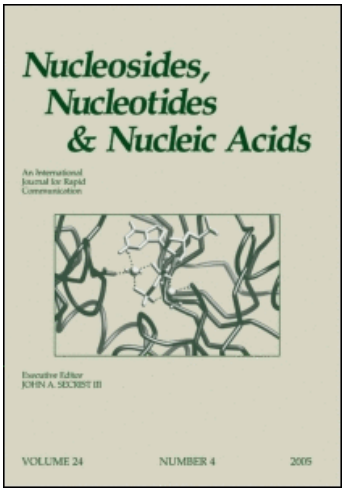

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Reaction of 5-αChloroacetyl-4-glycosylaminopyrimidines with Thiourea. Synthesis of 4-Glycosylaminofuro[2,3-d]pyrimidines and 4-Glycosylamino-5-(2-amino-4-thiazolyl)pyrimidines

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REACTION OF 5-α-CHLOROACETYL-4-GLYCOSYLAMINOPYRIMIDINES WITH THIOUREA. SYNTHESIS OF 4-GLYCOSYLAMINOFURO[2,3-d]PYRIMIDINES AND 4-GLYCOSYLAMINO-5-(2-AMINO-4-THIAZOLYL)PYRIMIDINES[1].

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Abstract : In the present paper we describe the preparation of some 4-glycosylamino-5-(2-amino-4-thiazolyl)pyrimidines **4**,**5** and the 4-glycopyranosylaminofuro[2,3-d]pyrimidine **3** by reaction of the corresponding 5-α-chloroacetylpyrimidine intermediate **2** with thiourea.

A large number of thiazole derivatives have been found to exhibit pharmacological activity[2-6]. It has been shown that they can possess diuretic[7], anthelmintic[7], mitostatic[2b], antiparasitic[2a] and antiviral[2b] properties. Furthemore they can act as mitodepressives[2b] and antihistaminics[7,8]. Among these products, there are also antibiotics such as sulfathiazole (synthetic derived from 2-aminothiazole) and a host of related compounds[9]. Moreover, the most important naturally occurring thiazole derivative is thiamine (vitamin B1)[10,11], which contains both thiazole and pyrimidine rings.

In the present paper we wish to describe the synthesis of some 4-glycosylamino-5-(2-amino-4-thiazolyl)pyrimidine and 4-

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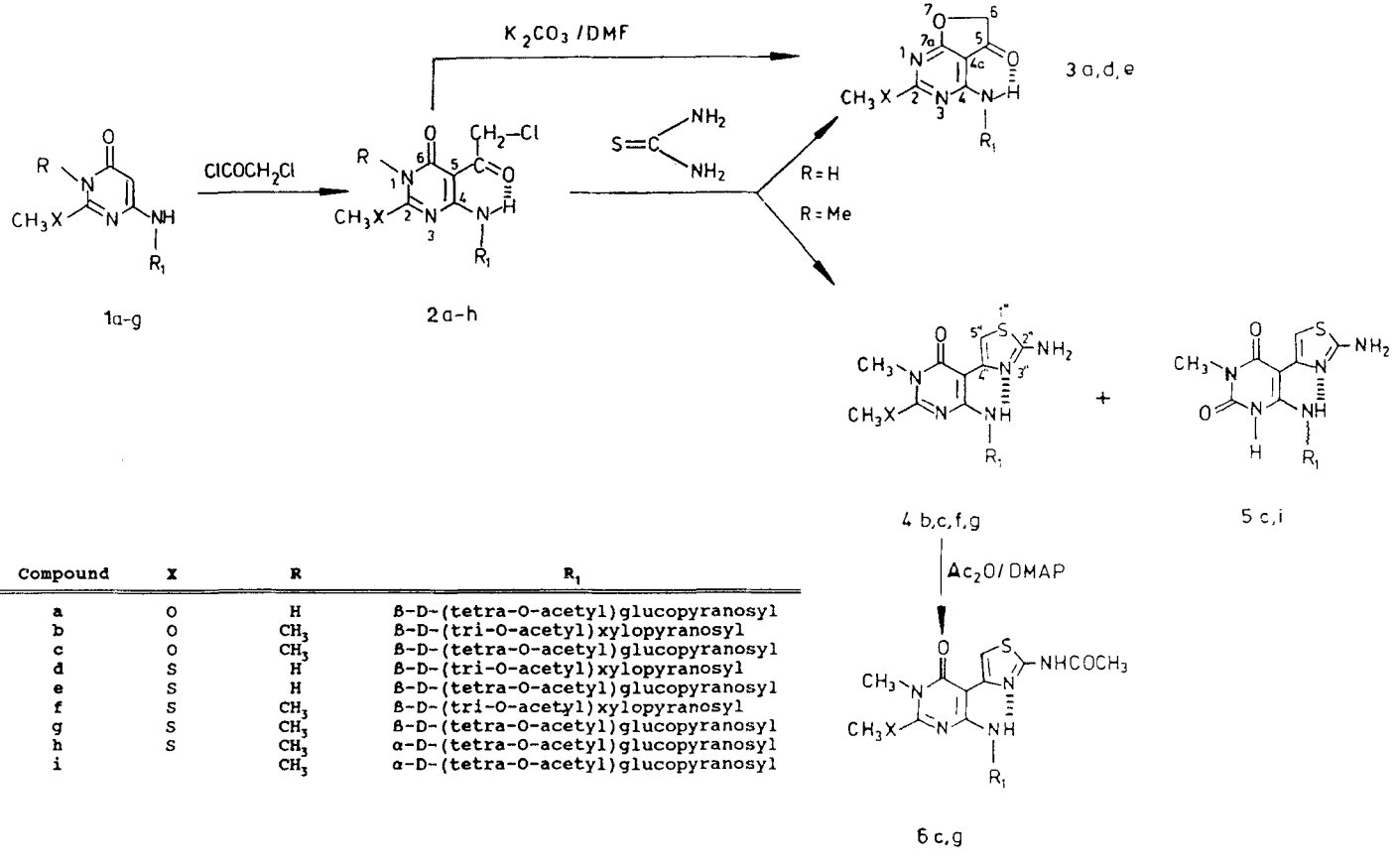

Compound	X	R	R_1
a	O	H	β-D-(tetra-O-acetyl)glucopyranosyl
b	O	CH_3	β-D-(tri-O-acetyl)xylopyranosyl
c	O	CH_3	β-D-(tetra-O-acetyl)glucopyranosyl
d	S	H	β-D-(tri-O-acetyl)xylopyranosyl
e	S	H	β-D-(tetra-O-acetyl)glucopyranosyl
f	S	CH_3	β-D-(tri-O-acetyl)xylopyranosyl
g	S	CH_3	β-D-(tetra-O-acetyl)glucopyranosyl
h	S	CH_3	α-D-(tetra-O-acetyl)glucopyranosyl
i		CH_3	α-D-(tetra-O-acetyl)glucopyranosyl

glycosylamino[2,3-d]pyrimidine derivatives in order that their anticancer and antiviral activities might be studied.

2-Amino and 2-guanidino-4-(2-amino-4-thiazolyl)pyrimidine derivatives have been synthesized by treatment of the corresponding 4-bromoacetylpyrimidines with thiourea[12]. However, Ross and coworkers[13] described the synthesis of 5-(2-methyl-4-thiazolyl)uracil and 5-(2-amino-4-thiazolyl)uracil by bromination of 5-acetyluracil and subsequent reaction with thioacetamide or thiourea respectively.

We have obtained the thiazolylpyrimidines **4**, **5** and the furo[2,3-d]pyrimidines **3** by a similar procedure (as the above mentioned) but by using 5-α-chloroacetyl derivatives **2** as starting products. These compounds **2** were obtained by reaction between the corresponding 4-glycopyranosylaminopyrimidines **1** and chloroacetyl chloride under conditions similar to those described in a previous publication[14] (compounds **2a-c**).

Thus, reaction of **1d-g** with an excess of freshly distilled $ClCOCH_2Cl$ in both anhydrous ethyl acetate and chloroform as solvent under reflux lead to the 5-α-chloroacetyl derivatives **2** with variable yields depending on the solvent used (see experimental part). Although the amount of chloroacetyl chloride and the reflux time were increased, the reaction to **2d** and **2e** did not take place completely in chloroform (36% of **2d** and no reaction to **2e**); but, significantly better yields were obtained when ethyl acetate was used as solvent (71% of **2d** and 56% of **2e**). When **1g** was reacted under the same conditions, anomerization was observed giving a mixture of 41-73% of the ß-anomer **2g** (^{1}H-NMR: $\delta H_{1'}$=5.8 ppm; $J_{1',2'}$=8.2 Hz) and 4-12% of the α-anomer **2h** (^{1}H-NMR: $\delta H_{1'}$=6.4 ppm; $J_{1',2'}$=5 Hz). In all these reactions, anomerization has been detected by TLC, nevertheless, when the reaction time was over only in the treatment of **1g** the α-anomer **2h** was isolated in low yield (4-12%). As we have observed in similar cases[14], hydrogen bonding between the C_4-NH- and C_5-CO- groups in compounds **2** (shown in scheme) has been detected by ^{1}H-NMR (see experimental part).

Reaction of **2a**, **2d** and **2e** with an excess of thiourea in hot 2-methoxyethanol and sodium acetate led to the furo[2,3-d] pyrimidines **3a**, **3d**, and **3e**, respectively. Compound **3a** was previously prepared in 78% yield by cyclization of **2a** with anhydrous K_2CO_3 in DMF[14]. Under these conditions and starting from **2d** and **2e**, compounds **3d** and **3e** have been prepared in 83% and 76% yields respectively.

Treatment of compounds **2b**, **2c**, **2f** and **2g** with thiourea under the same conditions described above, led to **4b**, **4c**, **4f** and **4g** as unique products, respectively, in good yields. When these reactions were carried out in the absence of sodium acetate a progressive complication (monitored by TLC) and a significant decrease of the yield was observed. However, in the reaction of **2c**, 13% of **4c**, 28% of **5c** (^{1}H-NMR: $\delta H_{1'}$=5.4 ppm; $J_{1',2'}$=5.5 Hz) and 21% of **5i** (α-anomer of **5c**. ^{1}H-NMR: $\delta H_{1'}$=6.1 ppm; $J_{1',2'}$=4.7 Hz) were obtained.

5-(2-amino-4-thiazolyl)pyrimidines **4** and **5** are formed by reaction between the 5-α-chloroacetyl group and thiourea. This reaction involves an isothiouronium salt (not isolable) the ring closure being accomplished by a condensation reaction using the carbonyl group of the acyl moiety. By contrast, treatment of compound **2a**, **2d** and **2e** under the same conditions led to the 4-glycopyranosylaminofuro[2,3-d]pyrimidines **3a**, **3d**, and **3e**, respectively. As we have observed in other cases[14], by using a basic medium, 5-α-chloroacetylpyrimidines can undergo cyclization giving furo[2,3-d]pyrimidines when N-1 is unsubstitued. Thiourea may provide the necessary basicity inducing cyclization towards **3**. On the other hand, formation of a highly conjugated carbonyl system can drive the reaction to furo[2,3-d]pyrimidines.

To corroborate the structures of compounds **4**, we have carried out acetylation with Ac_2O and dimethylaminopyridine (DMAP). The purification of compounds **6b** and **6f** has been attempted from the crude reaction mixtures by using column

chromatography , the isolation of these compounds being impossible due to the complexity of the obtained mixtures. The ^{1}H-NMR, ^{13}C-NMR and Mass spectra of compounds **6c** and **6g** were consistent with the proposed structures.

EXPERIMENTAL

Melting points were determined with a Gallemkamp Apparatus and are uncorrected. Proton nuclear magnetic resonance spectra were recorded with Hitachi Perkin-Elmer R-600 and Bruker AM-300 spectrometers, using tetramethylsilane as an internal standard. Carbon-13 nuclear magnetic resonance spectra were recorded with Bruker WP-805 and Bruker AM-300 spectrometers. Specific rotation values were determined with a Perkin-Elmer 141 polarimeter. Ultraviolet and visible spectra were recorded with a Beckman Model 25 spectrophotometer. Infrared spectra were recorded with Beckman 4250 and Perkin-Elmer 983 spectrophotometers. The analysis of C, H and N have been performed by "Servicios Técnicos de la Universidad de Granada", in Granada. Mass spectra were recorded with a Hewlett-Packard HP-5988-A spectrometer. Thin Layer chromatography (TLC) was performed on Merck pre-coated TLC aluminum sheets silicagel $60F_{254}$ using the eluent indicated in each case, visualization was accomplished by ultraviolet absorbance followed by charring with a 4% sulphuric acid/methanol solution. Column chromatography was done on Merck silicagel 60 (70-230 mesh) using CH_2Cl_2-AcOEt (0-20% of AcOEt).

Compounds **1** were prepared by previously reported methods[15].

5-α-chloroacetyl-1,6-dihydro-2-methylthio-6-oxo-4-ß-D-(2,3,4-tri-O-acetyl)xylopyranosylaminopyrimidine, 2d.

1.5 ml (18.52 mmol) of freshly distilled $ClCOCH_2Cl$ were added to a solution containing 1.66 g (4 mmol) of **1d** in 50 ml of anhydrous ethyl acetate. A white solid precipitated after 20-30 minutes. The mixture was stirred under reflux for 5-5.30 hours (at this time no starting product was detected in TLC, eluent CH_2Cl_2/MeOH, 9:1) and next was allowed to stand at room temperature for 12 h. The solid was filtered, washed with ethyl acetate and recrystallized from EtOH. This compound was identified as the 5-α-chloroacetyl derivative **2d**. 1.40 g (71%). M.P.: 219°C (dec.). $[\alpha]_D^{25}$= +27.5° (c 1, $CHCl_3$). Rf 0.65, CH_2Cl_2/MeOH (9:1). UV (MeOH): λ_{max}nm (ϵ): 227 (27900), 249 (shoulder), 271 (6700), 310 (14500). IR (KBr) ν_{max}(cm^{-1}): 3080 m, 3000 m, 2920 m, 2860 w, 1740 s, 1660 s, 1570 s, 1470 s, 1430 m, 1380 m, 1250 s, 1230 s, 1080 s, 1065 s, 1040 s. Mass spectrum, m/z (abundance %): 456 (1) M^+-Cl, 260 (1), 233 (1), 198 (24), 184 (1), 157 (2), 78 (1), 43 (100). ^{1}H-NMR (DMSO-d_6) δ(ppm): 2.6 (3H,s, CH_3S), 4.9 (2H,s, $COCH_2$), 5.8 (1H,st, H-1'), 10.8 (1H, d, $J_{1',NH}$= 8.2 Hz, D_2O exchangeable, C_4-NH), 12.8 (1H, s broad, D_2O exchangeable, N_1-H). ^{13}C-NMR (DMSO-d_6) δ (ppm): 13.0 (CH_3S), 51.2 ($CO\underline{C}H_2$), 62.9 (C-5'), 78.5 (C-1'), 94.4 (C-5), 161.4, 162.2, 166.5 (C-2, C-4, C-6), 190.6 ($\underline{C}OCH_2$). Anal. Calcd. for $C_{18}H_{22}N_3O_9Cl$: C, 43.95; H, 4.51; N, 8.54. Found: C, 44.20; H, 4.52; N, 8.92.

When chloroform (50 ml) was used as solvent, the mixture was stirred under reflux for 4-5 h (at this time no departure product was detected by TLC). The reaction crude was neutralized with a saturated $NaHCO_3$ aqueous solution, washed with water, dried over Na_2SO_4 and evaporated under reduced pressure. The excess of solvent was removed by dissolving in EtOH and evaporating several times. The obtained residue was then crystallized from EtOH and identified as **2d**. 0.71 g (36%).

5-α-chloroacetyl-1,6-dihydro-4-ß-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-2-methylthio-6-oxopyrimidine, 2e.

Reaction of 1.95 g (4 mmol) of **1e** with $ClCOCH_2Cl$ in ethyl acetate was carried out as described above for **1d**, leading to compound **2e** which was recrystallized from EtOH/DMSO. 1.26 g (56%). M.P.: 230°C (dec.). $[\alpha]_D^{25}$= +4.0° (c 1, DMSO). Rf 0.63, CH_2Cl_2/MeOH (9:1). UV (MeOH): λ_{max}nm (ε): 228 (28300), 249 (shoulder), 271 (6500), 310 (15100). IR (KBr) $\nu_{max}(cm^{-1})$: 3140 w, 3080 m, 3000 m, 2920 m, 2860 w, 1745 s, 1650 s, 1565 s, 1465 s, 1420 m, 1380 m, 1245 s, 1225 s, 1070 s, 1040 s. Mass spectrum, m/z (abundance %): 527 (1) M^+-Cl, 334 (4), 234 (1), 198 (12), 78 (12), 43 (100). ^{1}H-NMR (DMSO-d_6) δ (ppm): 2.6 (3H, s, CH_3S), 4.9 (2H, s, $COCH_2$), 5.8 (1H, st, with D_2O to d, $J_{1',2'}$= 8.2 Hz, H-1'), 10.6 (1H, d, $J_{1',NH}$= 8.2 Hz, D_2O exchangeable, C_4-NH), 12.8 (1H, s broad, D_2O exchangeable, N_1-H). ^{13}C-NMR (DMSO-d_6) δ (ppm): 13.0 (CH_3S), 51.2 ($CO\underline{C}H_2$), 61.9 (C-6'), 78.1 (C-1'), 94.6 (C-5), 161.3,162.2, 166.5 (C-2, C-4, C-6), 190.7 ($\underline{C}OCH_2$). Anal. Calcd. for $C_{21}H_{26}N_3O_{11}SCl$: C, 44.72; H, 4.65; N, 7.45. Found: C, 44.10; H, 4.36; N, 7.65.

5-α-chloroacetyl-1,6-dihydro-1-methyl-2-methylthio-6-oxo-4-ß-D-(2,3,4-tri-O-acetyl)xylopyranosylaminopyrimidine, 2f.

Compound **1f** (4 mmol, 1.72 g) was transformed to **2f** according to the procedure described for the preparation of **2d**. In both solvents, ethyl acetate and chloroform, reactions gave after 2 hours 5-α-chloroacetyl derivative **2f** which was recrystallized from EtOH. 1.86 g (92%, in ethyl acetate), 1.92 g (95%, in chloroform). M.P.: 257°(dec.). $[\alpha]_D^{25}$= -0.2° (c 1, $CHCl_3$). Rf 0.79, CH_2Cl_2/MeOH (9:1). UV (MeOH): λ_{max}nm (ε): 227 (26500), 249 (shoulder), 278 (7100), 310 (13600). IR (KBr) $\nu_{max}(cm^{-1})$: 3480 w, 3190 w, 3010 m, 2940 m, 1760 s, 1680 s, 1640 s, 1570 s, 1525 s, 1470 s, 1410 s, 1370 s, 1300 m, 1240 s, 1215 s, 1120 m, 1070 s. Mass spectrum, m/z (abundance %): 506 (1) M^+, 470 (1), 456 (1), 260 (1), 247 (1), 212 (8), 198 (4), 170 (1), 78 (1), 43 (100). ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.6 (3H, s, CH_3S), 3.5 (3H, s,

CH_3N),4.9 (2H,s,$COCH_2$), 5.8 (1H,st, with D_2O to d,$J_{1',2'}$= 6.8 Hz, H-1'), 11.1 (1H, d, $J_{1',NH}$= 8.2 Hz, D_2O exchangeable, C_4-NH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 15.3 (CH_3S), 30.0 (CH_3N), 51.8 ($CO\underline{C}H_2$), 62.8 (C-5'), 78.6 (C-1'),94.9 (C-5), 160.8, 161.2, 167.7 (C-2, C-4, C-6), 192.2 ($\underline{C}OCH_2$). Anal. Calcd. for $C_{19}H_{24}N_3O_9SCl$: C, 45.10; H, 4.78; N, 8.31. Found: C, 45.11; H, 4.71; N, 8.45.

Reaction of 1g with chloroacetyl chloride.

Treatment of 2.01 g (4 mmol) of **1g** with 1.5 ml (18.52 mmol) of $ClCOCH_2Cl$ in ethyl acetate was carried out under the same conditions as we described for **1d**. The mixture was stirred under reflux for 3 hours (no starting product was then detected by TLC). The solid was filtered, washed with ethyl acetate and recrystallized from EtOH. This compound was identified as **5-α-chloroacetyl-1,6-dihydro-4-ß-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-1-methyl-2-methylthio-6-oxopyrimidine, 2g**. 0.95-1.57 g (41-68 %). M.P.: 222°C. $[\alpha]_D^{25}$= +15° (c 1, $CHCl_3$). Rf 0.74, CH_2Cl_2/MeOH (9:1). Rf 0.23, CH_2Cl_2/Hexane/EtOH (7:5:0.4). UV (MeOH): λ_{max}nm (ϵ): 228 (26100), 248 (shoulder), 277 (6600), 312 (13600). IR (KBr) ν_{max}(cm^{-1}): 3480 w, 3210 w, 3090 w, 2950 m, 1755 s, 1730 s, 1675 s, 1635 s, 1575 s, 1525 s, 1470 s, 1420 s, 1370 s, 1315 m, 1240 s, 1210 s, 1085 s, 1065 s, 1035 s. Mass spectrum, m/z (abundance %): 578 (1) M^+, 542 (1), 528 (1), 499 (1), 331 (1), 247 (1), 212 (7), 198 (3), 169 (4), 78 (1), 43 (100). ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.6 (3H, s, CH_3S), 3.4 (3H, s, CH_3N), 4.9 (2H, s, $COCH_2$), 5.8 (1H, st, with D_2O to d, $J_{1',2'}$= 8.2 Hz, H-1'), 10.9 (1H, d, $J_{1',NH}$= 8.2 Hz, D_2O exchangeable, C_4-NH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 15.2 (CH_3S), 30.1 (CH_3N), 51.6 ($CO\underline{C}H_2$), 62.3 (C-6'), 79.6 (C-1'), 95.1 (C-5), 161.0, 161.1, 167.7 (C-2, C-4, C-6), 192.1 ($\underline{C}OCH_2$). Anal. Calcd. for $C_{22}H_{28}N_3O_{11}SCl$: C, 45.71; H, 4.88; N, 7.27. Found: C, 46.27; H, 4.78; N, 7.33.

The mother liquors were neutralized with a saturated $NaHCO_3$ solution, washed with water, dried over $CaCl_2$ and evaporated

under reduced pressure. The syrupy residue was recrystallized from ethanol and identified as **5-α-chloroacetyl-1,6-dihydro-4-α-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-1-methyl-2-methylthio-6-oxopyrimidine**, **2h**. 0.09-0.14 g (4-6 %). M.P.: 167°C. $[\alpha]_D^{25}$= +96° (c 1, $CHCl_3$). Rf 0.76, CH_2Cl_2/MeOH (9:1). Rf 0.30, CH_2Cl_2/Hexane/EtOH (7:5:0.4). UV (MeOH): λ_{max}nm (ε): 228 (26500), 249 (shoulder), 278 (7300), 312 (13800). IR (KBr) $\nu_{max}(cm^{-1})$: 3460 w, 3200 m, 3080 m, 3000 m, 2950 m, 2930 w, 1745 s, 1660 s, 1620 s, 1565 s, 1525 s, 1470 s, 1405 s, 1365 s, 1305 m, 1240 s, 1210 s, 1165 m, 1075 s, 1040 s, 1020 s. Mass spectrum, m/z (abundance %): 580 (1), 578 (3) M^+, 542 (5), 528 (3), 500 (1), 482 (56), 331 (4), 248 (10), 212 (57), 198 (24), 169 (32), 77 (1), 43 (100). ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.5 (3H, s, CH_3S), 3.4 (3H, s, CH_3N), 4.9 (2H, s, $COCH_2$), 6.4 (1H, st, with D_2O to d, $J_{1',2'}$= 5 Hz, H-1'), 11.3 (1H, d, $J_{1',NH}$= 8.2 Hz, D_2O exchangeable, C_4-NH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 15.3 (CH_3S), 30.1 (CH_3N), 51.9 ($CO\underline{C}H_2$), 61.7 (C-6'), 75.4 (C-1'), 95.0 (C-5), 161.1, 161.2, 168.2 (C-2, C-4, C-6), 192.6 ($\underline{C}OCH_2$). Anal. Calcd. for $C_{22}H_{28}N_3O_{11}SCl$: C, 45.71; H, 4.88; N, 7.27. Found: C, 45.98; H, 4.93; N, 7.50.

In the reaction of **1g** with chloroacetyl chloride in chloroform, after 4-5 hours according to the procedure described for the preparation of **2g**, compounds **2g** (ß-anomer, 1.69 g, 73%) and **2h** (α-anomer, 0.28 g, 12%) were successively obtained by fractionated crystallization.

Reaction of 2a, 2d and 2e with thiourea.

0.152 g (2 mmol) of thiourea were added to a solution of 1 mmol of **2a**, **2d** or **2e** and 0.164 g (2 mmol) of anhydrous sodium acetate in 15 ml of hot 2-methoxyethanol. The reaction mixture was stirred on a hot plate until no starting product was detected by TLC (eluent CH_2Cl_2/AcEt, 3:2). The mixture was poured into cold water and allowed to stand in the refrigerator for 10 hours. The solid, which precipitated on cooling, was

collected by filtration, washed with water and ethanol to afford a white powder. This product was recrystallized from ethanol and identified as:

5,6-dihydro-4-ß-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-2-methoxy-5-oxo furo[2,3-d]pyrimidine, 3a. Reaction time: 25 minutes. 0.25 g (49%)[14].

5,6-dihydro-2-methylthio-5-oxo-4-ß-D-(2,3,4-tri-O-acetyl)xylopyranosylamino furo[2,3-d]pyrimidine, 3d. Reaction time: 5 minutes. 0.43 g (95%). M.P.: 198°C. $[\alpha]_D^{25}$= -1.2° (c 1, $CHCl_3$). Rf 0.59, CH_2Cl_2/AcEt (3:2). UV (MeOH): λ_{max}nm (ϵ): 230 (16400), 249 (10500), 302 (23400). IR (KBr) $\nu_{max}(cm^{-1})$: 3380 m, 2980 w, 2930 w, 2840 w, 1745 s, 1710 s, 1600 s, 1500 m, 1425 m, 1390 m, 1365 m, 1330 m, 1300 m, 1250 s, 1225 s, 1170 m, 1135 m, 1105 m, 1070 s, 1030 s, 1010 s. Mass spectrum, m/z (abundance %): 455 (1) M^+, 335 (10), 260 (1), 198 (18), 43 (100). ^{1}H-NMR (DMSO-d_6) δ (ppm): 2.5 (3H, s, CH_3S), 4.8 (2H, s, C_6-H_2), 5.8 (1H, m, with D_2O to d, $J_{1',2'}$= 8.2 Hz, H-1'), 8.1 (1H, s broad, D_2O exchangeable, C_4-NH). ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.6 (3H, s, CH_3S), 4.7 (2H, s, C_6-H_2), 5.7 (1H, st, with D_2O to d, $J_{1',2'}$= 8.2 Hz, H-1'), 7.3 (1H, d, $J_{1',NH}$= 9.6 Hz, D_2O exchangeable, C_4-NH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 14.6 (CH_3S), 63.8 (C-5'), 74.6 (C-6), 78.7 (C-1'), 92.4 (C-4a), 157.5 (C-4), 169.8 (C-2), 182.8 (C-7a), 193.2 (C-5).Anal. Calcd. for $C_{18}H_{21}N_3O_9S$: C, 47.46; H, 4.65; N, 9.23. Found: C, 47.57; H, 4.50; N, 9.30.

5,6-dihydro-4-ß-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-2-methylthio-5-oxo furo[2,3-d]pyrimidine, 3e. Reaction time: 10 minutes. 0.47 g (89%). M.P.:210°C. $[\alpha]_D^{25}$= -22.8° (c 1, $CHCl_3$). Rf 0.53, CH_2Cl_2/AcEt (3:2). UV (MeOH): λ_{max}nm (ϵ): 231 (16000), 249 (10200), 301 (23000). IR (KBr) $\nu_{max}(cm^{-1})$: 3385 m, 2930 w, 2860 w, 1740 s, 1700 s, 1590 s, 1505 m, 1420 m, 1365 m, 1330 m, 1290 m, 1245 s, 1225 s, 1175 m, 1160 m, 1135 m, 1090 m, 1035 s, 1000 m. Mass spectrum, m/z (abundance %): 527 (1) M^+, 331 (1), 198 (9), 154 (1), 43 (100). ^{1}H-NMR (DMSO-d_6) δ

(ppm): 2.5 (3H, s, CH_3S), 4.8 (2H, s, C_6-H_2), 5.9 (1H, m, with D_2O to d, $J_{1',2'}$= 8.2 Hz, H-1'), 8.1 (1H, s broad, D_2O exchangeable, C_4-NH). ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.7 (3H, s, CH_3S), 4.7 (2H, s, C_6-H_2), 5.8 (1H,m,with D_2O to d,$J_{1',2'}$= 8.2 Hz, H-1'), 7.3 (1H, d, $J_{1',NH}$= 9.6 Hz, D_2O exchangeable, C_4-NH). ^{13}C-NMR ($CDCl_3$) δ(ppm): 14.6 (CH_3S),61.8 (C-6'),74.6 (C-6),78.9 (C-1'), 92.5 (C-4a), 157.5 (C-4),169.5 (C-2),182.8 (C-7a),193.1 (C-5). Anal. Calcd. for $C_{21}H_{25}N_3O_{11}S$: C, 47.81; H, 4.78; N, 7.96. Found: C, 47.34; H, 4.50; N, 8.08.

Reaction of 2b with thiourea.

Under the same conditions as described for **2a**, 0.49 g (1 mmol) of **2b** reacted with thiourea (0.152 g, 2 mmol) in the presence of sodium acetate (0.164 g, 2 mmol) leading to a solid which was recrystallized from ethanol being identified as **5-(2-amino-4-thiazolyl)-1,6-dihydro-1-methyl-2-methoxy-6-oxo-4-ß-D-(2,3,4-tri-O-acetyl)xylopyranosylaminopyrimidine, 4b.** Reaction time: 10 minutes. 0.13 g (26 %). M.P.: 230°C (dec.). $[\alpha]_D^{25}$= -11.5° (c 1, $CHCl_3$). Rf 0.44, CH_2Cl_2/AcEt (3:2). UV (MeOH): λ_{max}nm (ϵ): 221 (22300), 249 (8800), 314 (11700). IR (KBr) ν_{max}(cm^{-1}): 3480 m, 3390 m, 3160 w, 2950 m, 1755 s, 1650 s, 1620 s, 1580 s, 1535 s, 1470 m, 1455 m, 1415 m, 1380 m, 1365 m, 1345 m, 1300 m, 1240 s, 1220 s, 1130 m, 1120 m, 1065 s, 1060 s, 1040 s, 1030 s. Mass spectrum, m/z (abundance %): 513 (1), 511 (9) M^+, 260 (1), 253 (1), 153 (1), 100 (1), 85 (6), 57 (2), 45 (3), 43 (100). ^{1}H-NMR (DMSO-d_6) δ (ppm): 3.2 (3H, s, CH_3N), 4.0 (3H, s, CH_3O),5.7 (1H,st,with D_2O to d,$J_{1',2'}$= 8.2 Hz, H-1'), 6.8 (2H, s, D_2O exchangeable, $C_{2''}$-NH_2), 7.4 (1H, s, H-5''), 10.8 (1H, d, $J_{1',NH}$= 8.2 Hz, D_2O exchangeable, C_4-NH). ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.4 (3H, s, CH_3N), 4.0 (3H, s, CH_3O), 5.3 (6H, m, with D_2O to 4H, $C_{2''}$-NH_2 and four sugar protons), 7.4 (1H, s, H-5''), 10.8 (1H, d, $J_{1',NH}$= 5.0 Hz, D_2O exchangeable, C_4-NH). ^{13}C-NMR ($CDCl_3$) δ(ppm):27.6 (CH_3N), 55.2 (CH_3O),64.1 (C-5'),80.9 (C-1'), 90.9 (C-5), 103.7 (C-5''), 144.0 (C-4''), 154.4 (C-2''), 156.8, 161.6, 165.1 (C-2, C-4, C-6). Anal. Calcd. for $C_{20}H_{25}N_5O_9S$: C, 46.96; H, 4.93; N, 13.69. Found: C, 46.93; H, 5.11; N, 13.59.

Reaction of 2c with thiourea.

According to the procedure described for **2a**, treatment of 0.56 g (1 mmol) of **2c** with 0.152 g (2 mmol) of thiourea in the presence of sodium acetate (0.164 g, 2 mmol), afforded a solid which was recrystallized from ethanol and identified as **5-(2-amino-4-thiazolyl)-1,6-dihydro-1-methyl-2-methoxy-4-ß-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-6-oxopyrimidine, 4c**. Reaction time: 10-15 minutes. 0.48 g (82%). M.P.: 240-5°C (dec.). $[\alpha]_D^{25}$= +6.3° (c 1, $CHCl_3$). Rf 0.41, CH_2Cl_2/AcEt (3:2). UV (MeOH): λ_{max}nm (ϵ): 221 (24400), 248 (10000), 313 (12700). IR (KBr) $\nu_{max}(cm^{-1})$: 3440 m, 3350 m, 3200 w, 3160 w, 2945 m, 1755 s, 1730 s, 1655 s, 1625 s, 1580 s, 1540 s, 1470 m, 1455 m, 1410 w, 1365 m, 1340 w, 1320 w, 1245 s, 1215 s, 1130 w, 1075 m, 1065 m, 1035 s. Mass spectrum, m/z (abundance %): 585 (0.4), 583 (3) M^+, 331 (1), 252 (1), 236 (5), 153 (1), 100 (1), 85 (2), 58 (1), 45 (1), 43 (100). ^{1}H-NMR (DMSO-d_6) δ (ppm): 3.2 (3H, s, CH_3N), 4.0 (3H, s, CH_3O), 5.7 (1H, st, with D_2O to d, $J_{1',2'}$= 9.2 Hz, H-1'), 6.7 (2H, s, D_2O exchangeable, $C_{2''}$-NH_2), 7.4 (1H,s,H-5''), 10.8 (1H,d,$J_{1',NH}$= 8.2 Hz,D_2O exchangeable, C_4-NH). ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.4 (3H, s, CH_3N), 4.0 (3H, s, CH_3O), 5.4 (6H, m, with D_2O to 4H, $C_{2''}$-NH_2 and four sugar protons), 7.6 (1H,s, H-5''), 10.8 (1H,d,$J_{1',NH}$= 6.2 Hz,D_2O exchangeable,C_4-NH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 27.6 (CH_3N), 55.1 (CH_3O), 62.5 (C-6'), 80.5 (C-1'), 91.0 (C-5), 103.7 (C-5''), 144.0 (C-4''), 154.4 (C-2''), 156.7, 161.5, 165.1 (C-2, C-4, C-6). Anal. Calcd. for $C_{23}H_{29}N_5O_{11}S$: C, 47.33; H, 5.01; N, 12.00. Found: C, 47.54; H, 5.00; N, 12.00.

Different results were obtained when the reaction was carried out in the absence of sodium acetate using the following method: to a solution of 0.56 g (1 mmol) of **2c** in 15 ml of hot 2-methoxyethanol, 0.152 g (2 mmol) of thiourea were added. The reaction mixture was stirred on a hot plate for 10-15 minutes (at this time no starting material was detected by TLC, eluent CH_2Cl_2/AcEt, 3:2). After this time the crude reaction mixture was evaporated under reduced pressure and the

obtained residue was extracted with four portions of 10 ml of hot CH_2Cl_2 to remove the excess of thiourea. The organic solution was then evaporated under reduced pressure. The solution of the syrupy residue in 1 ml of CH_2Cl_2 was applied on a short chromatographic column and eluted by using CH_2Cl_2-AcEt (0-20 %) mixtures. The eluted fractions containing the compounds were evaporated under reduced pressure and crystallized from ethanol. Three products were obtained; the first one was identified as the previously described **5-(2-amino-4-thiazolyl)-1,6-dihydro-1-methyl-2-methoxy-4-ß-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-6-oxopyrimidine, 4c**. 0.07 g (13%).

The second collected fraction was identified as **5-(2-amino-4-thiazolyl)-1,2,3,6-tetrahydro-1-methyl-4-α-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-2,6-dioxopyrimidine, 5i**. 0.12 g (21%). M.P.: 192-4°C. $[\alpha]_D^{25}$= +216.3° (c 1, $CHCl_3$). Rf 0.33, CH_2Cl_2/AcEt (3:2). UV (MeOH): λ_{max}nm (ϵ): 224 (11400), 245 (12900), 307 (13100). IR (KBr) ν_{max}(cm^{-1}): 3460 m, 3360 m, 3210 w, 3160 w, 2950 m, 1740 s, 1700 s, 1630 s, 1515 m, 1460 m, 1365 m, 1220 s, 1165 m, 1060 s, 1035 s, 990 m. Mass spectrum, m/z (abundance %): 571 (6), 569 (57) M^+, 331 (1), 239 (17), 139 (8), 99 (3), 83 (2), 59(3), 45 (3), 43 (100). ^{1}H-NMR (DMSO-d_6) δ (ppm): 3.1 (3H, s, CH_3N), 6.1 (1H, st, with D_2O to d, $J_{1',2'}$= 4.7 Hz, H-1'), 6.9 (2H, s, D_2O exchangeable, $C_{2''}$-NH_2), 7.4 (1H, s, H-5''), 10.8 (1H, s, D_2O exchangeable, N_3-H), 11.6 (1H, d, $J_{1',NH}$= 7.9 Hz, D_2O exchangeable, C_4-NH). ^{13}C-NMR (DMSO-d_6) δ (ppm): 26.5 (CH_3N), 61.6 (C-6'), 75.4 (C-1'), 84.9 (C-5), 100.4 (C-5''), 142.9 (C-4''),149.1 (C-2''), 149.2,161.1,169.1 (C-2, C-4, C-6). Anal. Calcd. for $C_{22}H_{27}N_5O_{11}S$: C, 46.39; H, 4.78; N, 12.29. Found: C, 46.30; H, 4.67; N, 13.01.

The third fraction was identified as **5-(2-amino-4-thiazolyl)-1,2,3,6-tetrahydro-1-methyl-4-ß-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-2,6-dioxopyrimidine, 5c**. 0.16 g (28%). M.P.: 214°C (dec.). $[\alpha]_D^{25}$= -90.5° (c 1,$CHCl_3$). Rf 0.26, CH_2Cl_2/AcEt (3:2). UV (MeOH): λ_{max}nm (ϵ): 245 (14000), 305

(12800), 358 (4800). IR (KBr) $\nu_{max}(cm^{-1})$: 3425 m, 3320 m, 3200 w, 3150 w, 2950 w, 1750 s, 1715 s, 1700 s, 1620 s, 1515 s, 1455 m, 1370 s, 1315 w, 1225 s, 1165 m, 1055 m, 1030 s. Mass spectrum, m/z (abundance %): 571 (1), 569 (6) M^+, 331 (1), 239 (7), 222 (5), 139 (5), 100 (1), 85 (2), 58 (1), 45 (2), 43 (100). ^{1}H-NMR (DMSO-d_6) δ (ppm): 3.2 (3H, s, CH_3N), 5.4 (1H, m, with D_2O to d $J_{1',2'}$= 5.5 Hz, H-1'), 6.8 (2H, s, D_2O exchangeable, $C_{2''}$-NH_2), 7.3 (1H,s, H-5''), 10.9 (1H,s,D_2O exchangeable,N_3-H), 11.6 (1H, d, $J_{1',NH}$= 6.8 Hz, D_2O exchangeable, C_4-NH). ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.4 (3H, s, CH_3N), 5.4 (6H, m, with D_2O to 4H, $C_{2''}$-NH_2 and four sugar protons), 7.6 (1H, s, H-5''), 9.9 (1H, s, D_2O exchangeable, N_3-H), 11.6 (1H, d, $J_{1',NH}$= 5.5 Hz, D_2O exchangeable, C_4-NH). ^{13}C-NMR ($CDCl_3$) δ(ppm): 27.5 (CH_3N), 62.2 (C-6'), 80.0 (C-1'), 86.6 (C-5), 103.2 (C-5''), 143.0 (C-4''), 149.1 (C-2''), 150.9, 161.7, 165.6 (C-2, C-4, C-6). Anal. Calcd. for $C_{22}H_{27}N_5O_{11}S \cdot H_2O$: C, 44.97; H, 4.97; N, 11.92. Found: C, 45.28; H, 4.88; N, 11.53.

Reaction of 2f with thiourea.

Under the same conditions as described for **2a**, 0.51 g (1 mmol) of **2f** reacted with 0.152 g (2 mmol) of thiourea in the presence of sodium acetate (0.164 g, 2 mmol) affording a white solid which was recrystallized from ethanol and identified as **5-(2-amino-4-thiazolyl)-1,6-dihydro-1-methyl-2-methylthio-6-oxo-4-ß-D-(2,3,4-tri-O-acetyl)xylopyranosylaminopyrimidine, 4f**. Reaction time: 10 minutes. 0.33 g (62%). M.P.: 230°C (dec.). $[\alpha]_D^{20}$= -6.6° (c 1, $CHCl_3$). Rf 0.53, CH_2Cl_2/AcEt (3:2). UV (MeOH): λ_{max}nm (ϵ): 221 (22300), 244 (21000), 333 (12300). IR (KBr) $\nu_{max}(cm^{-1})$: 3440 m, 3340 m, 3200 w, 3140 w, 2930 w, 1750 s, 1635 s, 1610 s, 1510 s, 1440 s, 1410 m, 1365 s, 1320 m, 1310 m, 1235 s, 1210 s, 1170 m, 1060 s, 1025 s, 965 m. Mass spectrum, m/z (abundance %): 529 (0.5), 527 (4) M^+, 252 (2), 168 (1), 85 (5), 58 (1), 45 (2), 43 (100). ^{1}H-NMR (DMSO-d_6) δ (ppm): 2.6 (3H, s, CH_3S), 3.4 (3H,s, CH_3N), 5.7 (1H,st,with D_2O to d,$J_{1',2'}$= 8.2 Hz, H-1'), 6.8 (2H, s, D_2O exchangeable, $C_{2''}$-NH_2), 7.4 (1H,s,H-5''),

10.7 (1H, d, $J_{1',NH}$= 8.2 Hz, D_2O exchangeable, C_4-NH). ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.6 (3H, s, CH_3S), 3.5 (3H, s, CH_3N), 5.3 (6H, m, with D_2O to 4 H, $C_{2''}$-NH_2 and four sugar protons), 7.7 (1H, s, H-5''), 10.8 (1H, s broad, D_2O exchangeable, C_4-NH). ^{13}C-NMR ($CDCl_3$) δ(ppm):14.9 (CH_3S),30.2 (CH_3N),64.1 (C-5'), 81.0 (C-1'), 92.2 (C-5), 105.2 (C-5''), 144.0 (C-4''), 155.7 (C-2''), 159.7, 160.8, 165.2 (C-2, C-4, C-6). Anal. Calcd. for $C_{20}H_{25}N_5O_8S_2$: C, 45.53; H, 4.78; N, 13.27. Found: C, 45.09; H, 4.81; N, 12.21.

Reaction of 2g with thiourea.

0.58 g (1 mmol) of **2g** were treated with 0.152 g (2 mmol) of thiourea in 2-methoxyethanol and sodium acetate (0.164 g, 2 mmol), according to the general procedure described for **2a**. The resulting solid was recrystallized from ethanol and identified as **5-(2-amino-4-thiazolyl)-1,6-dihydro-1-methyl-2-methylthio-4-ß-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-6-oxopyrimidine, 4g**. Reaction time: 10 minutes. 0.54 g (87%). M.P.: 240°C (dec.). $[\alpha]_D^{25}$= -9.0° (c 1, $CHCl_3$). Rf 0.51, CH_2Cl_2/AcEt (3:2). UV (MeOH) λ_{max}nm (ϵ): 222 (19500), 243 (18700), 336 (11200). IR (KBr) ν_{max}(cm^{-1}): 3450 s, 3360 s, 3200 w, 3160 w, 2950 m, 1760 s, 1740 s, 1655 s, 1615 s, 1520 s, 1450 s, 1410 m, 1365 s, 1320 m, 1310 m, 1250 s, 1215 s, 1175 m, 1150 w, 1065 s, 1030 s, 980 m. Mass spectrum, m/z (abundance %): 601 (0.4), 599 (3) M^+, 269 (3), 253 (5), 169 (3), 85 (1), 45 (1), 43 (100). ^{1}H-NMR (DMSO-d_6) δ (ppm): 2.6 (3H, s, CH_3S), 3.4 (3H, s, CH_3N), 5.8 (1H, st, with D_2O to d, $J_{1',2'}$= 8.5 Hz, H-1'), 6.8 (2H, s, D_2O exchangeable, $C_{2''}$-NH_2), 7.4 (1H, s, H-5''), 10.8 (1H, d, $J_{1',NH}$= 8.2 Hz, D_2O exchangeable, C_4-NH). ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.6 (3H, s, CH_3S), 3.6 (3H, s, CH_3N), 5.5 (6H, m, with D_2O to 4 H, $C_{2''}$-NH_2 and four sugar protons), 7.7 (1H, s, H-5''), 10.9 (1H, s broad, D_2O exchangeable, C_4-NH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 14.8 (CH_3S), 30.2 (CH_3N), 62.5 (C-6'), 80.5 (C-1'), 92.4 (C-5), 105.2 (C-5''), 144.0 (C-4''), 155.6 (C-2''), 159.5, 160.8, 165.2 (C-2, C-4, C-6). Anal. Calcd. for $C_{23}H_{29}N_5O_8S_2 \cdot H_2O$: C, 44.72; H, 5.06; N, 11.34. Found: C, 45.20; H, 4.90; N, 11.65.

Cyclization of 5-α-chloroacetyl derivatives 2c and 2e.

To 3 ml of DMF, 1 mmol of the corresponding 5-α-chloroacetyl derivative (**2c** or **2e**) was added. To the resulting solution 0.14 g (1 mmol) of anhydrous K_2CO_3 were added. The reaction mixture was stirred at 80-90°C for variable period of time until no starting product was detected by TLC (eluent CH_2Cl_2/AcEt, 3:2). The reaction mixture was poured into cold water and allowed to stand into the refrigerator for 10 hours. A solid precipitated which was filtered, washed with water and recrystallized from EtOH yielding the corresponding furo[2,3-d]pyrimidine **3d** (Reaction time: 5 minutes. 0.38 g, 83%) or **3e** (Reaction time: 10 minutes. 0.40 g, 76%).

Acetylation of compounds 4c and 4g.

To a suspension of 0.5 mmol of the corresponding 5-(2-amino-4-thiazolyl)pyrimidine derivative, **4**, in 5 ml of methanol, 10 ml of Ac_2O and a catalytic amount of DMAP were added. After 30 minutes the solution became clear. The reaction mixture was stirred at room temperature until no starting product was detected by TLC (eluent CH_2Cl_2/AcEt, 3:2). The crude reaction mixture was then evaporated under reduced pressure removing the excess of reagent by coevaporating with MeOH several times. The residue was crystallized from MeOH yielding the corresponding 5-(2-acetamido-4-thiazolyl)pyrimidine **6**.

5-(2-acetamido-4-thiazolyl)-1,6-dihydro-1-methyl-2-methoxy-4-ß-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-6-oxopyrimidine, 6c.

Reaction time: 10 hours. 0.21 g (67 %). M.P.: 246-8°C (dec.). $[\alpha]_D^{20}$= +12.0°(c 1, $CHCl_3$). Rf 0.83, CH_2Cl_2/AcEt (3:2). UV (MeOH): λ_{max}nm (ϵ): 226 (26900), 244 (shoulder), 271 (10400), 301 (16300). IR (KBr) ν_{max}(cm^{-1}): 3440 w, 3320 m, 3120 w, 2950 w, 1755 s, 1730 s, 1680 s, 1655 s, 1620 s, 1580 s, 1545

s, 1470 m, 1445 m, 1410 m, 1365 s, 1310 m, 1285 m, 1245 s, 1220 s, 1140 w, 1030 s. Mass spectrum, m/z (abundance %): 626 (24) M^+, 582 (0.5), 567 (1), 296 (10), 295 (6), 331 (1), 165 (3), 142 (8), 100(3), 85 (1), 58 (1), 45 (2), 43 (100). ^{1}H-NMR (DMSO-d_6) δ (ppm): 2.1 (3H, s, CH_3CO thiazole), 3.3 (3H, s, CH_3N), 4.0 (3H, s, CH_3O), 5.8 (1H, st,with D_2O to d,$J_{1',2'}$=8.2 Hz, H-1'), 7.9 (1H, s, H-5''), 10.3 (1H, d, $J_{1',NH}$= 8.2 Hz, D_2O exchangeable, C_4-NH), 11.8 (1H, s, D_2O exchangeable, $C_{2''}$-NH). ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.3 (3H, s, CH_3CO thiazole), 3.4 (3H, s, CH_3N), 4.0 (3H, s, CH_3O), 8.1 (1H, s, H-5''), 10.0 (1H, s, D_2O exchangeable, $C_{2''}$-NH), 10.6 (1H, d, $J_{1',NH}$= 3.8 Hz, D_2O exchangeable, C_4-NH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 27.6 (CH_3N), 55.2 (CH_3O), 62.5 (C-6'), 80.4 (C-1'), 90.7 (C-5), 108.8 (C-5''), 143.1 (C-4''), 154.6 (C-2''), 155.1, 156.6, 161.5 (C-2, C-4, C-6). Anal. Calcd. for $C_{25}H_{31}N_5O_{12}S$: C, 47.99; H, 4.99; N, 11.19. Found: C, 47.64; H, 4.90; N, 11.51.

5-(acetamido-4-thiazolyl)-1,6-dihydro-1-methyl-2-methylthio-4-ß-D-(2,3,4,6-tetra-O-acetyl)glucopyranosylamino-6-oxopyrimidine, 6g.

Reaction time: 24 hours. 0.19 g (58%). M.P.: 218-220°C (dec.). $[\alpha]_D^{20}$= +1.2° c 1, $CHCl_3$). Rf 0.85, CH_2Cl_2/AcEt (3:2). UV (MeOH): λ_{max}nm (ϵ): 226 (26400), 244 (28500), 280 (7400), 320 (16300). IR (KBr) ν_{max}(cm^{-1}): 3450 w, 3335 m, 3215 m, 3145 m, 2945 w, 1760 s, 1740 s, 1700 m, 1660 s, 1600 s, 1535 s, 1460 m, 1445 s, 1420 m, 1370 s, 1290 s, 1240 s, 1180 m, 1150 w, 1060 s, 1040 s. Mass spectrum, m/z (abundance %): 642 (2), 641 (8) M^+, 312 (6), 311 (3), 165 (2), 141 (7), 99 (3), 85 (2), 58 (1), 45 (1), 43 (100). ^{1}H-NMR (DMSO-d_6) δ (ppm): 2.2 (3H, s, CH_3CO thiazole), 2.6 (3H,s,CH_3S), 3.4 (3H,s,CH_3N), 7.9 (1H, s, H-5''), 10.3 (1H, d, $J_{1',NH}$= 8.2 Hz, D_2O exchangeable, C_4-NH), 11.7 (1H, s, D_2O exchangeable, $C_{2''}$-NH). ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.3 (3H, s, CH_3CO thiazole), 2.6 (3H, s, CH_3S), 3.5 (3H, s, CH_3N), 8.1 (1H, s, H-5''), 10.0 (1H, s, D_2O exchangeable, $C_{2''}$-NH), 10.6 (1H, d, $J_{1',NH}$= 4.0 Hz, D_2O exchangeable, C_4-NH). ^{13}C-NMR ($CDCl_3$) δ (ppm): 14.8 (CH_3S), 30.2 (CH_3N), 62.5 (C-6'), 80.4 (C-1'),

92.1 (C-5), 110.2 (C-5''), 142.9 (C-4''), 155.2 (C-2''), 155.4, 160.0, 160.9 (C-2, C-4, C-6). Anal. Calcd. for $C_{25}H_{31}N_5O_{11}S_2$: C, 46.79; H, 4.87; N, 10.91. Found: C, 46.58; H, 4.71; N, 10.91.

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