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DERIVATIVES OF *N*-(2,3,4,6-TETRA-*O*-ACETYL-*β*-D-GLUCOPYRANOSYL)-*N'*-(BENZOTHIAZOLE-2'-YL)THIOUREAS

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Abstract

Some compounds of N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-N'-(benzothiazole-2'-yl)thioureas have been synthesized from corresponding 2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl isothiocyanate and the substituted derivatives of 2-aminobenzothiazoles executing in home microwave oven. Their spectroscopic properties have been recorded and the relationships between their structures and spectral properties (IR, ^{1}H- and ^{13}C-NMR) have been discussed.

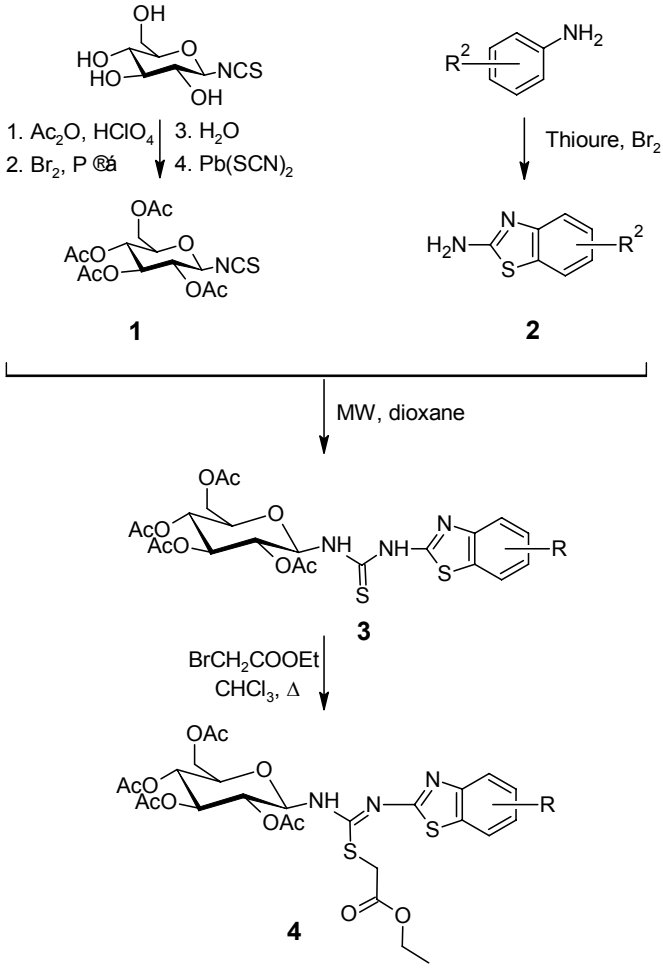
INTRODUCTION

Certain sugars express important biological function [1-4]. They can control various gene expressions to adjust the upgrowth, development and reaction of organs. Glycosyl isothiocyanates have been widely used as valuable intermediates in the synthesis of glycosyl derivatives [2]. The isothiocyanates and glycosyl isothiocyanates have been the focus of synthetic attention during recent years because of their potential pharmacological properties [3]. They have also considerable interests due to the anti-HIV activity, for examples, 1-deoxyno-jirimycin, castanospermine and some of their derivatives [5-6]. Many biologically important products have a sugar unit joined by an atom (O, S, N or C) or a group of atom [5].

Some thioureas containing glucose moiety and benzothiazole ring have been synthesized [6a] In the previous papers, we have reported on the synthesis of some series of *N*-(2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranosyl)-*N'*-(4',6'-diarylpyrimidine-2'-yl)thioureas and *N*-(2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranosyl)-*N'*-(4'-arylthiazole-2'-yl)thioureas using microwave-assisted method [6-12]. This method is becoming an increasingly popular method of heating which replaces the classical one because it proves to be a clean, cheap, and conventional method [7]. In this paper, some other peracetated glucopyranosyl thioureas containing benzothiazole ring were synthesized.

RESULTS AND DISCUSSION

Some derivatives of *N*-(2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranosyl)-*N'*-(benzothiazole-2'-yl)thioureas (**4a-n**) could be easily synthesized by the addition of corresponding amino compounds (**2**) on isothiocyanate derivatives (**1**). We reported here that reaction could be executed in microwave oven in several minutes (*see Scheme 1, Table 1*). We have found that nucleophiles addition the derivatives of 2-aminobenzothiazole to 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl isothiocyanate has taken place fairly easily. The yields were rather high in this method. All these synthesized thioureas could be dissolved in a mixture of ethanol and toluene (1:1 in volume) solvent, and could not be dissolved in ethanol and water. Their structures have been confirmed by spectroscopic data (such as IR, NMR spectra and mass spectra) [13,14].



where, R=6-COOMe (a); 6-COOEt (b); 6-COOPr (c); 6-COO-*i*Pr (d); 6-COOBut (e); 6-COO-iBut (f); 6-COOAm (g); 6-COO*i*Am (h); 6-COOOct (i); 6-Cl (j); 6-Br (k); 6-Me (l); 6-OEt (m); 4,6-$(Me)_2$ (n).

Scheme 1. Synthesis and transformations of substituted N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-N'-(benzothiazole-2'-yl)thioureas.

Table 1. Some substituted *N*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-*N'*-(benzothiazole-2'-yl)thioureas (3a-g)

Compd.	mp (°C)	Yield (%)	IR spectra (cm–1)				Color
			ν_{NH}	$\nu_{C=O}$ (ester)	ν_{C-O-C} (ester)	$\nu_{C=S}$ (thiourea)	
3a	202 - 203	57	3182; 3024	1750	1223; 1038	1373	White
3b	203 - 205	48	3170; 3030	1751	1228; 1040	1372	White
3c	205 - 206	60	3172; 3036	1748	1227; 1042	1370	White
3d	212 - 214	68	3182; 3039	1748	1227; 1042	1373	White
3e	197 - 198	88	3171; 3036	1750	1227; 1039	1374	White
3f	204 - 206	62	3188; 3031	1749	1222; 1042	1373	White
3g	212 - 214	78	3171; 3029	1751	1222; 1040	1379	White
3h	213 - 215	58	3168; 3031	1753	1226; 1043	1373	White
3i	198 - 200	52	3174; 3031	1750	1229; 1047	1370	White
3j	210 - 212	65	3175; 3032	1746	1223; 1042	1373	White
3k	200 - 202	62	3168; 3024	1747	1224; 1044	1367	White
3l	201 - 203	54	3175; 3032	1748	1231; 1039	1370	White
3m	202 - 204	76	3196; 3039	1747	1221; 1042	1368	Light violet
3n	206 - 208	78	3174; 3024	1750	1226; 1036	1370	White

In the IR spectra of the above glucopyranosyl thioureas, the stretching band of C=S bond in thiourea linkage appeared in the regions of 1367-1373 cm^{-1}, and N-H bonds in thiourea linkage have absorption band in the regions of 3490-3168 cm^{-1}, specified for stretching vibrations of these bonds. These bands sometimes have been superimposed each other, hence in several cases, one absorption band was appeared in their IR spectra. These bands also appeared in IR-spectra of some *N*-(2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranosyl)-*N'*-(4',6'-diarylpyrimidine-2'-yl)thioureas [6], and *N*-(2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranosyl)-*N'*-(4"-

arylthiazole-2-yl)thioureas [8]. The characteristics of penta-*O*-acetated glucopyranose ring was confirmed by the present of absorption band in the region of 1750-1692 cm^{-1} that specified for stretching vibration of C=O bond of ester function (*see Table 1*).

The ^{1}H-NMR spectra of the above thioureas, for example, the compound 3l, are represented in Fig.1. There are resonance signals which specified for protons in thioureas N-H groups at δ 11.966 and 8.889 ppm. Some resonance signals are in the regions δ 2.096 and 1.902 ppm belong to some protons in methyl and acetyl groups. Protons C-H in pyranose ring of monosaccharide have chemical shifts from δ 5.878 ppm to 3.986 ppm which usually are observed in ^{1}H-NMR spectra of monosaccharide compounds. Proton H-1 has chemical shift in the region δ 5.878 ppm (triplet) with coupling constant J= 9.0 Hz. Resonance signal of proton H-2 appeared as triplet in the region δ 5.094 ppm with coupling constant J= 5.0 Hz. The values of coupling constants correlated with *trans* H-H coupling interactions and indicated the β-anomer configuration of NH-thiourea group [9]. Other protons, such as H-3 and H-4 have triplet resonance signals in the regions δ 5.452 ppm (with coupling constants $J_{3,4}$= 9.5 Hz) and δ 4.928 ppm (with coupling constants $J_{4,3}$=$J_{4,5}$= 9.5 Hz), respectively. Three protons in benzothiazole have two chemical shifts in the regions from δ 7.617 ppm to δ 7.016 ppm. In the COSY spectra of thiourea **3l**, it was shown that proton H-1 interacted with proton H-2 and proton in NH bond of thiourea linkage, and that these signals appeared in triplet. Protons H-2 interacted with proton H-3 and proton H-1. Protons in phenyl moiety also have some interactions each other in AX type (*see Fig. 1, Table 2*) [12]

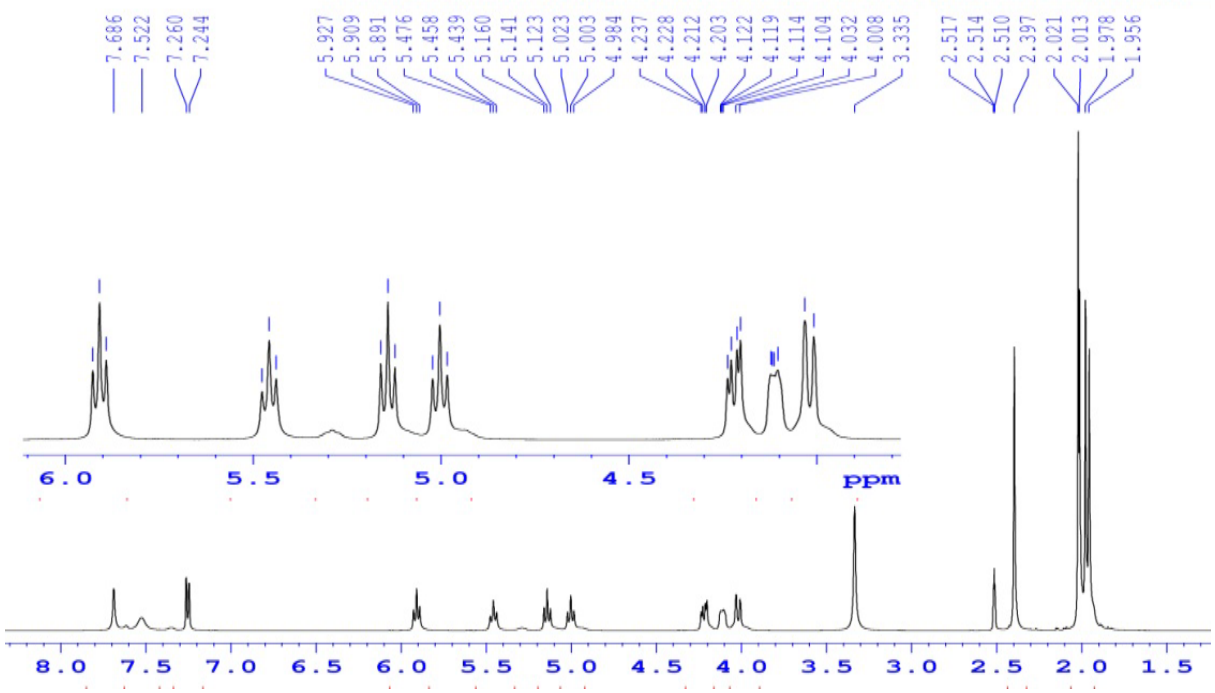


Figure 1. ^{1}H-NMR spectrum of thiourea 2l.

In the ^{13}C-NMR spectra, it could be noticed that the number of carbon atoms in spectra and this one in molecular formulas of each thioureas were identical each other. For example, the compound of thiourea **3l**, there were some resonance peaks in high-field region of 30.609-14.605 ppm that's indicated the presence of ethoxy group and methyl groups on acetyl function. Six carbon atoms in pyranose ring have clearly resonance signal in the region of 81.347-61.690 ppm. The carbon atoms in benzothiazole rings have chemical shifts in the region of 115.195-106.004 ppm. The magnetic resonance signals of the thiocarbonyl and carbonyl groups have appeared in the low-field region of 206.473 and 169.992-169.336 ppm, respectively. The ^{13}C-NMR spectrum of compound **3l** is represented in Fig. 2 and Table 3 [12]

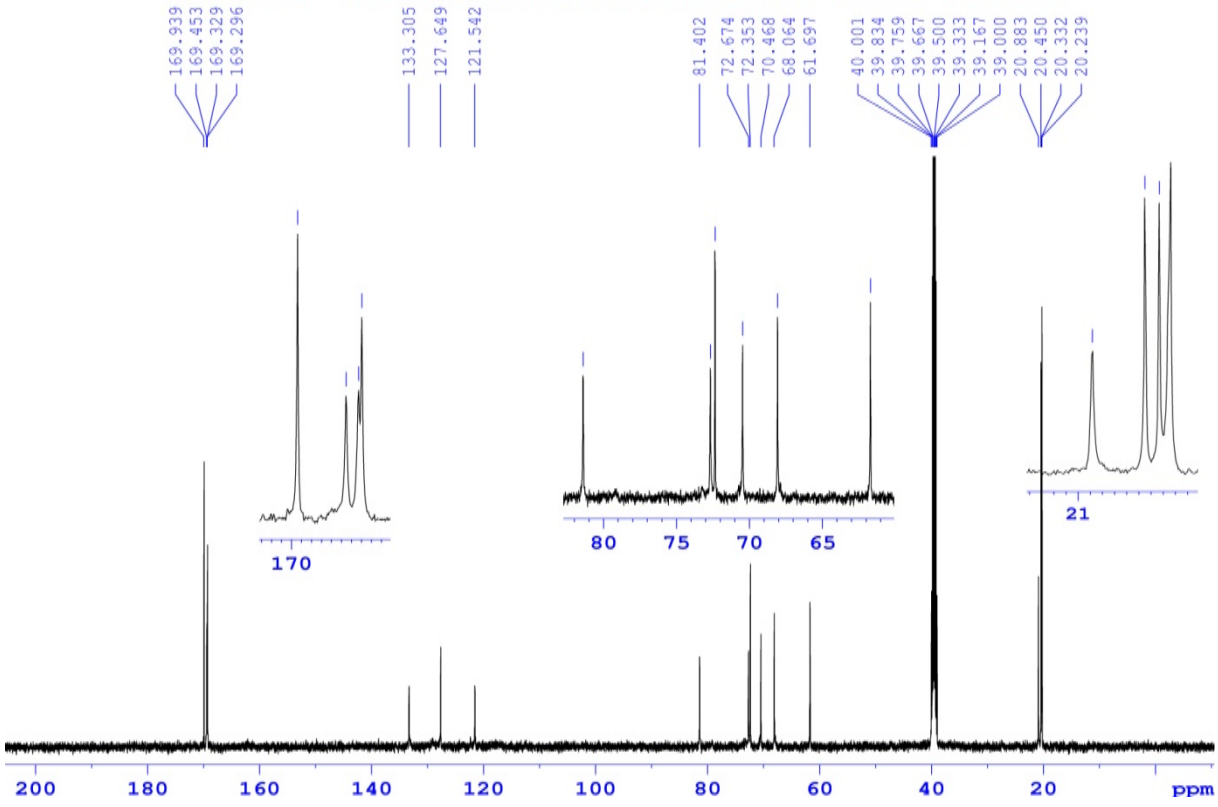


Figure 2. ^{13}C-NMR spectrum of compound 3l.

In the NMR spectra using HMBC and HSQC experiments of thiourea **3c**, the long-range and the short-range C-H interactions were indicated clearly (*see Fig. 2*), for examples, carbon atom C-1 had long-range interaction with proton H-2 and proton H-1; carbon atom C-2 interacted with protons H-2 and H-3, etc...

Table 2. ^{1}H-NMR Spectral Data of thioureas 4a-n

Proton	Compounds						
	3a (δ, J, Hz)	3b (δ, J, Hz)	3c (δ, J, Hz)	3d (δ, J, Hz)	3e (δ, J, Hz)	3f (δ, J, Hz)	3g (δ, J, Hz)
N-H	13.22, br; 12.33, br	12.28, br	12.26, br; 13.35, br	13.32, br; 12.26, br	13.34, br; 12.24, br	13.44, br; 12.31, br	13.31, br; 12.21, br
N'-H	9.85, br; 9.23, br	9.23, br	9.23, br, 9.86, br	9.86, br 9.23, br	9.66, br; 9.18, br	9.80, br; 9.15, br	9.72, br; 9.16, br
H-1	5.90, t, 8.9	5.90, t, 8.9	5.91, t, 8.7	5.90, t, 8.7	5.90, t, 8.7	5.91, t, 8.9	5.90, t, 8.9
H-2	5.12, t, 9.0; 9.3	5.12, t, 9.0; 9.3	5.13, t, 8.7; 8.9	5.13, t, 8.7; 8.9	5.12, t, 8.7; 8.9	5.13, t, 9.0; 9.3	5.12, t, 9.0; 9.3
H-3	5.46; t, 9.3; 9.3	5.46; t, 9.3; 9.3	5.46; t, 8.9; 8.7	5.46; t, 8.9; 8.7	5.45; t, 8.9; 8.7	5.45; t, 9.3; 9.3	5.45; t, 9.3; 9.3
H-4	5.00, t, 9.2; 9.5	5.00, t, 9.2; 9.5	4.99, t, 8.7; 8.5	4.99, t, 8.7; 8.5	4.99, t, 8.7; 8.5	4.99, t, 9.2; 9.5	4.99, t, 9.2; 9.5
H-5	4.12, m	4.12, m	4.12, m	4.12, m	4.11, m	4.12, m	4.10, m
H-6a	4.21, dd, 12.3; 4.6	4.21, dd, 12.3; 4.6	4.22, dd, 12.3; 4.6	4.22, dd, 12.3; 4.6	4.23, dd, 12.3; 4.6	4.22, dd, 12.3; 4.6	4.26, dd, 12.3; 4.6
H-6b	4.01, dd, 12.3; 4.5	4.01, dd, 12.3; 4.5	4.03, dd, 12.3; 4.5	4.01, dd, 12.3; 4.5	4.01, dd, 12.3; 4.5	4.01, dd, 12.3; 4.5	4.01, dd, 12.3; 4.5
H-4'	7.68, br	7.68, br	7.80, br	7.71, br	7.69, br	7.71, br	7.68, br
H-5'	8.00, d, 8.4	8.00, d, 8.5	8.02, d, 8.4	8.01, d, 8.4	8.00, d, 8.4	8.02, d, 8.3	8.00, d, 8.3
H-7'	8.54, br	8.54, br	8.56, br	8.56, br	8.55, br	8.58, br	8.53, br
CH_3CO	2.02, s; 2.01, s; 2.00, s; 1.95, s	2.02, s; 2.01, s; 2.00, s; 1.95, s	2.01, s; 2.00, s; 1.97, s; 1.96, s	2.01, s; 2.00, s; 1.97, s; 1.96, s	2.01, s; 2.00, s; 1.97, s; 1.96, s	2.02, s; 2.01, s; 1.97, s; 1.96, s	2.01, s; 2.00, s; 1.97, s; 1.95, s
Other Proton	3.91, s (CH_3)	4.35, q (CH_2) 2.40, s (CH3)	4.03, t (CH_2) 1.77, m (CH_2) 1.10, s (CH_3)	4.25, m (CH) 1.30, d (CH_3) 1.30, d (CH_3)	4.29, t (CH_2) 1.70, m (CH_2) 1.48, m (CH_2) 0.92, s (CH_3)	4.09, d, 1.01, m (CH); 1.00, d (CH_3); 1.00, d (CH_3)	4.27, t, 1.71, m, 1.79, m, 1.36, m CH_2); 0.91, d (CH_3)

Table 2. ^{1}H-NMR Spectral Data of thioureas 5a-n (continuing)

Proton	Hợp chất						
	3h (δ, J, Hz)	**3i** (δ, J, Hz)	**3j** (δ, J, Hz)	**3k** (δ, J, Hz)	**3l** (δ, J, Hz)	**3m** (δ, J, Hz)	**3n** (δ, J, Hz)
N-H	13.34, br; 12.31, br	13.32, br; 12.29, br	13.22, br; 12.19, br	13.21, br; 12.22, br	13.12, br; 12.23, br	13.11, br; 11.97, br	12.10, br; 8.91, br
N'-H	9.82, br; 9.15, br	9.75, br; 9.20, br	9.65, br, 9.13, br	9.65, br; 9.13, br	10.01, br; 8.90, br	11.12, br; 8.84, br	12.76, br, 12.10, s
H-1	5.90, t, 8.9	5.91, t, 8.9	5.89, t, 8.9	5.88, t, 9.4	5.91, t, 9.0	5.91, t, 9.0	5.95, t, 9.0
H-2	5.12, t, 9.0; 9.3	5.13, t, 9.0; 9.3	5.12, t, 8.9; 9.1	5.11, t, 9.4; 9.0	5.12, t, 9.0; 9.3	5.12, t, 9.0; 9.3	5.10, t, 9.0; 9.1
H-3	5.45; t, 9.3; 9.3	5.46; t, 9.3; 9.3	5.45; t, 9.1; 9.2	5.45; t, 9.0; 9.0	5.46; t, 9.3; 9.4	5.46; t, 9.3; 9.4	5.45; t, 9.1; 9.2
H-4	4.99, t, 9.2; 9.5	5.00, t, 9.2; 9.5	4.99, t, 9.2; 9.5	4.99, t, 9.9; 9.5	5.00, t, 9.4; 9.7	4.93, t, 9.5; 9.5	5.00, t, 9.2; 9.4
H-5	4.12, m	4.12, m	4.11, m	4.11, m	4.12, m	4.10, m	4.12, m
H-6a	4.18, dd, 12.3; 4.6	4.28, dd, 12.3; 4.6	4.21, dd, 12.5; 4.7	4.19, dd, 12.0; 3.2	4.23, dd, 12.4; 4.7	4.22, dd, 12.4; 4.7	4.22, dd, 12.5; 4.4
H-6b	4.00, dd, 12.3; 4.5	4.02, dd, 12.3; 4.5	3.99, dd, 12.5; 4.5	4.02, dd, 12.0; 3.0	4.03, dd, 12.4; 1.9	4.00, dd, 12.4; 4.7	4.05, dd, 12.3; 1.9
H-4'	7.72, br	7.69, br	7.63, br	7.57, br	7.52, br	7.34, br	-
H-5'	8.00, d, 8.2	8.00, d, 8.0	7.45, d, 8.0	7.57, dd, 1.1; 7.8	7.24, d, 7.8	7.02, d, 7.1	7.07, s
H-7'	8.55, br	8.54, br	8.08, br	8.17, br	7.69, br	7.62, br	7.57, br
CH_3CO	2.01, s; 2.00, s; 1.97, s; 1.96, s	2.02, s; 2.01, s; 1.97, s; 1.92, s	2.01, s; 2.00, s; 1.97, s; 1.96, s	2.01, s; 1.96, s; 1.96, s; 1.95, s	2.02, s; 2.01, s; 2.00, s; 1.95, s	2.01, s; 2.00, s; 1.97, s; 1.95, s	2.02, s; 2.01, s; 1.98, s; 1.97, s
others	4.32, t, và 1.63, m (CH_2); 1.79, m (CH); 0.56, d (CH_3); 0.56, d (CH_3)	4.28, t, và 1.71, m; 1.40, m và 1.30, m; 1.29, m và 1.27, m); 1.25, m (CH_2); 0.85, s (CH_3)	-	-	2.40, s (CH_3)	4.06, q, 7.0 (CH_2) 1.35, t, 7.0 (CH_3)	2.52, q (CH_3)

Table 3. ^{13}C-NMR Spectral Data and MS of thioureas 5a-n

δ (ppm)	Compounds						
	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
C-1	81.2	81.3	81.3	81.3	81.3	81.3	81.8
C-2	73.2	72.3	72.3	72.3	72.3	72.3	72.9
C-3	73.5	72.6	72.6	72.6	72.6	72.6	73.3
C-4	71.4	71.4	70.4	70.4	70.4	70.4	71.1
C-5	68.8	67.9	67.9	67.9	67.9	67.9	68.6
C-6	62.5	61.6	61.6	61.7	61.6	61.6	62.2
C-4'	124.8	123.7	123.8	123.8	123.7	123.8	124.3
C-5'	125.6	125.0	124.9	125.4	124.9	124.9	125.6
C-7'	128.4	127.4	127.5	127.5	127.3	127.4	127.9
CH_3CO	20.5; 20.4; 20.3; 20.2	20.4; 20.3; 20.2; 20.1	20.4; 20.3; 20.3; 20.2	20.5; 20.4; 20.3; 20.2	20.4; 20.3; 20.3; 20.2	20.5; 20.4; 20.3; 20.2	20.9; 20.8; 20.7; 20.7
CH_3***C***O	170.8; 170.7; 170.4; 170.2	169.8; 169.7; 169.3; 169.2	169.9; 169.8; 169.4; 169.3	169.9; 169.8; 169.4; 169.3	169.8; 169.8; 169.3; 169.1	169.9; 169.8; 169.4; 169.3	170.4; 169.9; 169.8; 169.7
Other Carbon	166.7 (CO); 53.0 (CH_3)	165.2 (CO); 60.6 (CH_2); 14.1 (CH_3)	165.3 (CO); 66.1 (CH_2); 21.6 (CH_2); 10.3 (CH_3)	164.7 (CO); 66.3 (CH); 21.7 (CH_3); 21.7 (CH_3)	165.2 (CO); 64.3 (CH_2); 30.2 (CH_2); 21.6 (CH_2); 13.4 (CH_3)	165.2 (CO); 70.3 (CH); 27.4 (CH_2); 18.8 (CH_3); 18.8 (CH_3)	165.8 (CO); 65.2 (CH_2); 28.4 (CH_2); 28.2 (CH_2); 19.2 (CH_2); 14.3 (CH_3)

Table 3. ^{13}C-NMR Spectral Data and MS of thioureas 5a-n (continuing)

δ (ppm)	Compounds						
	3h	**3i**	**3j**	**3k**	**3l**	**3m**	**3n**
C-1	81.3	81.3	81.3	81.2	81.3	81.3	81.2
C-2	72.3	72.3	72.3	72.3	72.3	72.3	72.3
C-3	72.6	72.6	72.6	72.6	72.7	72.6	72.5
C-4	70.4	70.4	70.4	70.4	70.5	70.4	70.5
C-5	68.9	67.9	67.9	67.9	68.1	68.0	68.1
C-6	61.6	61.6	61.6	61.6	61.7	61.7	61.6
C-4’	123.8	123.7	121.6	115.4	121.6	115.2	118.6
C-5’	124.9	124.9	126.7	124.4	127.6	115.2	128.2
C-6’	-	-	-	-	-	155.5	-
C-7’	127.4	127.3	127.6	129.3	133.3	106.0	133.3
CH_3CO	20.4; 20.3; 20.2; 20.1	20.3; 20.2; 20.1; 20.1	20.4; 20.3; 20.3; 20.2	20.4; 20.3; 20.3; 20.2	20.5; 20.4; 20.3; 20.2	20.4; 20.3; 20.3; 18.5	20.3; 20.2; 20.1; 20.0
CH_3***C***O	169.8; 169.8; 169.3; 169.2	169.8; 169.3; 169.2; 169.1	169.9; 169.4; 169.3; 169.2	169.9; 169.4; 169.3; 169.2	169.9; 169.4; 169.3; 169.2	170.0; 169.4; 169.4; 169.3	169.8; 169.3; 169.2; 169.1
Other Carbon	165.2 (CO); 63.0(CH); 24.5 (CH_2); 22.2 (CH_2); 16.2 (CH_2); 10.9 (CH_3)	165.2 (CO); 64.6 (CH_2); 31.1 (CH_2); 28.5 (CH_2); 28.4 (CH_2); 28.0 (CH_2); 25.3 (CH_2); 21.9 (CH_2); 13.7 (CH_3)	-	-	20.8 (CH_3)	56.0 (OCH_2); 14.6 (CH_3)	20.8 (CH_3); 17.4 (CH_3)

Table 4. Mass spectra of thioureas 1a-g

Fragment	3a m/z*; m/z (%)	3b m/z*; m/z (%)	3c m/z*; m/z (%)	3e m/z*; m/z (%)	3f m/z*; m/z (%)	3g m/z*; m/z (%)	3h m/z*; m/z (%)
$M^{+\bullet}$	597.1078*; 597.1094 (1.2)	611.1243*; 611.1208 (0.2)	625.1339*; 625.0510 (0.1)	639.1556*; 639.2317 (0.2)	639.1556*; 639.2040 (0.3)	653.1713*; 653.1948 (0.1)	653.1713*; 653.1634 (0.1)
$[M\text{-}AcOH]^{+\bullet}$	537.0875*; 537.0587 (0.7)	551.1032*; 551.9715 (0.5)	565.1188*; 565.0741 (0.4)	579.1345*; 579.1551 (0.9)	579. 1345*; 579.1086 (1.4)	593.1502*; 593.1833 (0.8)	593.1502*; 593.1633 (0.9)
$[M\text{-}AcOH\text{-}AcO]^{+}$	478.0782*; 477.9927 (0.9)	492.0899*; 492.1002 (1.1)	506.1056*; 506.0767 (0.6)	520.1212 *; 520.0832 (1.2)	520.1212 *; 520.1058 (3.8)	534.1368*; 534.0844 (2.2)	534.1368*; 534.1144 (2.1)
$[M\text{-}2AcOH\text{-}AcO]^{+}$	418.0531*; 417.9919 (1.6)	432.0878*; 432.0918 (1.2)	446.0844*; 446.0607 (0.5)	460.1000*; 460.0963 (0.6)	460.1000*; 460.1129 (1.2)	474.1157*; 474.0866 (3.2)	474.1157*; 474.1126 (2.3)
$[F_4]^{+}$	331.1029*; 331.0256 (4.2)	331.1029*; 331.0402 (7.4)	331.1029*; 331.0509 (2.2)	331.1029*; 331.1221 (10.6)	331.1029*; 331.1263 (11.1)	331.1029*; 331.1048 (14.2)	331.1029*; 331.1067 (11.2)
$[F_4\text{-}AcOH+H]^{+}$	271.0483*; 271.0562 (5.6)	271.0483*; 271.0205 (2.4)	271.0483*; 271.0005 (0.4)	271.0483*; 271.0935 (4.4)	271.0483*; 271.0858 (3.1)	271.0483*; 171.0778 (2.0)	271.0483*; 171.0323 (2.5)
$[F_4\text{-}3AcOH\text{-}CH_2CO]^{+}$	109.1027*; 109.0188 (40.1)	109.1027*; 109.1182 (16.7)	109.1027*; 109.0175 (25.6)	109.1027*; 109.0175 (39.2)	109.1027*; 109.0226 (25.3)	109.1027*; 109.0079 (24.2)	109.1027*; 109.0123 (21.2)
$[F_5\text{-}H]^{+\bullet}$	288.1083*; 288.0783 (3.8)	288.1083*; 288.0929(3.2)	288.1083*; 288.0829(0.9)	288.1083*; 288.0883(1.2)	288.1083*; 288.0843(0.8)	288.1083*; *not observed*	288.1083*; *not observed*
$[F_6]^{+\bullet}$	249.9870*; 249.9841(100)	264.0027*; 264.0102 (74.1)	278.0183*; 277.9951 (30.7)	292.0340*; 292.0486 (21.1)	292.0340*; 292.045 (20.8)	306.0497*; 306.0480 (14.8)	306.0497*; 306.0480 (14.8)
$[F_6\text{-}R+H]^{+\bullet}$	235.9714*; *not observed*	235.9714*; 235.9686 (100)	235.9714*; 235.9691 (100)	235.9714*; 235.9681 (100)	235.9714*; 235.9695 (100)	235.9714*; 235.9515 (100)	235.9714*; 235.9515 (100)
$[F_6\text{-}RO]^{+\bullet}$	218.9686*; 218.9683^{+} (52.1)	218.9686*; 218.9697 (58.8)	218.9686*; 218.9521 (71.8)	218.9686*; 218.9637 (61.1)	218.9686*; 218.9632 (93.2)	218.9686*; 218.9502 (58.2)	218.9686*; 218.9661 (66.2)
$[F_6\text{-}ROOC]^{+\bullet}$	190.9737*; 190.9689 (38.8)	190.9737*; 190.9678 (35.3)	190.9737*; 190.9202 (21.1)	190.9737*; 190.9993 (19.1)	190.9737*; 190.9632 (26.6)	190.9737*; 190.9511 (16.6)	190.9737*; 190.9643 (20.2)
$[F_7+H]^{+}$	208.0306*, 208.0237 (46.2)	222.0463*; 222.0515(23.4	236.0619*; *not observed*	250.0776*; 250.0792 (24.6)	250.0776*; 250.0800 (15.7)	264.0932*; 264.0836 (13.2)	264.0932*; 264.0966 (11.8)
$[F_7+H\text{-}RO]^{+\bullet}$	177.0122*; 177.0038 (56.3)	177.0122*; 177.0012 (26.8)	177.0122*; 176.9991 (35.6)	177.0122*; 176.9989 (58.6)	177.0122*; 177.0011 (49.1)	177.0122*; 176.9980 (35.1)	177.0122*; 177.0012 (27.1)
$[F_8]^{+}$	192.0119*; 190.9689 (31.2)	206.0276*; 206.0243 (25.4)	220.0432*; 219.9586 (11.8)	234.0588*; *not observed*	234.0588*; 234.0256 (0.6)	234.0588*; *not observed*	234.0588*; *not observed*
$[F_8\text{-}ROOC]^{+\bullet}$	132.9986*; 132.9900(21.2)	132.9986*; 132.9887 (20.3)	132.9986*; 132.9900 (18.8)	132.9986*; 132.9864 (1.5)	132.9986*; 132.9844 (21.3)	132.9986*; 132.9749 (12.3)	132.9986*; 132.9865 (31.3)

Note : m.z* is calculated; $m.z^{+}$ is (m/z+nH) fragment.

The mass spectral data of *N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-*N'*-(6'-alkoxycarbonylbenzothiazole-2'-yl)thioureas are representedin Table 4. Mass spectra of these thioureas show some features that are similar with ones of typical hexopyranose pentaacetates containing pyrimidine ring [1]. As expected of such a highly substituted molecule of carbohydrate, the molecular ion $M^{+\bullet}$ appears in very low intensive peak (1-3%) and is hardly observed in the spectra. The only observable peaks in the higher mass number range were due to loss of the substituents and fall, therefore, at position of fragment ions such as $[M\text{-}AcOH]^+$, $[M\text{-}AcOH,\text{-}AcO]^+$ and $[M\text{-}2AcOH,\text{-}AcO]^+$, and some peaks such as $[M\text{-}2AcOH,\text{-}C_2H_2O]^+$, $[M\text{-}3AcOH,\text{-}AcO]^+$ could be specified for glycosides having amino structure. A very important mode of fragmentation of these acetated compounds was the loss of acetic acid (*m/z* 60), a process well known for most esters of acetic acid, and the loss of ketene (*m/z* 42) [12]. The fragment ion *m/z* 242 is formed from cleavage of pyranose ring. The fragmentations of this ion fragment give fragments with *m/z* 200, 140, 98 due to the cleavage of neutral molecules such as CH_3COOH and $CH_2=C=O$ [12].

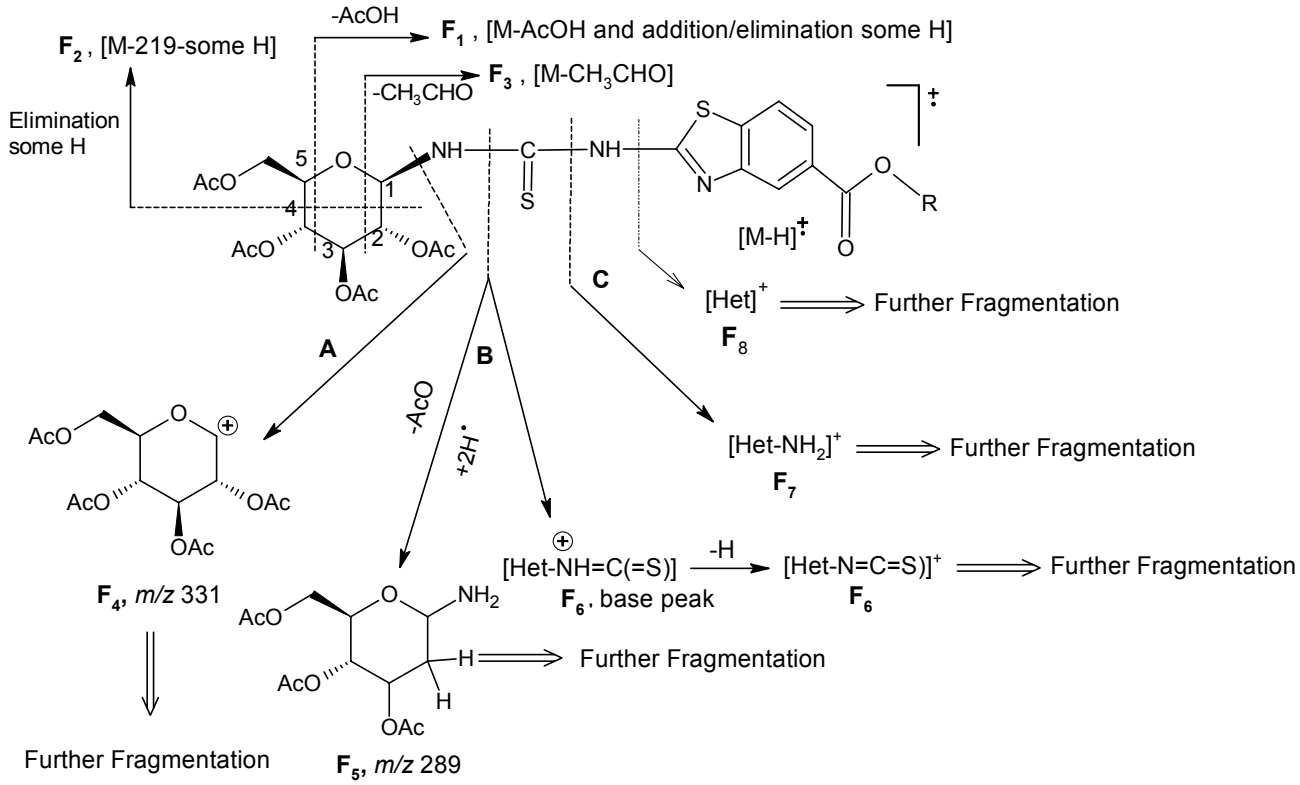


Figure 3. General fragmentations of some thioureas 3a-h.

Fragment ion F_4 (*m/z* 331) usually appears in small intensity peaks (5-15%) in spectra. These fragments are formed from the cleavage of the monosaccharide moiety and remained component of thiourea molecule. The secondary fragmentation of fragment ion F_4 occurred by the elimination of neutral molecules, such as CH_3COOH and $CH_2=C=O$ to form fragment ions with *m/z* 271, 211, 169,

109, 69 [1]. Fragment ion in (*m/z* 235-R+H)-type appears in high intensity (100%, base peak) indicating the high stability of this ion in mass spectra and tendency of fragmentation type is characteristic for *N-(*2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-*N'*-(6'-alkxoycarbonyl benzothiazole-2'-yl)thioureas. The secondary fragmentation of ion F_6 lead to form the fragment ions F_6-RO (*m/z* 219), F_6-ROOC (*m/z* 191), F_8 (*m/z* 177+R), F_8-ROOC+H (*m/z* 134) … due to elimination of C=S, N=C=S groups, R radical, benzothiazole ring or the cleavage of benzothiazole ring.

The reaction of ethyl bromoacetate with corresponding *N*-(per-*O*-acetyl-β-D-glucopyranosyl)-*N*'-(benzothiazole-2'-yl) thioureas lead to new ethyl 2-[*N'*-(6-substituted-benzothiazole-2'-yl)-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)carbamimidoylthio]acetates **4a-n** (Scheme 2). We used chloroform as the reaction medium and molar ratios of ethyl bromoacetate and thioureas **3a-n** in 3:1 in order to obtain the higher transformation yields. Reaction mixtures were stirred in room temperature for one hour, after that, heated with reflux for 8-10 h. A reaction time of over 10 h at reflux in chloroform was kept since a longer time did not improve the yield. The appearance of white precipitate in the reaction beginning was the evidence indicating the reaction was taken place. The products were insoluble in ethanol, methanol, it facilitated for purification. Reaction yields are 50-68% (Table 5).

Table 5. Ethyl carbamimidoylthioacetate 4a-m

Compd.	Reaction time	Mp (°C)	Yield (%)	IR spectra (cm^{-1})			
				ν_{NH2}	$\nu_{C=N}$	$\nu_{C=O}$ (ester)	ν_{C-O-C} (ester)
4a	30 min* 6 h**	172-174	58	-	1568	1749	1278; 1228; 1036
4c	30 min* 6 h**	174-176	74	3164	1568	1754	1271; 1225; 1040
4e	30 min* 6 h**	178-179	57	3138	1567	1751	1271; 1230; 1040
4f	30 min* 6 h**	180-182	58	3157	1570	1750	1270; 1223; 1041
4g	30 min* 6 h**	180-182	62	3154	1574	1756	1273; 1230; 1039
4h	30 min* 6 h**	186-187	60	3144	1567	1754	1277; 1219; 1042
4j	30 min* 6 h**	163-164	66	3156	1570; 1566	1752	1224; 1047
4k	30 min* 6 h**	172-173	62	3178	1594; 1569	1753	1224; 1037
4l	30 min* 6 h**	176-178	72	3170	1581; 1579	1745	1214; 1039
4m	30 min* 6 h**	160-162	65	3166	1574; 1572	1750	1212; 1034

Note: * in room temperature, ** at refluxing.

Table 6. ^{1}H-NMR spectra of ethyl carbamimidoylthioacetate 4a-m (DMSO-d_6)

Proton	7a (δ, J, Hz)	7c (δ, J, Hz)	7e (δ, J, Hz)	7f (δ, J, Hz)	7g (δ, J, Hz)
N-H	11.02, br	11.09, br	11.05, br	11.04, br	11.06, br
H-4''	8.01, d, 7.5	8.01, d, 7.8	8.00, d, 7.6	8.01, d, 8.2	8.00, d, 8.2
H-5''	7.81, d, 8.0	7.81, d, 7.6	7.81, d, 7.8	7.81, d, 8.3	7.80, d, 8.3
H-7''	8.55, s	8.54, s	8.54, s	8.55, s	8.54, s
H-1'	5.49, br	5.49, br	5.49, br	5.48, br	5.48, br
H-2'	5.18, br	5.19, br	5.19, br	5.19, t, 8.9, 9.2	5.17, br
H-3'	5.57, br	5.58, br	5.57, br	5.57, t, 9.2, 8.9	5.55, br
H-4'	5.00, br	5.01, br	5.00, br	5.01, t, 9.2, 9.2	4.99, br
H-5'	4.23, br	4.24, br	4.29, br	4.24, br	4.29, br
H-6'a	4.22, br	4.23, br	4.24, br	4.22, br	4.27, br
H-6'b	3.98, s m	3.98, m	3.98, m	3.98, m	3.98, m
H-3	4.02,	4.03, s	4.02, s	4.02, s	4.01, s
H-6	4.14, q, 5.7	4.14, q, 6.3	4.14, q, 6.2	4.14, q, 6.8	4.13, q, 6.9
H-7	1.23, t, 7.1	1.23, t, 7.1	1.23, t, 7.1	1.23, t, 7.1	1.23, t, 7.1
CH_3CO	2.02, s; 2.01, s; 1.99, s; 1.98, s	2.02, s; 2.01, s; 1.99, s; 1.98, s	2.01, s; 2.00, s; 1.99, s; 1.98, s	2.01, s; 2.00, s; 1.99, s; 1.98, s	2.01, s; 2.00, s; 1.98, s; 1.97, s
Other Protons	3.88, s (CH_3)	3.99, t, 6.6 (CH_2) 1.73, m (CH_2) 0.99, t, 7.1 (CH_3)	4.22, br (CH_2) 1.71, m (CH_2) 1.44, m (CH_2) 0.95, t, 8.8 (CH_3)	4.08, d, 6.3 (CH_2) 2.04, m (CH) 0.99, d, 6.5 (CH_3) 0.99, d, 6.5 (CH_3)	4.23, br (CH_2) 2.04, m (CH_2) 1.70, m (CH_2) 1.44, m (CH_2) 0.94, t, 7.2 (CH_3)

Table 6. ^{1}H-NMR spectra of ethyl carbamimidoylthioacetate 4a-m (DMSO-d_6) (continuing)

Proton	7h (δ, J, Hz)	7j (δ, J, Hz)	7k (δ, J, Hz)	7l (δ, J, Hz)	7m (δ, J, Hz)
N-H	11.06, br	10.99, br	11.00, br	11.09, br	10.98, br
H-4''	7.81, d, 7.8	7.73, d, 8.6	7.66, d,	7.64, d, 8.1	7.63, d, 8.3
H-5''	8.00, dd, 7.8, 1.2	7.48, dd, 7.0, 1.7	7.59, d,	7.25, d, 8.2	7.03, d, 8.2
H-7''	8.52, s	8.03, d, 1.5	8.16, s	7.68, s	7.47, s
H-1'	5.49, br	5.47, t, 7.9, 8.0	5.45, br	5.45, br	5.44, br
H-2'	5.19, t, 9.1, 9.1	5.19, t, 9.1, 9.1	5.16, t, 8. 9, 9.1	5.16, t, 8.8, 8.8	5.16, t, 8. 9, 9.1
H-3'	5.58, t, 9.3, 9.4	5.58, t, 9.2, 9.2	5.56, t, 9.4, 9.4	5.55, t, 8.8, 9.3	5.58, t, 9.1, 8.9
H-4'	5.02, t, 9.3, 9.3	5.02, t, 9.2, 9.3	5.00, t, 9.2, 9.3	5.00, t, 9.2, 8.8	5.01, t, 8.9, 9.7
H-5'	4.32, q, 7.6, 6.6	4.25, br	4.22, q, 9.3	4.23, br	4.23, br
H-6'a	4.32, t, 7.6, 6.6	4.23, br	4.23, br	4.22, br	4.21, br
H-6'b	3.99, m	3.98, m	3.98, m	3.98, m	3.98, m
H-3	4.03, s	4.05, s	4.05, s	4.03, s	4.06, s
H-6	4.23, q, 8.7	4.14, q, 7.1	4.13, q, 9.1	4.13, q, 5.2	4.14, q, 6.6
H-7	1.23, t, 7.1	1.23, t, 7.1	1.23, t, 7.1	1.23, t, 7.1	1.23, t, 7.1
CH_3CO	2.02, s; 2.02, s; 2.01, s; 2.00, s	2.03, s; 2.02, s; 1.99, s; 1.99, s	2.02, s; 2.01, s; 1.98, s; 1.97, s	2.03, s; 2.01, s; 1.99, s; 1.98, s	2.03, s; 2.01, s; 1.99, s; 1.98, s
Other Protons	4.22, m (CH_2) 1.76, m (CH) 1.61, m (CH_2) 0.94, d, 6.6 (CH_3) 0.94, d, 6.6 (CH_3)	-	-	3.39, s (CH_3)	3.93, q, 7.1 (CH_2) 1.34, t, 6.2 (CH_3)

Table 7. ^{13}C-NMR spectra of ethyl carbamimidoylthioacetate 4a-m (DMSO-d_6)

Carbon	7a	7c	7e	7f	7g
C-2	-	172.7	-	172.4	-
C-1'	80.3	80.4	80.4	80.4	80.2
C-2'	70.3	70.3	70.3	70.5	70.3
C-3'	72.1;	72.1	72.1	72.1	72.1
C-4'	68.2	68.2	68.2	68.2	68.2
C-5'	71.9	71.9	71.9	71.9	71.9
C-6'	61.7	61.7	61.7	61.7	61.7
C-2''	-	-	-	-	-
C-4''	120.4	120.4	120.4	120.4	120.4
C-5''	124.9	125.2	125.2	125.2	125.2
C-6''	-	144.2	-	-	-
C-7''	123.6	127.0	123.5	123.5	123.5
C-4''a	153.2	153.6	153.6	153.7	153.6
C-7'a'	127.1	133.1	127.1	127.1	127.1
C-3	33.2	33.0	33.2	33.2	33.2
C-4	165.9	165.4	165.4	165.4	165.4
C-6	61.1	61.0	61.1	61.2	61.2
C-7	14.1	14.1	14.1	14.1	14.1
COOCH_3	169.9; 169.5; 169.3; 168.3	169.9; 169.5; 169.3; 168.2	169.9; 169.5; 169.3; 168.3	170.0; 169.5; 169.3; 168.3	170.0; 169.5; 169.3; 168.3
COO*CH_3*	20.5; 20.4; 20.3; 20.2	20.5; 20.4; 20.3; 20.2	20.5; 20.4; 20.3; 20.2	20.5; 20.4; 20.3; 20.2	20.5; 20.4; 20.3; 20.2
Other Carbons	52.1 (CH_3)	153.7 (COO); 66.1 (CH_2); 21.6 (CH_2); 10.3 (CH_3)	153.7 (COO); 64.4 (CH_2); 30.3 (CH_2); 18.7 (CH_2); 3.6 (CH_3)	153.7 (COO); 70.3 (CH_2); 27.4 (CH); 18.9 (CH_3); 18.9 (CH_3)	153.6 (COO); 64.4 (CH_2); 30.2 (CH_2); 20.2 (CH_2); 18.7 (CH_2); 13.6 (CH_3)

Table 7. ^{13}C-NMR spectra of ethyl carbamimidoylthioacetate 4a-m (DMSO-d_6) (continuing)

Carbon	7h	7j	7k	7l	7m
C-2	172.7	170.3	-	-	170.0
C-1'	80.4	80.3	80.3	80.3	80.4
C-2'	70.3	70.3	70.3	70.3	70.3
C-3'	72.2	72.1	72.1	72.1	72.1
C-4'	68.1	68.2	68.1	68.2	68.3
C-5'	72.0	71.9	71.9	70.0	72.1
C-6'	61.7	61.7	61.6	61.6	61.7
C-2''	-	-	-	-	167.7
C-4''	120.4	121.3	116.1	120.3	105.5
C-5''	125.2	126.6	124.2	127.4	121.3
C-6''	-	150.0	149.3	147.6	144.1
C-7''	123.5	121.7	122.2	121.2	115.5
C-4''a	153.7	-	-	-	155.7
C-7'a'	127.1	132.0	129.3	133.3	132.8
C-3	33.2	33.0	33.2	33.0	33.0
C-4	165.4	168.3	167.8	168.4	168.4
C-6	61.2	60.1	60.1	61.0	60.1
C-7	14.1	14.1	14.1	14.1	14.1
COOCH_3	170.0; 169.5; 169.3; 168.3	170.3; 169.9; 169.5; 168.3	170.0; 169.5; 169.3; 168.4	169.9; 169.4; 169.4; 169.3	169.9; 169.4; 168.4; 167.8

COO*CH*$_3$	20.5; 20.4; 20.3; 20.2	20.5; 20.4; 20.3; 20.2	20.5; 20.4; 20.3; 20.2	20.5; 20.4; 20.3; 20.2	20.5; 20.4; 20.3; 20.2
Other Carbons	153.7 (COO); 63.2 (CH_2); 36.9 CH); 24.6 (CH_2); 22.3 (CH_3); 22.3 (CH_3)	-	-	20.9 (CH_3)	63.6 (CH_2); 14.6 (CH_3)

It is of interest that the reaction of thioureas **3a-n**, which includes a benzothiazole-2-yl substituent, with ethyl bromoacetate leads to the formation of N-3′ tautomeric isomers **4a-m** instead for N-1′ tautomeric isomers **4'a-m**. ^{1}H and ^{13}C NMR spectra of final products **4a-m** (after work-up) suggest absence of any trace of the isomers, indicating that the final products are isomerically pure. Due to the absence of the imino group at N-1′, the chemical shift value of H-1 for **3a** (5.45 ppm) is larger than H-1 (4.39-5.22 ppm), as it were previously reported [14], and the chemical shift value of C-1' for **3a** (80.34 ppm) is smaller than C-1′ (89.73-86.74 ppm). These differences in chemical shifts may indicate different disposition of attack of tautomeric types. Formation of the tautomeric N-3′ *versus* tautomeric N-1′ type attack for the ethyl (carbamimidoylthio)acetates derivatives **4a-m** has now been proven by HMBC experiments (Table 6 and 7). HMBC spectrum of ethyl 2-[*N'*-(6-methyl-benzothiazole-2'-yl)-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)carbamimidoylthio]acetate **4a** confirms these nucleophilic substitutions S_N2. Based on the HMBC, HSQC and COSY correlations, we can unambiguous assign all chemical shift values of carbon and proton atoms in the sugar ring (The detail discursion on NMR spectra of compounds **4a-m** will be published in another paper). On the other hand, H-1′ at δ 5.45 ppm has no the three-bond connectivity with any carbon atoms, and the three-bond connectivity of S–CH_2 group at δ 3.07 ppm with C-2′ at δ 163.5 ppm and with C=O (of ethoxyacetyl group) at δ 168.4 ppm in the HMBC spectrum confirmed the addition of thioureas **3a-n** with ethyl bromoacetate at tautomeric N-3′. Other evidence is the disappearance of C=S signals at δ 206-208 ppm and the appearance of C=N signals at 163.9-160.0 ppm.

(*E*)-Configuration in C=N bond of compounds **4a-m** confirm by NH signal: in case of (*E*)-configuration the hydrogen bond of NH with nitrogen atom of benzothiazole ring make NH signal lie in downfield region at δ 11.09-10.98 ppm; in case of (*Z*)-configuration it has no hydrogen bond (Fig. 4).

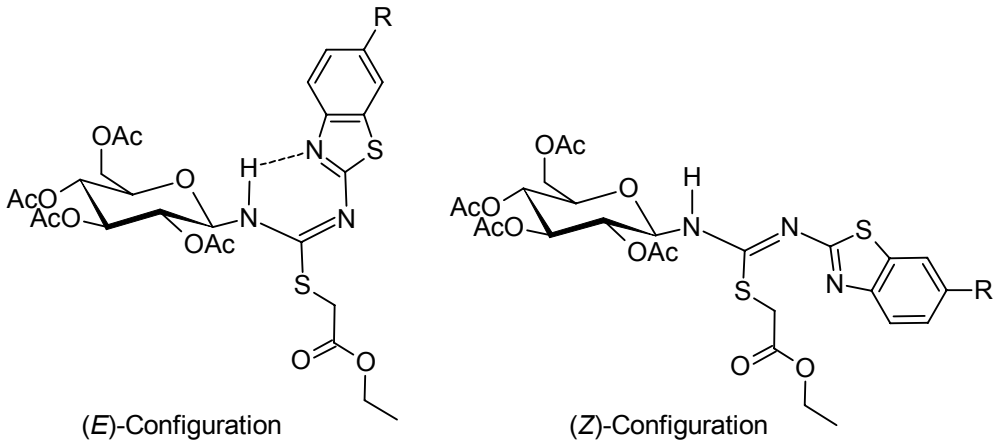


Figure 4.

EXPERIMENTAL

Melting points of the synthesized compounds were measured on STUART SMP3 (BIBBY STERILIN-UK). The FTIR-spectra was recorded on Magna 760 FT-IR Spectrometer (Nicolet, USA) in form of KBr and using reflex-measure method. ^{1}H- and ^{13}C-NMR spectra was recorded on an Advance AMX500 FT-NMR Spectrometer (Bruker, Germany) at 500.13 MHz and 125.76 MHz, respectively, using DMSO-d_6 as solvent and TMS as an internal reference. 2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl isothiocyanate was synthesized by known method [9,10]. High-resolution mass spectra (HR-MS) were recorded on Micromass AutoSpec Premier instrument (WATERS, USA).

General method for synthesis of substituted 1-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyl)-3-(benzo-thiazole-2-yl)thioureas (3a-n). A reaction mixture of (0.002 mole) of the corresponding substituted 2-aminobenzothiazoles (**2**) and 0.778 g (0.002 mole) of 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl isothiocyanate (**1**) was grinned carefully. This mixture was irradiated for 4-5 minutes in home microwave oven at 750 Watts. Then mixture had become dark-yellow. Cooled it to room temperature, recrystallized from a mixture of ethanol and toluene (1:1 in volume) obtained ivory-white crystal. The synthesized compounds were represented in Table 1.

Synthesis of ethyl 2-[(*E*)-*N'*-(benzothiazole-2'-yl)-*N*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-carbamimidoylthio]acetate (4a-m). To a solution of thioureas **3a-m** (5 mmol) in $CHCl_3$ (20 mL), ethyl bromoacetate (1.0 g, 0.2 mL, 6 mmol) was added dropwise with stirring. The mixture was heated at reflux for 8-10 h and the solvent was removed under diminished pressure until the volume was in 10 mL, and ethanol (20 mL) was added and left overnight. A white separated crude product was filtered and purified by recrystallization from toluene:ethanol (1:1) to afford the title compounds **4a-m**.

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