uracil (24): Colourless foam, yield 0.57 g,(90 %) R_f 0.35 (3:2 hexane/ethyl acetate). $[\alpha]_D^{25}$ −14.6 (*c* 0.20, $CH_3COOC_2H_5$). MS (FAB): *m/z* 513 $(M + H)^+$. IR (Neat) ν_{max} cm^{-1}: 3455, 2939, 2370, 1679, 1597, 1454, 1202, 1078, 1019, 755. ^1H NMR ($CDCl_3$): δ 7.49–7.41 (m, 3H, ArH), 7.18–7.15 (d, *J* = 6.5 Hz, 2 H, ArH), 6.93–6.85 (m, 3H, ArH), 5.98 (d, *J* = 3.8 Hz, 1H, H-1′), 5.37 and 4.21 (2 d, *J* = 14.8 Hz, each 1H, N^1CH_A and N^1CH_B), 4.61 (d, *J* = 3.8 Hz, 1H, H-2′), 4.52 (dd, *J* = 9.9 and 3.1 Hz, 1H, H-4′), 3.92–3.89 (m, 1H, H-6), 3.87 (s, 6H, $Ar-OCH_3$), 3.71 (d, *J* = 3.1 Hz, 1H, H-3′), 3.38 (s, 3H, OCH_3), 2.85 (dd, *J* = 16.8 and 6.5 Hz, 1H, H-5_A), 2.55 (d, *J* = 16.8 Hz, 1H, H-5_B), 1.52 and 1.35 [2 s, each 3H, $-C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): 168.7 (C = O), 153.3 (NC = ON), 149.7, 149.2, 135.9, 130.3, 129.6, 129.0, 128.8, 121.4, 112.4, 112.4 (Ar-C), 111.7 [$C(CH_3)_2$], 105.5 (C-1), 84.2 (C-2), 81.3 (C-4), 80.9 (C-3), 57.9 ($-OCH_3$), 56.5, 56.3 ($Ar-OCH_3$), 51.6 (C-6), 49.9 ($-NCH_2$), 35.2 (C-5), 27.2, 26.6. Anal. Calcd for $C_{27}H_{32}N_2O_8$: C, 63.28; H, 6.25; N, 5.46. Found: C, 64.33; H, 6.58; N, 5.31.

(6*S*)-3-Benzyl-1-(3,4-dimethoxybenzyl)-5,6-dihydro-6-(1,2-*O*-isopropylidene-3-*O*-methyl-α-D-*xylo*-tetrofuranos-4-yl)uracil (25): Colourless foam, yield 0.61 g (95 %), R_f 0.45 (3:2 hexane/ethyl acetate). $[\alpha]_D^{25}$ −22.4 (*c* 0.2, $CH_3COOC_2H_5$). MS (FAB): *m/z* 527 $(M + H)^+$. IR (Neat) ν_{max}: 3431, 2939, 2378, 2148, 1597, 1521, 1456, 1367, 1260, 1162, 1077, 1023, 700.5, 631, 556 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.39–7.33 (m, 2H, ArH), 7.30–7.24 (m, 4H, ArH), 6.82 (s, 2H, ArH), 5.90 (d, *J* = 3.8 Hz, 1H, H-1′), 5.34 and 4.13 (2 d, *J* = 14.9 Hz, each 1H, N^1CH_A and N^1CH_B), 4.54 (s, 2H, $-N^3CH_2$), 4.53 (d, *J* = 3.8 Hz, 1H, H-2′), 4.14 (dd, *J* = 9.7 and 3.0 Hz, 1H, H-4′), 3.85 and 3.83 (2 s, each 3H, $Ar-OCH_3$), 3.74–3.70 (m, 1H, H-6), 3.61 (d, *J* = 3.0 Hz, 1H, H-3′), 3.31 (s, 3H, OCH_3), 2.65 (dd, *J* = 16.8 and 6.7 Hz, 1H, H-5_A), 2.43 (d, *J* = 16.8 Hz, 1H, H-5_B), 1.27 [s, 6H, $-C(CH_3)_2$].^{13}C NMR ($CDCl_3$): δ 168.6(C = O), 158.5 (NC = ON), 149.6, 149.0, 139.7, 130.5, 129.09, 128.9, 128.8, 127.8, 127.6, 127.5, 121.0 (Ar-C), 112.00 [$C(CH_3)_2$], 111.7, 111.4 (Ar-C) , 105.5 (C-1), 84.1 (C-2), 81.4 (C-4), 80.9 (C-3), 57.7 ($-OCH_3$), 56.3, 56.2 ($Ar-OCH_3$), 51.6 (C-6), 49.7, 44.2 ($-NCH_2$), 34.6 (C-5), 27.1 and 26.5 [$C(CH_3)_2$]. Anal. Calcd for $C_{28}H_{34}N_2O_8$: C, 63.87; H, 6.46; N, 5.32. Found: C, 64.19; H, 6.81; N, 5.11.

(6*S*)-6-(3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-tetrofuranos-4-yl)-1-(2-chlorobenzyl)-5,6-dihydro-3-phenyluracil (26): Colourless foam, yield 0.55 g (85 %), R_f 0.35 (3:2 hexane/ethyl acetate). $[\alpha]_D^{20}$ −25.6 (*c* 0.1875, $CHCl_3$). MS (FAB): *m/z* 564 $(M + H)^+$. IR (Neat) ν_{max}: 2927, 2371, 1682, 1597 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.42–7.32 (m, 8H, ArH), 7.25–7.19 (m, 4H, ArH), 7.14–7.10 (m, 2H, ArH), 6.01 (d, *J* = 3.7 Hz, 1H, H-1′), 5.26 (d, *J* = 14.9 Hz, 1H, NCH_AAr), 4.70 and 4.58 (2 d, *J* = 11.9 Hz, each 1H, $-OCH_APh$ and $-OCH_BPh$), 4.65 (d, *J* = 3.7 Hz, 1H, H-2′), 4.51–4.43 (m, 2H, H-4′ and $-NCH_BAr$), 4.21–4.15 (m, 1H, H-6), 3.95 (d, *J* = 3.1 Hz, 1H, H-3′), 2.92 (dd, *J* = 16.9 and 5.6 Hz, 1H, H-5_A), 2.32 (d, *J* = 16.9 Hz, 1H, H-5_B), 1.51 and 1.33 [2 s, each 3H, $C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 168.7 (C = O), 153.3 (NC = ON), 137.1, 135.8, 135.2,

134.3, 132.2, 130.1, 129.5, 129.5, 129.1, 129.0, 128.7, 128.0, 127.3 (Ar-C), 112.5 [$C(CH_3)_2$], 105.7 (C-1), 81.9 (C-2), 81.1 (C-4), 81.3 (C-3), 72.2 (–OCH_2Ph), 51.3 (C-6), 51.2 (–NCH_2), 34.7 (C-5), 27.2 and 26.6 [$C(CH_3)_2$]. Anal. Calcd for $C_{31}H_{31}N_2O_6Cl$: C, 66.13; H, 5.51; N, 4.97. Found: C, 66.46; H, 5.72; N, 4.83.

(6*S*)-6-(3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-tetrofuranos-4-yl)-3-(4-chlorophenyl)-5,6-dihydro-1-(4-methoxybenzyl)uracil (27): Colourless foam, yield 0.58 g (90 %), R_f 0.35 (3:2 hexane/ethylacetate). $[\alpha]_D^{25}$ −4.36 (*c* 0.1375, $CHCl_3$). MS (FAB) *m/z* = 593 $(M + H)^+$. IR (Neat) ν_{max} : 3450, 2931, 2374, 1678, 1603, 1509 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.39 (d, *J* = 8.6 Hz, 2H, ArH), 7.34–7.18 (m, 7H, ArH), 7.07 and 6.87 (2 d, *J* = 8.6 Hz, each 2H, ArH), 6.0 (d, *J* = 3.7 Hz, 1H, H-1′), 5.33 and 4.20 (2 d, *J* = 14.8 Hz, each 1H, NCH_AAr and NCH_BAr), 4.68 (d, *J* = 11.9 Hz, 1H, OCH_APh), 4.64 (d, *J* = 3.7 Hz, 1H, H-2′), 4.45–4.39 (m, 2H, OCH_BPh and H-4′), 3.93–3.89 (m, 2H, H-6 and H-3′), 3.80 (s, 3H, $ArOCH_3$), 2.65 (dd, *J* = 16.9 and 6.5 Hz, 1H, $H\text{-}5_A$), 2.26 (d, *J* = 16.9 Hz, 1H, $H\text{-}5_B$), 1.49 and 1.33 [2 s, each 3H, $C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 168.5 (C = O), 159.7 (NC = ON), 153.0, 136.9, 134.6, 134.4, 130.4, 130.4, 129.7, 129.6, 129.1, 128.8, 128.1, 114.6 (Ar-C), 112.5 [$C(CH_3)_2$], 105.6 (C-1), 81.8 (C-1), 81.7 (C-1), 81.3 (C-1), 72.2 (–OCH_2Ph), 55.7 (Ar–OCH_3), 51.4 (C-6), 49.5 (–NCH_2), 34.9 (C-5), 27.2 and 26.6 [$C(CH_3)_2$]. Anal. Calcd for $C_{32}H_{33}N_2O_7Cl$: C, 64.81; H, 5.57; N, 4.72. Found: C, 65.19; H, 5.94; N, 4.68.

(6*S*)-6-(3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-tetrofuranos-4-yl)-1-(3,4-dimethoxybenzyl)-5,6-dihydro-3-phenyluracil (28): Colourless foam, yield 0.41 g (90 %), R_f 0.35 (3:2 hexane/ethyl acetate). MS (FAB): *m/z* 589 $(M + H)^+$. IR (Neat) ν_{max}: 3433, 2263, 1670, 1594, 1503, 1425, 1387, 1248, 1155, 1062, 1003, 875, 821 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.44–7.31 (m, 5H, ArH), 7.21–7.12 (m, 5H, ArH), 6.87–6.84 (m, 3H, ArH), 6.01 (d, *J* = 3.7 Hz, 1H, H-1′), 5.30 and 4.22 (2 d, *J* = 14.7 Hz, each 1H, NCH_A and NCH_B), 4.67 and 4.43 (2 d, *J* = 11.7 Hz, each 1H, OCH_APh and OCH_BPh), 4.65 (d, *J* = 3.7 Hz, 1H, H-2′), 4.49 (dd, *J* = 9.9 and 3.0 Hz, 1H, H-4′), 3.95 (m, 1H, H-6), 3.96–3.92 (m, 2H, H-6 and H-3′), 3.87 and 3.83 (2 s, each 3H, $ArOCH_3$), 2.69 (dd, *J* = 16.9 and 6.5 Hz, 1H, $H\text{-}5_A$), 2.30 (d, *J* = 16.9 Hz, 1H, $H\text{-}5_B$), 1.51 and 1.33 [2 s, each 3H, $C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 168.5 (C = O), 153.0 (NC = ON), 149.7,149.2, 135.9, 137.0, 130.3, 129.5, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 128.1, 121.6,112.5, 112.5 (Ar-C), 111.8 [$C(CH_3)_2$], 105.6 (C-1), 81.9 (C-2), 81.7 (C-4), 81.4 (C-3), 72.2 (–OCH_2Ph), 56.4, 56.3 (Ar–OCH_3), 51.7 (C-6), 49.4 (–NCH_2), 34.9 (C-5), 27.2, 26.6. Anal. Calcd for $C_{33}H_{36}N_2O_8$: C, 67.34; H, 6.12; N, 4.76. Found: C, 67.67; H, 6.35; N, 4.62.

(6*S*)-3-(3-Acetylphenyl)-6-(3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-tetrofuranos-4-yl)-1-(3,4-dimethoxybenzyl)-5,6-dihydrouracil (29): Colourless foam; yield 0.42 g (89 %), R_f 0.3 (3:2 hexane/ethyl acetate). $[\alpha]_D^{25}$ + 33 (*c* 0.1, $CHCl_3$). MS (FAB): *m/z* 631 $(M + H)^+$. IR (Neat) ν_{max}: 3018, 2438,1681, 1597, 1513 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.97 (d, *J* = 7.8 Hz, 1H, ArH), 7.73 (s, 1H, ArH), 7.51 (dd, *J* = 7.8 and 7.31 Hz, 1H, ArH), 7.37–7.21 (m, 4H, ArH), 7.23–7.19 (m, 2H, ArH), 6.88–6.85 (m, 3H, ArH), 6.03 (d, *J* = 3.6 Hz, 1H, H-1′), 5.34 and 4.21 (2 d, *J* = 14.7 Hz, each 1H, NCH_AAr and NCH_BAr), 4.70 and 4.42 (2 d, *J* = 11.7 Hz, each 1H, OCH_APh and OCH_BPh), 4.67 (d, *J* = 3.6 Hz, 1H, H-2′), 4.47 (dd, *J* = 9.1 and 2.8 Hz, 1H, H-4′), 4.03–3.97 (m, 1H, H-6), 3.95 (d, *J* = 2.8 Hz, 1H, H-3′), 3.88 and 3.84 (2 s, each 3H,

$ArOCH_3$), 2.70 (dd, J = 16.9 and 6.5 Hz, 1H, H-5_A), 2.58 (s, 3H, $ArCOCH_3$), 2.30 (d, J = 16.9 Hz, 1H, H-5_B), 1.53 and 1.35 [2 s, each 3H, $C(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 197.1 (C = OCH_3), 168.5 (C = O), 153.0 (NC = ON), 149.6,149.2, 138.5, 136.9,136.3, 133.8, 129.8, 129.2, 129.1, 128.8, 128.6, 128.1, 121.6 (Ar-C), 112.4 [$C(CH_3)_2$], 111.7, 112.6 (Ar-C), 105.7 (C-1), 81.3 (C-2), 81.7 (C-4), 81.3 (C-3), 72.2 (–OCH_2Ph), 56.3, 56.4 (Ar–OCH_3), 51.8 (C-6), 49.4, 34.9 (C-5), 27.2, 27.0, 26.6. Anal. Calcd for $C_{35}H_{38}N_2O_9$: C, 66.66; H, 6.03; N, 4.44. Found: C, 66.92; H, 6.32; N, 4.39.

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