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An Efficient Route to Pyrimidine Nucleoside Analogues by [4 + 2] Cycloaddition Reaction

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We report here an efficient synthesis for pyrimidine nucleoside analogues by [4 + 2] cycloaddition reaction. These compounds were obtained by convergent chemistry from glycosyl isothiocyanates **3a**−**f** (pyranoses, furanoses, and dissaccharides) and diazadienium salt **5**. In fact, diazapentadienium iodide **5** prepared from vinylthioamide **4** is an efficient intermediate in heterocyclic synthesis and reacts with isothiocyanates **3a**−**f** affording β-D-uracil analogues **7a**−**f** in good yields and with total regiocontrol. All compounds were fully characterized by IR, HRMS, and ^{13}C and ^{1}H NMR (COSY and HMQC).

Introduction

For many years, modified nucleosides have been widely used as antiviral and antitumor agents.[1] Considerable efforts have been undertaken to exploit synthetic routes to these compounds.[2] In the course of the preparation of nucleosides, base moieties are generally introduced by substitution or more rarely by construction.[3] Conventionally, synthesis of *N*-linked oligosaccharides has been achieved by coupling of activated glycosyl derivatives with heterocyclic nucleobase analogues such as pyrimidinones.[4] Alternative methods for *N*-alkylation include heating with trimethyl phosphate[5] and alkylation of *O*-silylated derivatives,[6] which is an important method for unambiguous *N*-alkylation especially ribosylation of uracils.[7] Complementary studies through an intramolecular transposition process were investigated in order to improve the synthesis of nucleoside pyrimidinone analogues.[8] Significant and diverse pharmaceutical values of various nucleosides have inspired investigations toward the development of new synthetic methods for their practical preparation.

Among the *N*-glycosides, glycosyl isothiocyanates are attracting much attention because of the synthetic flexibility of the isothiocyanate function.[9] In fact, sugar isothiocyanates play a key role in the preparation of a variety of functional groups as well as in the construction of heterocyclic ring systems. In particular, they have been used for the synthesis of a wide spectrum of carbohydrate derivatives with thiourea structure.[10] Recently, glycosyl isothiocyanates were used to prepare galactofuranosidase inhibitors,[11] β-amphiphilic compounds,[12] hydantocidin,[13] spironucleosides,[14] and glycodendrimers.[15] Paradoxically, only few syntheses of nucleoside analogues by [4 + 2]

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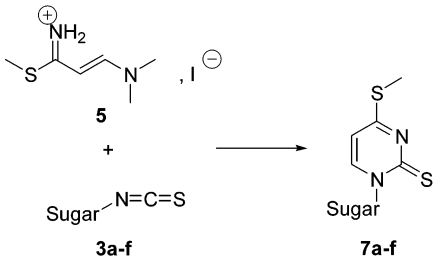
SCHEME 1. Synthetic Route to Nucleosides 7a−f



cycloaddition or addition−cyclization reactions of glycosyl isothiocyanates have been described.[14a,16] Therefore, it would be interesting to establish simple synthetic approaches and novel concepts in the synthesis and development of pyrimidine nucleoside analogues.

During the last years, we have focused our research on the development of efficient methodologies to build heterocyclic compounds.[17] In our previous paper, we described the versatility of cationic dienes as stable synthons for the preparation of various heterocyclic rings.[18] We report here the reactivity of diazadienium iodide **5** in a [4 + 2] cycloaddition reaction with glycosyl isothiocyanates **3a**−**f** affording sugar pyrimidines **7a**−**f** (Scheme 1).[19] This type of derivatives opens a new route to original functionalized six-membered ring heterocycles with strong biological potential.

Results and Discussion

Starting glycosyl isothiocyanates **3a**−**f** were obtained in two steps in good to moderate overall yields. Thus, acetylated (for **3a**−**d**) or benzoylated (for **3e**,**f**) glycosyl bromides were prepared by stirring the respective acetates in HBr−acetic acid solution.[20] A subsequent step in a phase-transfer reaction using thiocyanate anion and tetrabutylammonium bromide as catalyst in acetonitrile in the presence of molecular sieves (4 Å) afforded the desired *N*-glycosides **3a**−**f** (Scheme 2) without yielding corresponding thiocyanates.[21,22] The reaction is totally diastereoselective affording only the 1,2-*trans*-isothiocyanates, probably due to the anchimeric participation of the vicinal 2-*O*-acyl group.[21a,23] The anomeric configuration could be easily determined by measuring the anomeric coupling constant $J_{1,2}$. The $J_{1,2}$ value (∼8.4 Hz) indicated pyranoses **3a**−**d** to be *β*. The *β*-D-furanose configuration of **3e**,**f** was equally established by means of H_1-H_2 coupling constant values, which being smaller than 1 Hz indicate a 1,2-trans relationship.[24] Compounds **2e**,**f** were reacted directly with an excess of potassium thiocyanate without purification. In fact, 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl bromide **2e** and 2,3,5-tri-*O*-benzoyl-D-xylofuranosyl bromide **2f** proved extremely unstable and degraded on silica gel during chromatography.

Rajappa and Advani have previously reported the condensation of *N*,*N*-dimethylformamide dimethyl acetal and thioacetamide to furnish vinylthioamide **4** in very poor yields (6.5%).[25] An alternative preparation consisting of sulfhydratation of the commercially available 3-dimethylaminoacrylonitrile (trans/cis ratio: 95/5) in the presence of triethylamine and pyridine permitted the isolation of compound **4** in more satisfactory yields (79%), and with exclusive *E* configuration (Scheme 3).

During the past years, different types of 2-amino-1-thiazabutadienes have been studied in our laboratory. We have reported that these compounds could react either as thiazadienes or diazadienes giving rise to tetrahydropyrimidines or 1,3-thiazines.[18a,26] Vinylthioamide **4** can have also two tautomeric forms either azadiene or thiadiene, and thus probably possess a wide reactivity. With the aim to investigate the synthesis of uracil analogues, we have rigidified the structure by alkylation of compound **4** to obtain only the azadiene chain. Alkylation of vinylthioamide afforded, as the sole product, the corresponding *S*-methyl salt **5**, due to the higher nucleophilicity of the sulfur. In contrast to the method developed in the literature, we never observed a dehydrohalogenation of iodide **5** in the basic medium to afford methylthioimine.[26a,27] In this case, the expected product was not stable enough to be isolated (Scheme 3). This problem was solved by the use of the cationic form. In fact, the reaction of diazadienium iodide **5** in a [4 + 2] cycloaddition reaction with glycosyl isothiocyanates **3a**−**f** afforded methylsulfanyldihydropyrimidinethiones **7a**−**f** in good yields (Table 1). In this reaction, the intermediate **6** was never isolated and the final step consisted in a

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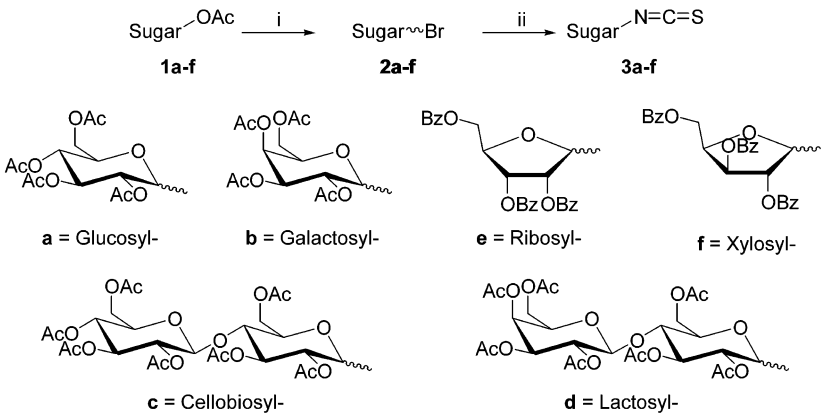
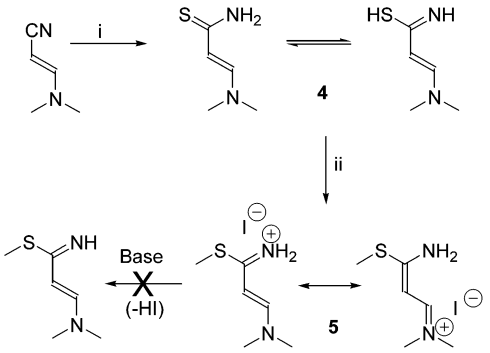
SCHEME 2. Synthetic Route to Glycosyl Isothiocyanates 3a−f[a]



[a] Reagents and conditions: (i) CH_2Cl_2, HBr in AcOH, 0°C, 2 h; (ii) CH_3CN, KSCN, molecular sieves 4 Å, Bu_4N^+ Br^-, reflux, 2 h.

SCHEME 3. Synthesis of *S*-Methyl Salt 5[a]



[a] Reagents and conditions: (i) Et_3N, pyridine, H_2S, rt, 48 h; (ii) CH_3I, THF, rt, 18 h.

TABLE 1. Yields of Compounds 7a−f and Selected NMR Data (δ, ppm; *J*, Hz))

compd	sugar	yield[a] (%)	H-1 (*J*)	C-1
7a	glucosyl	84	7.23 (9.5)	85.7
7b	galactosyl	82	7.21 (8.3)	86.2
7c	cellobiosyl	82	7.14 (9.2)	87.0
7d	lactosyl	73	7.28 (8.9)	86.4
7e	ribosyl	72	7.22 (3.0)	92.0
7f	xylosyl	83	6.79	94.2

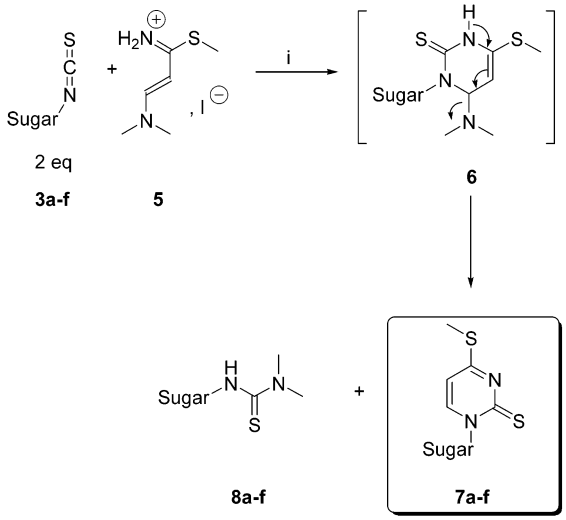
[a] Isolated yields. Yields of **7a−f** are based on diazadienium **5**.

deamination of the formed cycloadduct giving sugar pyrimidines **7a−f** (Scheme 4).

Starting from salt **5**, triethylamine can be added to remove hydriodic acid. This [4 + 2] cycloaddition reaction occurs in a regiocontrolled manner. The structures of compounds **7a−f** were determined unequivocally by the complementary of the $^1H/^{13}C$-2D NMR techniques (COSY and HMQC) (Table 1). The β anomeric configuration was fully preserved, and we observed only 1,2-trans glycosidic linkage. In this reaction, the dimethylamine generated in the mixture reacted with a second equivalent of the dienophile to provide glycosyl thioureas **8a−f**.

These types of *N*-nucleosides may be attracting much attention from the viewpoint of antiviral and antitumor drugs. Preliminary biological tests (antiviral and cytotoxicity assays) with pyrimidine glycoside **7a** against Herpes simplex virus type 1 (HSV-1) showed a significant

SCHEME 4. Synthesis of *N*-Nucleosides 7a−f[a]



[a] Reagents and conditions: (i) CH_2Cl_2, Et_3N, rt, 3 h.

in vitro activity.[28] Their evaluation as antitumor agents is in progress, and these promising results led us to develop new *N*-nucleosides.

In summary, we have developed an effective method for the synthesis of various pyrimidine nucleoside analogues by [4 + 2] cycloaddition reaction between glycosyl isothiocyanates and diazadienium iodide. Advantages of the present method are: easy availability of starting materials, good yields in the [4 + 2] cycloaddition reaction, high diastereoselectivity and regioselectivity, and experimental simplicity of the procedure. Substitution of methylsulfanyl group using diverse nucleophiles is now under investigation.

Experimental Section

2-Amino-4-(dimethylamino)-1-thiabuta-1,3-diene (4). Hydrogen sulfide was passed at room temperature for 4 h through a solution of 3-dimethylaminoacrylonitrile (3.84 g, 40

(28) Cytotoxic effect of pyrimidine glycoside **7a** on the Vero cells was not observed in the range of the concentrations tested. After 3 days of treatment, 39% cellular destruction was observed at 200 μg/mL (CC_{50} > 200 μg/mL). Compound **7a** is efficient against HSV-1 in vitro. 59% cellular protection was obtained for 200 μg/mL 72 h after infection (EC_{50} 111.20 μg/mL).

mmol) in triethylamine (25 mL) and pyridine (25 mL). The solvents were removed, and the residue was crystallized from dichloromethane then methanol to provide **4** as a white solid (4.12 g, 31.7 mmol, 79%). Mp: 189−191 °C. IR (KBr): 3342, 1605, 1344, 1116 cm^{-1}. ^1H NMR (DMSO-d_6) δ: 2.88 (br s, 6H, N(CH_3)$_2$), 5.20 (d, 1H, J = 12.2 Hz, CHCS), 7.69 (d, 1H, J = 12.2 Hz, CHN), 7.85 (br s, 1H, NH_2), 7.99 (br s, 1H, NH_2). ^{13}C NMR (DMSO-d_6) δ: 38.7 and 43.76 (N(CH_3)$_2$), 96.4 (CHCS), 155.2 (CHN), 194.6 (CS). MS: m/z 130 (M^+, 100), 97 [M − SH]$^+$, 86 (10). Anal. Calcd for $C_5H_{10}N_2S$: C, 46.12; H, 7.74; N, 21.51. Found: C, 46.34; H, 7.54; N, 21.74.

1,1-Dimethyl-4-methylsulfanyl-1,5-diazapentadienium Iodide (5). A suspension of thiabutadiene **4** (1 g, 7.7 mmol) in methyl iodide (6 mL) and tetrahydrofuran (6 mL) was stirred for 18 h at room temperature. The mixture was evaporated under reduced pressure. After addition of diethyl ether (40 mL), compound **5** was precipitated and collected by filtration to leave a white solid, which was dried under vacuum (2.02 g, 74.3 mmol, 96%). Mp: 182−184 °C. IR (KBr): 3257, 3107, 1632, 1533, 1282, 1056 cm^{-1}. ^1H NMR (D_2O) δ: 2.55 (s, 3H, CH_3S), 3.03 (s, 3H, N(CH_3)$_2$), 3.27 (s, 3H, N(CH_3)$_2$), 5.36 (d, 1H, J = 12.2 Hz, CHCS), 7.95 (d, 1H, J = 12.2 Hz, CHN). ^{13}C NMR (D_2O) δ: 13.1 (CH_3S), 37.5 and 45.6 (N(CH_3)$_2$), 89.2 (CHCS), 156.7 (CHN), 176.3 (CSCH$_3$). Anal. Calcd for $C_6H_{13}IN_2S$: C, 26.48; H, 4.81; N, 10.29. Found: C, 26.22; H, 5.03; N, 10.97.

Pyrimidine Nucleoside (7). Diazapentadienium iodide **5** (0.42 mmol) was added to a solution of glycoside isothiocyanates **3a**−**f** (0.85 mmol) in dichloromethane (20 mL). After 1 h of stirring at room temperature, the reaction mixture was cooled to 0 °C, and triethylamine (0.85 mmol) was added. The mixture was stirred at room temperature for an additional 2 h, and then the solvent was removed in vacuo. The resulting residue was partitioned between CH_2Cl_2 (20 mL) and water (2 × 20 mL). The organic extract was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash chromatography on silica using hexane/AcOEt (9/1) and then hexane/AcOEt (4/6) mixture as eluent to give compounds **7** and **8**.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-4-methylsulfanyl-1,2-dihydropyrimidin-2-thione (7a). Yellow crystals (yield 84%). Mp: 94−96 °C. IR (KBr): 1753, 1612, 1492, 1223 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.00 (s, 3H, COCH_3), 2.02 (s, 3H, COCH_3), 2.06 (s, 3H, COCH_3), 2.08 (s, 3H, COCH_3), 2.60 (s, 3H, CH_3S), 4.01 (ddd, 1H, J = 9.5, 5.1, 2.0 Hz, glu H_5), 4.10 (dd, 1H, J = 12.6, 2.0 Hz, glu H_{6b}), 4.29 (dd, 1H, J = 12.6, 5.1 Hz, glu H_{6a}), 5.14 (t, 2H, J = 9.5 Hz, glu H_2 and H_4), 5.49 (t, 1H, J = 9.5 Hz, glu H_3), 6.56 (d, 1H, J = 7.2 Hz, H_5 pyr), 7.23 (d, 1H, J = 9.5 Hz, glu H_1), 7.49 (d, 1H, J = 7.2 Hz, H_6 pyr). ^{13}C NMR ($CDCl_3$) δ: 13.1 (CH_3S), 20.5 and 20.7 (4 COCH_3), 61.6 (glu C_6), 67.9 and 71.0 (glu C_2 and C_4), 72.4 (glu C_3), 75.2 (glu C_5), 85.7 (glu C_1), 108.6 (C_5 pyr), 139.4 (C_6 pyr), 169.6, 170.0, 170.5 and 173.1 (4 COCH$_3$ and C=N), 181.3 (C=S). MS: m/z 489 ([M + H]$^+$), 331 (100). HRMS (CI): m/z calcd for $C_{19}H_{25}N_2O_9S_2$ [M + H]$^+$ 489.1002, found 489.1005.

1-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl)-4-methylsulfanyl-1,2-dihydropyrimidin-2-thione (7b). Yellow crystals (yield 82%). Mp: 93−95 °C. IR (KBr): 1749, 1613, 1493, 1224 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.01 (s, 3H, COCH_3), 2.03 (s, 3H, COCH_3), 2.06 (s, 3H, COCH_3), 2.20 (s, 3H, COCH_3), 2.62 (s, 3H, CH_3S), 4.11−4.22 (m, 2H, gal H_{6a} and H_{6b}), 4.13 (dd, 1H, J = 7.1, 2.7 Hz, gal H_4), 5.27−5.31 (m, 1H, gal H_5), 5.29 (dd, 1H, J = 8.3, 0.8 Hz, gal H_2), 5.54 (dd, 1H, J = 2.7, 0.8 Hz, gal H_3), 6.58 (d, 1H, J = 7.3 Hz, H_5 pyr), 7.21 (d, 1H, J = 8.3 Hz, gal H_1), 7.54 (d, 1H, J = 7.3 Hz, H_6 pyr). ^{13}C NMR ($CDCl_3$) δ: 13.1 (CH_3S), 20.5 and 20.7 (4 COCH_3), 61.2 (gal C_6), 67.0 (gal C_3), 68.7 (gal C_2), 70.6 (gal C_5), 74.1 (gal C_4), 86.2 (gal C_1), 108.6 (C_5 pyr), 139.8 (C_6 pyr), 169.0 and 170.4 (4 COCH$_3$ and C=N), 180.0 (C=S). MS: m/z 489 ([M + H]$^+$), 331 (100). HRMS (CI): m/z calcd for $C_{19}H_{25}N_2O_9S_2$ [M + H]$^+$ 489.1002, found 489.0999.

1-(2,3,6,2′,3′,4′,6′-Hepta-*O*-acetyl-*β*-D-cellobiopyranosyl)-4-methylsulfanyl-1,2-dihydropyrimidin-2-thione (7c). Yellow crystals (yield 82%). Mp: 124−126 °C. IR (KBr): 1750, 1613, 1493, 1228 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.99 (s, 3H, COCH_3), 2.00 (s, 3H, COCH_3), 2.01 (s, 3H, COCH_3), 2.03 (s, 3H, COCH_3), 2.04 (s, 3H, COCH_3), 2.10 (s, 3H, COCH_3), 2.12 (s, 3H, COCH_3), 2.60 (s, 3H, CH_3S), 3.68 (ddd, 1H, J = 9.4, 4.5, 2.2 Hz, glu $H_{5'}$), 3.85 (dd, 1H, J = 10.3, 9.2 Hz, glu H_4), 3.93 (ddd, 1H, J = 10.3, 5.5, 1.6 Hz, glu H_5), 4.04 (dd, 1H, J = 12.5, 2.2 Hz, glu $H_{6'b}$), 4.15 (m, 1H, glu H_{6b}), 4.35 (dd, 1H, J = 12.5, 4.5 Hz, glu $H_{6'a}$), 4.48 (dd, 1H, J = 12.2, 1.6 Hz, glu H_{6a}), 4.55 (d, 1H, J = 8.0 Hz, glu $H_{1'}$), 4.94 (dd, 1H, J = 9.4, 8.0 Hz, glu $H_{2'}$), 5.08 (t, 1H, J = 9.2 Hz, glu H_2), 5.10 (t, 1H, J = 9.4 Hz, glu $H_{4'}$), 5.18 (t, 1H, J = 9.4 Hz, glu $H_{3'}$), 5.47 (t, 1H, J = 9.2 Hz, glu H_3), 6.51 (d, 1H, J = 7.3 Hz, H_5 pyr), 7.14 (d, 1H, J = 9.2 Hz, glu H_1), 7.41 (d, 1H, J = 7.3 Hz, H_6 pyr). ^{13}C NMR ($CDCl_3$) δ: 14.3 (CH_3S), 21.7 and 22.0 (7 COCH_3), 62.8 and 63.0 (glu $C_{6'}$ and C_6), 69.0 (glu C_2), 72.1 (glu $C_{5'}$), 72.1 (glu $C_{4'}$), 73.0 (glu $C_{2'}$), 73.3 (glu C_3), 74.0 (glu $C_{3'}$), 77.2 (glu C_4 and C_5), 87.0 (glu C_1), 101.7 (glu $C_{1'}$), 109.6 (C_5 pyr), 140.4 (C_6 pyr), 170.2, 170.5, 171.4 and 171.7 (7 COCH$_3$ and C=N), 183.0 (C=S). MS: m/z 777 ([M + H]$^+$), 717 (100), 331. HRMS (DCI): m/z calcd for $C_{31}H_{41}N_2O_{17}S_2$ [M + H]$^+$ 777.1847, found 777.1851.

1-(2,3,6,2′,3′,4′,6′-Hepta-*O*-acetyl-*β*-D-lactopyranosyl)-4-methylsulfanyl-1,2-dihydropyrimidin-2-thione (7d). Yellow crystals (yield 73%). Mp: 131−133 °C. IR (KBr): 1753, 1613, 1493, 1226 cm^{-1}. ^1H NMR (CD_3COCD_3) δ: 1.92 (s, 3H, COCH_3), 1.94 (s, 3H, COCH_3), 2.07 (s, 3H, COCH_3), 2.09 (s, 3H, COCH_3), 2.10 (s, 3H, COCH_3), 2.11 (s, 3H, COCH_3), 2.16 (s, 3H, COCH_3), 2.59 (s, 3H, CH_3S), 4.17−4.29 (m, 6H, glu H_4, H_5, H_{6b} and gal H_5, H_{6a}, H_{6b}), 4.64 (d, 1H, J = 10.3 Hz, glu H_{6a}), 4.94 (m, 1H, gal H_1), 5.08−5.15 (m, 2H, gal H_2 and H_3), 5.25 (t, 1H, J = 8.9 Hz, glu H_2), 5.39 (s, 1H, gal H_4), 5.58 (t, 1H, J = 8.9 Hz, glu H_3), 6.81 (d, 1H, J = 7.1 Hz, H_5 pyr), 7.28 (d, 1H, J = 8.9 Hz, glu H_1), 8.06 (d, 1H, J = 7.1 Hz, H_6 pyr). ^{13}C NMR (CD_3COCD_3) δ: 12.8 (CH_3S), 20.6 (7 COCH_3), 61.9 (gal C_6), 62.9 (glu C_6), 68.1 (gal C_5), 69.9 (gal C_4), 71.5 and 71.7 (gal C_2 and C_3), 72.5 (glu C_2 and C_3), 76.7 (glu C_4 and C_5), 86.4 (glu C_1), 101.6 (gal C_1), 108.6 (C_5 pyr), 142.4 (C_6 pyr), 169.6, 169.8, 170.2, 170.8 and 171.5 (7 COCH$_3$ and C=N), 182.0 (C=S). MS: m/z 777 ([M + H]$^+$), 71, 559, 331 (100). HRMS (DCI): m/z calcd for $C_{31}H_{41}N_2O_{17}S_2$ [M + H]$^+$ 777.1847, found 777.1836.

1-(2,3,5-Tri-*O*-benzoyl-*β*-D-ribofuranosyl)-4-methylsulfanyl-1,2-dihydropyrimidin-2-thione (7e). Yellow crystals (yield 72%). Mp: 89−91 °C. IR (KBr): 1727, 1601, 1450, 1269 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.61 (s, 3H, CH_3S), 4.66 (dd, 1H, J = 12.6, 3.2 Hz, rib H_{5b}), 4.84 (ddd, 1H, J = 7.0, 3.2, 2.4 Hz, rib H_4), 4.91 (dd, 1H, J = 12.6, 2.4 Hz, rib H_{5a}), 5.77 (dd, 1H, J = 7.0, 5.3 Hz, rib H_3), 5.94 (dd, 1H, J = 5.3, 3.0 Hz, rib H_2), 6.32 (d, 1H, J = 7.3 Hz, H_5 pyr), 7.22 (d, 1H, J = 3.0 Hz, rib H_1), 7.30−7.69 (m, 9H, CHar meta and CHar para), 7.86 (d, 2H, J = 8.5 Hz, CHar ortho), 7.96 (d, 1H, J = 7.3 Hz, H_6 pyr), 8.07 (m, 4H, CHar ortho). ^{13}C NMR ($CDCl_3$) δ: 13.1 (CH_3S), 62.6 (rib C_5), 69.4 (rib C_3), 75.0 (rib C_2), 80.1 (rib C_4), 92.0 (rib C_1), 108.3 (C_5 pyr), 128.5, 128.8, 129.6 and 130.1 (3 Car, 6 CHar meta, 3 CHar para), 133.7 (6 CHar ortho), 138.1 (C_6 pyr), 164.8 and 172.8 (3 COC$_6$H$_5$ and C=N), 180.0 (C=S). MS m/z 603 ([M + H]$^+$), 359 (100), 297, 123. HRMS (DCI): m/z calcd for $C_{31}H_{27}N_2O_7S_2$ [M + H]$^+$ 603.1260, found 603.1302.

1-(2,3,5-Tri-*O*-benzoyl-*β*-D-xylofuranosyl)-4-methylsulfanyl-1,2-dihydropyrimidin-2-thione (7f). Yellow crystals (yield 83%). Mp: 89−91 °C. IR (KBr): 1728, 1600, 1450, 1260, 1090, 707 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.65 (s, 3H, CH_3S), 4.73 (dd, 1H, J = 12.3, 4.2 Hz, xyl H_{5a}), 4.87 (dd, 1H, J = 12.3, 4.2 Hz, xyl H_{5b}), 5.03 (m, 1H, xyl H_4), 5.77 (d, 1H, J = 3.1 Hz, xyl H_3), 5.94 (s, 1H, xyl H_2), 6.55 (d, 1H, J = 7.3 Hz, H_5 pyr), 6.79 (s, 1H, xyl H_1), 7.34−7.64 (m, 9H, CHar meta and CHar para), 7.77 (dd, 2H, J = 8.5, 1.4 Hz, CHar ortho), 7.92 (dd, 2H, J = 8.5, 1.4 Hz, CHar ortho), 8.15 (dd, 2H, J = 8.6, 1.5 Hz, CHar ortho), 8.21 (d, J = 7.3 Hz, H_6 pyr). ^{13}C NMR ($CDCl_3$) δ: 13.1 (CH_3S), 61.4 (xyl C_5), 74.6 (xyl C_3), 80.2 and 81.9 (xyl C_2 and C_4), 94.2 (xyl C_1), 107.5 (C_5 pyr), 128.1, 128.5, 128.6, 129.1, 129.7, 129.9, 130.2, 133.5, 133.8 and 134.1 (3 Car, 6 CHar

meta, 3 *C*Har para, and 6 *C*Har ortho), 139.3 (C_6 pyr), 164.3, 164.4, 166.1 and 172.8 (3 COC_6H_5 and *C*═N), 179.4 (*C*═S). MS: *m*/*z* 603 ([M + H]$^+$), 359, 123 (100). HRMS (DCI): *m*/*z* calcd for $C_{31}H_{27}N_2O_7S_2$ [M + H]$^+$ 603.1260, found 603.1267.

***N*,*N*-Dimethyl-*N*′-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)thiourea (8a).** Yellow crystals (yield 72%). Mp: 72−74 °C. IR (KBr): 1750, 1550, 1229, 1067 cm^{-1}. ^{1}H NMR ($CDCl_3$) *δ*: 2.03 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 3.25 (br s, 6H, $N(CH_3)_2$), 3.88 (ddd, 1H, *J* = 9.5, 4.6, 2.0 Hz, glu H_5), 4.11 (dd, 1H, *J* = 12.5, 2.0 Hz, glu H_{6b}), 4.32 (dd, 1H, *J* = 12.5, 4.6 Hz, glu H_{6a}), 5.00 (t, 1H, *J* = 9.5 Hz, glu H_2), 5.08 (t, 1H, *J* = 9.5 Hz, glu H_4), 5.40 (t, 1H, *J* = 9.5 Hz, glu H_3), 5.77 (dd, 1H, *J* = 8.2, 9.5 Hz, glu H_1), 6.41 (d, 1H, *J* = 8.2 Hz, N*H*). ^{13}C NMR ($CDCl_3$) *δ*: 20.6, 20.8 and 20.9 (4 $COCH_3$ and $N(CH_3)_2$), 61.7 (glu C_6), 68.5 (glu C_4), 71.2 (glu C_2), 72.6 (glu C_5), 73.2 (glu C_3), 83.7 (glu C_1), 169.7, 170.7 and 172.2 (4 $COCH_3$), 182.1 (*C*═S). MS: *m*/*z* 435 ([M + H]$^+$), 403, 331 (100), 213. HRMS (CI): *m*/*z* calcd for $C_{17}H_{27}N_2O_9S$ [M + H]$^+$ 435.1436, found 435.1440.

***N*,*N*-Dimethyl-*N*′-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galactopyranosyl)thiourea (8b).** Yellow crystals (yield 82%). Mp: 192−194 °C. IR (KBr): 1746, 1548, 1227, 1084 cm^{-1}. ^{1}H NMR ($CDCl_3$) *δ*: 2.01 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$), 2.15 (s, 3H, $COCH_3$), 3.26 (br s, 6H, $N(CH_3)_2$), 4.07−4.19 (m, 3H, gal H_4, H_{6a} and H_{6b}), 5.19 (d, 1H, *J* = 8.1 Hz, gal H_2), 5.18−5.21 (m, 1H, gal H_5), 5.47 (d, 1H, *J* = 2.7 Hz, gal H_3), 5.77 (t, 1H, *J* = 8.1 Hz, gal H_1), 6.44 (d, 1H, *J* = 8.1 Hz, N*H*). ^{13}C NMR ($CDCl_3$) *δ*: 19.5, 19.6, 19.8 and 20.0 (4 $COCH_3$ and $N(CH_3)_2$), 60.1 (gal C_6), 66.0 (gal C_3), 67.8 (gal C_2), 70.0 (gal C_5), 71.1 (gal C_4), 83.0 (gal C_1), 168.7, 169.1, 169.5 and 171.3 (4 $COCH_3$), 181.0 (*C*═S). MS: *m*/*z* 435 ([M + H]$^+$, 100), 403, 331. HRMS (CI): *m*/*z* calcd for $C_{17}H_{27}N_2O_9S$ [M + H]$^+$ 435.1436, found 435.1431

***N*,*N*-Dimethyl-*N*′-(2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-*β*-D-cellobiopyranosyl)thiourea (8c).** Yellow crystals (yield 80%). Mp: 112−114 °C. IR (KBr): 1748, 1548, 1230, 1040 cm^{-1}. ^{1}H NMR ($CDCl_3$) *δ*: 1.98 (s, 3H, $COCH_3$), 2.00 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.09 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 3.21 (br s, 6H, $N(CH_3)_2$), 3.65 (ddd, 1H, *J* = 9.2, 4.6, 2.1 Hz, glu $H_{5'}$), 3.70−3.77 (m, 2H, glu H_4 and glu H_5), 4.03 (dd, 1H, *J* = 12.4, 2.1 Hz, glu $H_{6'b}$), 4.14 (dd, 1H, *J* = 11.7, 4.5 Hz, glu H_{6b}), 4.35 (dd, 1H, *J* = 12.4, 4.6 Hz, glu $H_{6'a}$), 4.47 (d, 1H, *J* = 8.0 Hz, glu $H_{1'}$), 4.45−4.55 (m, 1H, glu H_{6a}), 4.91 (t, 1H, *J* = 9.3 Hz, glu H_2), 4.93 (dd, 1H, *J* = 9.2, 8.0 Hz, glu $H_{2'}$), 5.05 (t, 1H, *J* = 9.2 Hz, glu $H_{4'}$), 5.13 (t, 1H, *J* = 9.2 Hz, glu $H_{3'}$), 5.33 (t, 1H, *J* = 9.3 Hz, glu H_3), 5.67 (dd, 1H, *J* = 9.3, 8.0 Hz, glu H_1), 6.37 (d, 1H, *J* = 8.0 Hz, N*H*). ^{13}C NMR ($CDCl_3$) *δ*: 20.5, 20.7 and 20.9 (7 $COCH_3$ and $N(CH_3)_2$), 61.7 (glu $C_{6'}$), 62.1 (glu C_6), 67.9 (glu $C_{4'}$), 71.5 (glu C_2, $C_{2'}$ and $C_{5'}$), 72.0 (glu C_3 and $C_{3'}$), 72.9 (glu C_5), 74.1 (glu C_4), 83.6 (glu C_1), 100.6 (glu $C_{1'}$), 169.0, 169.3, 170.2, 170.4, 170.5 and 172.5 (7 $COCH_3$), 182.1 (*C*═S). MS: *m*/*z* 723 ([M + H]$^+$), 619, 331 (100). HRMS (DCI): *m*/*z* calcd for $C_{29}H_{43}N_2O_{17}S$ [M + H]$^+$ 723.2282, found 723.2301.

***N*,*N*-Dimethyl-*N*′-(2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-*β*-D-lactopyranosyl)thiourea (8d).** Yellow crystals (yield 73%). Mp: 123−125 °C. IR (KBr): 1749, 1548, 1231, 1083 cm^{-1}. ^{1}H NMR ($CDCl_3$) *δ*: 1.96 (s, 3H, $COCH_3$), 2.06 (s, 6H, 2 $COCH_3$), 2.07 (s, 6H, 2 $COCH_3$), 2.12 (s, 3H, $COCH_3$), 2.17 (s, 3H, $COCH_3$), 3.22 (br s, 6H, $N(CH_3)_2$), 3.76−3.86 (m, 2H, glu H_4 and gal H_5), 4.07−4.15 (m, 3H, glu H_{6b}, gal H_{6a} and H_{6b}), 4.20 (dd, 1H, *J* = 4.5, 2.2 Hz, glu H_5), 4.43 (d, 1H, *J* = 7.8 Hz, gal H_1), 4.41−4.46 (m, 1H, glu H_{6a}), 4.92 (t, 1H, *J* = 9.1 Hz, glu H_2), 4.94 (dd, 1H, *J* = 10.4, 2.9 Hz, gal H_3), 5.11 (dd, 1H, *J* = 10.4, 7.8 Hz, gal H_2), 5.36 (d, 1H, *J* = 2.9 Hz, gal H_4), 5.39 (m, 1H, glu H_3), 5.69 (dd, 1H, *J* = 9.1, 7.9 Hz, glu H_1), 6.38 (d, 1H, *J* = 7.9 Hz, N*H*). ^{13}C NMR ($CDCl_3$) *δ*: 20.6 and 20.9 (7 $COCH_3$ and $N(CH_3)_2$), 61.0 and 62.1 (glu C_6 and gal C_6), 66.7 (gal C_4), 68.9 (gal C_2), 70.8 and 71.0 (gal C_3 and C_5), 71.5 and 72.0 (glu C_2, C_3 and C_5), 74.1 (glu C_4), 83.6 (glu C_1), 100.8 (gal C_1), 169.0, 169.3, 170.1, 170.4 and 172.5 (7 $COCH_3$), 182.1 (*C*═S). MS: *m*/*z* 723 ([M + H]$^+$), 331 (100). HRMS (DCI): *m*/*z* calcd for $C_{29}H_{43}N_2O_{17}S$ [M + H]$^+$ 723.2282, found 723.2296.

***N*,*N*-Dimethyl-*N*′-(2,3,5-tri-*O*-benzoyl-D-ribofuranosyl)thiourea (8e).** Yellow oil (yield 75%). Mixture of anomer α and *β*. Mp: 69−71 °C. IR (KBr): 1726, 1600, 1538, 1269, 709 cm^{-1}. ^{1}H NMR ($CDCl_3$) *δ*: 3.22 (br s, 12H, $N(CH_3)_2$), 4.57−4.75 (m, 6H, rib H_4, H_{5a} and H_{5b}), 5.82−5.92 (m, 4H, rib H_2 and H_3), 6.39 (d, 1H, *J* = 7.3 Hz, N*H* of one anomer), 6.50−6.57 (m, 2H, N*H* of one anomer and rib H_1 of one anomer), 6.93 (dd, 1H, *J* = 8.5, 4.8 Hz, rib H_1 of one anomer), 7.34−7.51 (m, 12H, C*H*ar meta), 7.51−7.62 (m, 6H, C*H*ar para), 7.89 (dd, 2H, *J* = 8.3, 1.3 Hz, C*H*ar ortho), 7.93 (dd, 2H, *J* = 8.4, 1.3 Hz, C*H*ar ortho), 7.97 (dd, 2H, *J* = 8.5, 1.4 Hz, C*H*ar ortho), 8.04 (dd, 2H, *J* = 8.5, 1.4 Hz, C*H*ar ortho), 8.10 (dd, 4H, *J* = 7.1 Hz, *J* = 1.2 Hz, C*H*ar ortho). ^{13}C NMR ($CDCl_3$) *δ*: 40.5 ($N(CH_3)_2$), 64.3 (rib C_5), 70.8, 71.9, 73.4 and 74.1 (rib C_2 and C_3), 78.8 and 79.4 (rib C_4), 84.6 (rib C_1 of one anomer), 87.6 (rib C_1 of one anomer), 128.5, 128.6, 129.5, 129.7, 129.8 and 129.9 (6 *C*ar, 12 *C*Har meta and 12 *C*Har ortho), 133.3, 133.4, 133.7 and 133.8 (6 *C*Har *para*), 164.5, 165.1, 165.6, 166.0 and 166.2 (6 COC_6H_5), 181.9 and 182.1 (*C*═S). MS: *m*/*z* 549 ([M + H]$^+$), 445 (100), 123. HRMS (DCI): *m*/*z* calcd for $C_{29}H_{29}N_2O_7S$ [M + H]$^+$ 549.1694, found 549.1680.

***N*,*N*-Dimethyl-*N*′-(2,3,5-tri-*O*-benzoyl-D-xylofuranosyl)thiourea (8f).** Yellow oil (yield 82%). Mixture of anomers α and *β*. **Anomer α or *β*:** R_f = 0.43 (hexane/AcOEt 6/4). IR (KBr): 1725, 1600, 1536, 1262, 708 cm^{-1}. ^{1}H NMR ($CDCl_3$) *δ*: 3.20 (br s, 6H, $N(CH_3)_2$), 4.64 (d, 2H, *J* = 5.3 Hz, xyl H_{5a} and H_{5b}), 4.86 (q, 1H, *J* = 5.3 Hz, xyl H_4), 5.82 (t, 1H, *J* = 3.7 Hz, xyl H_2), 5.90 (dd, 1H, *J* = 5.3, 3.7 Hz, xyl H_3), 6.27 (d, 1H, *J* = 7.7 Hz, N*H*), 6.49 (dd, 1H, *J* = 7.7, 3.7 Hz, xyl H_1), 7.35−7.65 (m, 9H, C*H*ar meta and para), 7.97−8.03 (m, 4H, *H*ar ortho), 8.07 (dd, 2H, *J* = 8.4, 1.3 Hz, *H*ar ortho). ^{13}C NMR ($CDCl_3$) *δ*: 40.6 ($N(CH_3)_2$), 62.5 (xyl C_5), 75.3 and 75.7 (xyl C_3 and C_4), 79.5 (xyl C_2), 88.6 (xyl C_1), 128.6, 128.7, 128.9, 129.7, 130.1, 133.3 and 133.8 (3 *C*ar, 6 *C*Har meta, 6 *C*Har ortho, and 3 *C*Har para), 165.0, 165.5 and 166.2 (3 COC_6H_5), 181.6 (*C*═S). **Anomer α or *β*:** R_f = 0.34 (hexane/AcOEt 6/4). IR (KBr): 1725, 1600, 1536, 1262, 708 cm^{-1}. ^{1}H NMR ($CDCl_3$) *δ*: 3.21 (br s, 6H, $N(CH_3)_2$), 4.56 (dd, 1H, *J* = 11.6, 5.8 Hz, xyl H_{5a}), 4.67 (dd, 1H, *J* = 11.6, 5.9 Hz, xyl H_{5b}), 4.87 (m, 1H, xyl H_4), 5.80 (dd, 1H, *J* = 4.2, 1.8 Hz, xyl H_2), 5.89 (dd, 1H, *J* = 4.2, 1.8 Hz, xyl H_3), 6.12 (d, 1H, *J* = 9.0 Hz, N*H*), 7.02 (dd, 1H, *J* = 9.0, 4.2 Hz, xyl H_1), 7.40−7.70 (m, 9H, C*H*ar meta and C*H*ar para), 8.01 (dd, 2H, *J* = 8.6 Hz, *J* = 1.5 Hz, C*H*ar ortho), 8.04−8.11 (m, 4H, C*H*ar ortho). ^{13}C NMR ($CDCl_3$) *δ*: 40.6 ($N(CH_3)_2$), 62.4 (xyl C_5), 75.3 and 75.6 (xyl C_2 and C_3), 76.2 (xyl C_4), 85.5 (xyl C_1), 128.4, 128.5, 128.6, 128.9, 130.0, 133.2, 133.3, 133.8 and 134.1 (3 *C*ar, 6 *C*Har meta, 6 *C*Har ortho, and 3 *C*Har para), 164.1, 165.0 and 166.1 (3 COC_6H_5), 181.5 (*C*═S). MS: *m*/*z* 549 ([M + H]$^+$), 445, 305, 123 (100). HRMS (DCI): *m*/*z* calcd for $C_{29}H_{29}N_2O_7S$ [M + H]$^+$ 549.1696, found 549.1688.

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Supporting Information Available: General procedures, copies of ^{1}H and ^{13}C NMR for compounds **4** and **5**, and copies of ^{1}H, ^{13}C NMR, and 2D NMR (COSY and HMQC) for compounds **7a**−**f** and **8a**−**f** (except COSY of one anomer **8f**). This material is available free of charge via the Internet at http://pubs.acs.org.

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