

Thionization Method of Glycosyl Urea and Carbamide Sugars

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Abstract

This work is describing a thionization method for glycosyl urea and carbamide of sugars by using the Lawesson's reagent. It is proposed the method based on the interaction of glycosyl urea and carbamide of sugars with the Lawessons reagent at a 1:1 ratio in the presence of a pyridine. As a result, sulfur-containing derivatives of sugar carbamides are obtained with the help of Lawesson's reagent. Obtained experimental data are indicating the developed new method for thionization of sugar carbamides, which opens up broad possibilities for synthesis of various carbohydrate derivatives of thiourea. Significance of this work is that, thiourea derivatives are promising bactericidal, fungicidal and anti-inflammatory drugs. Therefore, the preparation of thiourea derivatives and the study of their properties remain topical tasks in the field of chemistry.

Keywords

Glycosyl Urea, Glycosyl Thiourea Synthesis, Lawesson's Reagent, Anti-Inflammatory, Bactericidal, Fungicidal Properties

1. Introduction

Thiourea has great medicinal applications promising bactericidal [1], fungicidal [2] and anti-inflammatory drugs [3], as well as non-medicinal activities in the industry [4], analytical chemistry and metallurgy [5]. It is known that the replacement of the oxygen heteroatom by sulfur leads to a significant change in the spectrum of the biological activity of compounds [6]. Carbohydrate derivatives of thiourea can be obtained by the thionization of glycosyl ureas. In addi-

tion, thionization of glycosyl urea derivatives is a practically unexplored area. The most common method for synthesis of glycosyl thiourea by isothiocyanate method was developed in 1914 by E. Fischer, which has several significant drawbacks, namely a multi-stage process, the use of expensive reagents (silver salt), the use of an expensive catalyst (platinum dioxide), aggressive and toxic reagents (sodium azide, bromine), deficient isothiocyanate, high pressure and reaction time [7]. We have developed a modified method for obtaining the Lawessons reagent, distinguished by its simplicity and accessibility [8], compared with the previous preparation method [9].

In this regard, it was of interest for us to develop a simplified and accessible method for obtaining of glycosyl thiourea derivatives. For these purposes, we have used the Lawessons reagent (2,4-bis(p-methoxyphenyl)-1,3-dithiadiphosphetan-2,4-disulfide) for thionization which allows us to eliminate the above-mentioned disadvantages of the isothiocyanate method of thionization as shown in **Figure 1**.

2. Experimental

A general method for thionization of sugar ureas conducted as following: 0.2 mmol of carbamide sugars, 0.2 mmol of Lawessons reagent, and 3 ml of abs. pyridine placed into the flask then boiled under reflux with the potassium chloride tube for 45 minutes. Then the solution evaporated under vacuum at the temperature of 50 °C - 60 °C until dryness. 3 ml of distilled water was added to this residue and refluxed for five minutes. Then the solution filtered and the filtrate evaporated. The residue recrystallized from alcohol: benzene mixture. Then precipitated crystals separated by filtration and dried in the air. Product yield was about 56% - 60%.

Sample Characterizations

Identification of the synthesized compounds carried out by using thin-layer chromatography on Silufol, IR-, NMR-¹³C, ¹H-spectroscopy, and elemental analysis. The ¹³C NMR spectra were taken on a Bruker AM-300, SF = 75.47 MHz instruments with an operating frequency of 126 MG at a temperature of 2950 K, where TMS was used as an internal standard. The spectra taken in deuterated solvents—DMSO-d₆. ¹H NMR spectra were taken on a Bruker AM-300, SF = 300.13 MHz instruments with an operating frequency of 500 MHz at a temperature of 2930 K, where TMS was used as an internal standard. The spectra taken

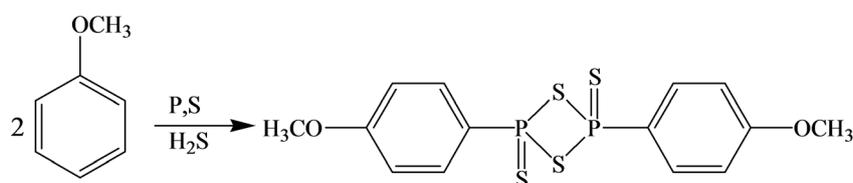


Figure 1. Simplified and accessible method for obtaining of glycosyl thiourea derivatives by the Lawessons reagent.

in deuterated solvents—DMSO- d_6 . The IR spectra of the compounds obtained were obtained on spectrophotometers IKS-29, SpecordM-80 with the program “Soft Spectra”, “SpectrumBXII” Fourier-IR spectrometer “NicoletAvatar 370” DTGS company Electron Corporation in the region of 500 - 4000 cm^{-1} (pressing with KBr). The melting point of the synthesized compounds measured on a microheater Boetuis. The rate of temperature rise on the table was 4°C per minute. Elemental analysis of synthesized compounds was determined by colorimetric method Dyumo-Pregl and Schöniger on the device VM-20 (VLM-20g-M), SMD-1000 (VLM-1g). The control throughout the reaction and the purity of the synthesized compounds carried out using thin-layer chromatography (TLC) on SilufolUV-254 plates (sorbent: silica gel). System: chloroform:methanol (3:1), chloroform-ethanol-methyl ethyl ketone (1:2:1).

3. Results and Discussions

3.1. Thionization of Glycosyl Urea

We then applied the synthesized Lawessons reagent to the thionization of glycosylurea derivatives. The proposed method of thionization was based on the interaction of N-methyl-N1-(β -D-glycopyranosyl)-urea (2 - 4) with the Lawessons (1) reagent at a 1:1 ratio of reagents in pyridine, where is formed N-methyl-N¹-(β -D-glycopyranosyl)-thioureas (8 - 10) (Figure 2) [10]. This reaction proceeds quickly, so we could not fix the intermediate formation of the corresponding

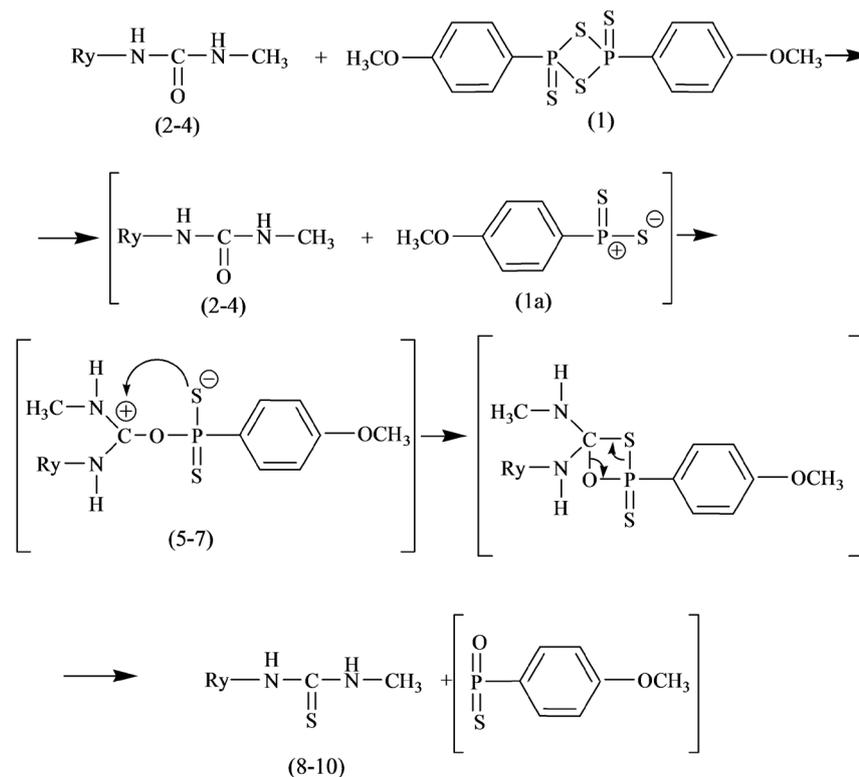


Figure 2. The thionization mechanism for glycosylurea (where Ry = xylose, glucose, and galactose).

products. This is most likely due to the decomposition of the Lawessons (1) reagent into dithiometaphosphonate (1a), which has a resonant structure. The interaction of dithiometaphosphonate with glycosylmethyl urea (2-4) leads to the formation of intermediate cyclic thioketals (5 - 7), with the subsequent decomposition, which produces the final products (8 - 10).

The advantage of this method is the simplicity, acceleration of the process, and elimination from the use of high-pressure technological processes and expensive platinum dioxide, poisonous sodium azide, and bromine reagents. Compounds synthesized by the new method are crystalline substances possessing chemical stability. They can be stored without decomposition at room temperature, stable under thin-layer chromatography (TLC) conditions. The individuality and structure of the target products were confirmed by the methods of nuclear magnetic resonance ^{13}C (NMR), ^1H NMR, infrared (IR)-spectroscopy, also elemental analysis. In the ^{13}C NMR and ^1H NMR spectra of as-synthesized compounds, we observed nuclei signals belonging to all presenting compounds (Table 1).

In the IR spectra, in particular of N-methyl-N¹-(β -D-glucopyranosyl)-thiourea, a broadband was observed in the region of 3000 - 3550 cm^{-1} , which is characteristic of the stretching vibrations of the OH- and NH- groups. Absorption bands in the regions of 1024 and 1108 cm^{-1} are related to the stretching vibrations of the carbohydrate ring. The presence of signals at 926 cm^{-1} is indicating β -position of the pyranotic ring. Oscillations in the region of 1256 - 1441 cm^{-1} can be attributed to the valence vibrations of the group (C=S). Peaks in the region of 2836 cm^{-1} are attributing to CH_3 group vibrations.

Important structural information was obtained by the ^1H NMR spectra. According to the proton magnetic resonance (PMR) spectrum, the structures of the products obtained are compounds formed from the glycosylamine bond with the β -arrangement of glucosyl methylthiourea. The low-field part of the PMR spectrum for the N-methyl-N¹-(β -D-glucopyranosyl)-thiourea contains signals that appearing as a multiplet centered at 3.6 ppm - 3.8 ppm, respectively, belonging to the fifth axial and the fifth equatorial hydrogen atom of the carbon-water ring. The equatorial hydrogen atom at C-2 appears as a doublet with a chemical shift at 3.8 ppm. A signal in the form of a broadened singlet, belonging to the protons of the methyl group CH_3 , is observed in the region of 2.7 ppm. The signal in the region of 4.6 ppm - 4.85 ppm refers to carbohydrate rings.

^{13}C NMR spectra of N-methyl-N¹-(β -D-glucopyranosyl) thiourea, the anomeric carbon atoms were found in the range of δ 60.69 - 81.09 ppm, which also testifies favor for the β -configuration of the glyosidic bond. Signals in the region of 60.69 ppm and δ 69.42 suggest that the glucoside residue in the compounds under discussion is in the pyranose form. Signals in the region of δ 26.28 ppm belonging to the methyl group, C=S signals were observed in the field of \approx 160.13 ppm. The set of spectral characteristics of the synthesized compounds do not doubt that all the substances obtained are individual compounds.

3.2. Synthesis of 2,4-Bis(p-methoxyphenyl)-1,3-dithiadiphosphetan-2,4-disulfide

In a flask equipped with a reflux condenser and a calcium chloride tube, 3.661 g (0.114 mol) of sulfur and 1.4 g (0.045 mol) of red phosphorus placed and boiled. The reaction mass was then cooled, 12 ml (0.11 mol) of anisole was added and boiled. After cooling up to the room temperature, the precipitated crystals filtered and washed with absolute ether and benzene, and then recrystallized from absolute toluene. Product yield: 4.36 g, (47.8%), $T_{\text{melt}} = 228^{\circ}\text{C} - 229^{\circ}\text{C}$. IR spectrum (KBr, ν , cm^{-1}): 689 (P = S), 615 (P = C), 1022, 1095, 1180 (R-O-CH₃), 1267, 1294, 1308, 1458, 1493, 1592 (arom.). C₁₄H₁₄O₂P₂S₄ 404.475 Calculated %: C-41.57; H-3.49; P-15.32; S-31.71. Found %: C-41.95; H-3.78; R-15.1; S-32.0.

3.3. Thionization of Carbamide Sugars

Lawessons reagent was used by us for thionization of carbamide derivatives of sugars to obtain thiocarbamide derivatives, 4-(N- β -D-glycopyranosyl)-thiosemicarbazide [11], previously synthesized by us, N-(β -D-glycopyranosyl) phenylsemicarbazide, 2,3,4,6-tetra-O-acetyl-(β -D-glycopyranosyl)-carbamoyl diethylenediamine, 1-[(N-glycopyranosyl) carbamoyl]-3,5-dimethylpyrazole [10] [12] [13] [14] as shown in **Figure 3**.

The reaction proceeds smoothly with the interaction of carbamide derivatives of sugars with Lawesson reagent in pyridine, for 20 minutes and leads to the formation of the corresponding 4-(N- β -D-glycopyranosyl)-thiosemicarbazide, N-(β -D-glycopyranosyl) phenylthiosemicarbazides, 1-[(N- β -glycopyranosyl) thiocarbamoyl]-3,5-dimethylpyrazoles, 2,3,4,6-tetra-O-acetyl-(β -D-glycopyranosyl)-thiocarbamoyl diethylenediamine diamine (**Figure 4**). The course of reactions and compositions of obtained compounds was controlled and carried out using the methods of thin-layer and paper chromatography in the systems: chloroform-ethanol-methyl ethyl ketone (1:2:1).

Compounds synthesized by the method are the crystalline substances possessing chemical stability. They can be stored without decomposition at room temperature, stable under TLC.



Figure 3. Synthesized samples of the Lawessons reagent and 4-(N- β -D-glycopyranosyl)-thiosemicarbazide.

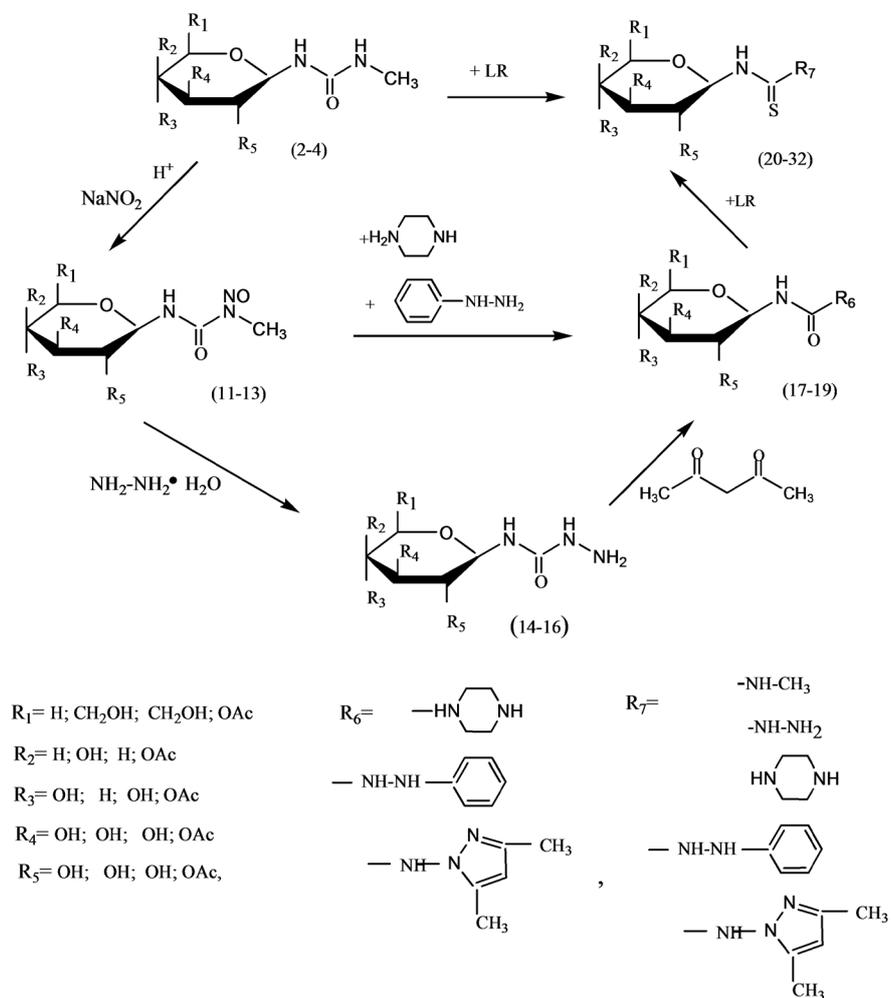


Figure 4. Thionization reaction for carbamide derivatives of sugars.

Individuality and structures of the target products confirmed by physico-chemical methods of ^{13}C and ^1H NMR, IR spectroscopy analyses. Results were presented in **Tables 1-4**, characteristic maximums of sugar thiocarbamides in the IR spectrum absorption bands, and chemical shifts for ^{13}C NMR of sugar thiocarbamides in **Figure 5**, **Figure 6**.

4. Conclusion

Thionization method of glycosyl urea and carbamide compounds of sugars is presented in this article. Obtained compounds are crystalline substances possessing chemical stability, and open up new ways of synthesizing various carbohydrate derivatives of thiourea. For thionization of carbamide derivatives of sugars, the Lawessons reagent is used to obtain thiocarbamide derivatives, 4-(N- β -D-glycopyranosyl)-semicarbazide which allows eliminating disadvantages of the isothiocyanate use. Obtained experimental data is useful for thionization of sugar derivatives and provides possibilities for the synthesis of various carbohydrate derivatives of thiourea.

Table 1. Physio-chemical property of thiocarbamide sugars.

No.	Compounds	Formula	T _{melt} , °C	Output %	Rf	Calculated % (found %) elemental compositions			
						C	H	N	S
20	N-methyl-N ¹ -(β-D-xylopyranosyl)-thiourea	C ₇ H ₁₄ N ₂ O ₄ S	122 - 125	53	0.2	37.82 (37.97)	6.34 (6.45)	12.60 (12.80)	14.42 (14.60)
21	N-methyl-N ¹ -(β-D-galactopyranosyl)-thiourea	C ₈ H ₁₆ N ₂ O ₅ S	168 - 170	48	0.8	38.08 (38.25)	6.39 (6.50)	11.10 (11.29)	12.71 (12.85)
22	N-methyl-N ¹ -(β-D-glucopyranosyl)-thiourea	C ₈ H ₁₆ N ₂ O ₅ S	165 - 167	58	0.6	38.08 (38.24)	6.39 (6.50)	11.10 (11.25)	12.71 (12.87)
23	N-(β-D-xylopyranosyl) phenylthiosemicarbazide	C ₁₂ H ₁₇ N ₃ O ₄ S	149 - 152	52	0.87	48.14 (48.04)	5.72 (5.98)	14.03 (13.94)	10.71 (10.86)
24	N-(β-D-galactopyranosyl) phenylthiosemicarbazide	C ₁₃ H ₁₉ N ₃ O ₅ S	137 - 140	56	0.84	47.40 (47.21)	5.81 (5.98)	12.75 (12.94)	9.73 (9.45)
25	N-(β-D-glucopyranosyl) -phenylthiosemicarbazide	C ₁₃ H ₁₉ N ₃ O ₅ S	142 - 144	55	0.75	47.40 (47.23)	5.81 (6.05)	12.75 (12.92)	9.73 (9.94)
26	1-[(N-β-xylopyranosyl)-thiocarbamoyl]-3,5-dimethylpyrazole	C ₁₁ H ₁₇ N ₃ O ₄ S	116 - 117	58	0.89	45.98 (46.07)	5.96 (6.13)	14.62 (14.80)	11.15 (11.25)
27	1-[(N-β-galactopyranosyl)-thiocarbamoyl]-3,5-dimethylpyrazole	C ₁₂ H ₁₉ N ₃ O ₅ S	146 - 148	61	0.6	45.41 (45.67)	6.03 (6.15)	13.24 (13.40)	10.10 (10.25)
28	1-[(N-β-glucopyranosyl)-thiocarbamoyl]-3,5-dimethylpyrazole	C ₁₂ H ₁₉ N ₃ O ₅ S	150 - 151	56.5	0.7	45.41 (45.52)	6.03 (5.96)	13.24 (13.45)	10.10 (10.35)
29	4-(N-β-D-xylopyranosyl)thiosemicarbazide	C ₆ H ₁₃ N ₃ O ₄ S	217 - 219	35.6	0.8	32.28 (32.40)	5.86 (6.10)	18.82 (18.97)	14.36 (14.47)
30	4-(N-β-D-galactopyranosyl)thiosemicarbazide	C ₇ H ₁₅ N ₃ O ₅ S	210 - 211	46	0.9	33.19 (33.36)	5.96 (6.28)	16.59 (16.75)	12.65 (12.98)
31	4-(N-β-D-glucopyranosyl)thiosemicarbazide	C ₇ H ₁₅ N ₃ O ₅ S	205 - 206	37	0.6	33.19 (33.32)	5.96 (6.26)	16.59 (16.64)	12.65 (12.85)
32	2,3,4,6-tetra-O-acetyl-(β-D-glycopyranosyl)-thiocarbamoyl diethylene diamine)	C ₂₂ H ₃₅ N ₃ O ₉ S	135 - 137	62.5	0.84	51.05 (50.97)	6.81 (6.98)	8.11 (8.33)	6.19 (6.35)

Table 2. Characteristic maximums of sugar thiocarbamides in the IR spectrum absorption bands.

No.	Fluctuations in the carbohydrate fragment, ν , cm^{-1}			Aglycone fluctuations, ν , cm^{-1}		
	-C-O-	OH	β -form	N-H	C=S	Other signals
20	1029	2838	955	3288	1257	2958 (CH ₃)
	1145	3046		1658 1602	1403 1439	
21	1024	2939	926	3403	1256	2836 (CH ₃)
	1108			1536 1649	1461 1441	
22	1030	2958	949	3288	1257	2837 (CH ₃)
	1074	3046		1572 1602	1453	
23	1233	3463	912	3269	1364	482 - 834 (C-H arom)
				1525 1748	1448	
24	1228	3339	915	2960	1371	492 - 831 (C-H arom)
				1536 1750	1499	
25	1230	3343	910	2950	1360	475 - 833 (C-H arom)
				1532 1730	1475	
26	1216	3453	909	3269	1424	2919 (CH ₃)
				1533 1626		
27	1220	3443	902	3250	1440	2930 (CH ₃)
				1536 1726		
28	1225	3450	905	3260	1445	2925 (CH ₃)
				1538 1722		
29	1108	3000	901	3251	1461	3377 (NH ₂)
		3500		1505		
30	1133	3000	908	3233	1332	3369 (NH ₂)
		3400		1530		
31	1140	3000	905	3235	1350	3360 (NH ₂)
		3400		1520		
32	1228	-	918	3371	1367	601 (CH arom) 1332 (OAc)
				1541	1421	

Table 3. Chemical shifts of thiocarbamide sugar protons.

No.	Carbonaceous part		Aglycone part	
	CH	OH	NH	Other signals
20	4.7 broad singlet 3.2 - 3.7 multiplet	4.5 - 4.8 broad singlet (3 OH)	5.4 singlet (1H)	2.7 broad singlet (3H) (CH ₃)
21	3.5 triplet 3.6 - 3.8 multiplet	4.6 - 4.8 broad singlet (4 OH)	5.4 singlet (1H)	2.7 broad singlet (3H) (CH ₃)
22	3.2 - 3.9 multiplet	4.6 - 4.7 broad singlet (4 OH)	5.4 singlet (1H)	2.7 broad singlet (3H) (CH ₃)
23	3.2 - 4 multiplet	4.8 broad singlet (3 OH)	7.2 duplet (1H) 6.8 duplet (1H)	2.0 - 2.2 (arom 5H)
24	4.2 broad singlet 3.5 triplet 3.6 - 4.0 multiplet	4.6 - 4.7 broad singlet (4 OH)	7.7 duplet (1H) 7.7 duplet (1H)	2.0 - 2.4 multiplet (arom 5H)
25	4.0 singlet 3.4 triplet 3.49 - 3.46 multiplet	4.8 singlet (4 OH)	7.5 duplet (1H) 7.6 duplet (1H)	2.0 - 2.2 (arom 5H)
26	3.7 singlet 3.2 triplet 3.5 - 3.7 multiplet	4.5 singlet (3 OH)	6.0 duplet (1H)	2.5 broad singlet (6H) (CH ₃) 5.8 singlet (pyrazole CH 1H)
27	3.79 singlet 3.4 triplet 3.5 - 3.76 multiplet	4.7 singlet (4 OH)	6.2 duplet (1H)	2.8 broad singlet (6H) (CH ₃) 5.9 singlet (pyrazole CH 1H)
28	3.79 singlet 3.4 triplet 3.49 - 3.76 multiplet	4.82 singlet (4 OH)	6.2 duplet (1H)	2.8 broad singlet (6H) (CH ₃) 5.9 singlet (pyrazole CH 1H)
29	3.88 quartet 3.41 triplet 3.49 - 3.76 multiplet	2.0 broad singlet (3OH)	4.81 duplet (1H)	2 broad singlet (NH ₂ ; NH) (3H)
30	3.79 multiplet 3.4 triplet 3.48 - 3.76 multiplet	2.1 broad singlet (4OH)	4.83 duplet (1H)	2 broad singlet (NH ₂ ; NH) (3H)
31	3.76 multiplet 3.4 triplet 3.48 - 3.76 multiplet	2.1 broad singlet (4OH)	4.80 duplet (1H)	2 broad singlet (NH ₂ ; NH) (3H)
32	4.16 multiplet 3.6 - 3.91 multiplet	4.09 - 4.34 multiplet (-CH ₂ O) (8H) 2.0 broad singlet (CH ₃ 12H)	4.72 duplet (1H)	3.37, 2.67, 3.57, 2.67, 2.0 (CH ₃ ; NH amine)

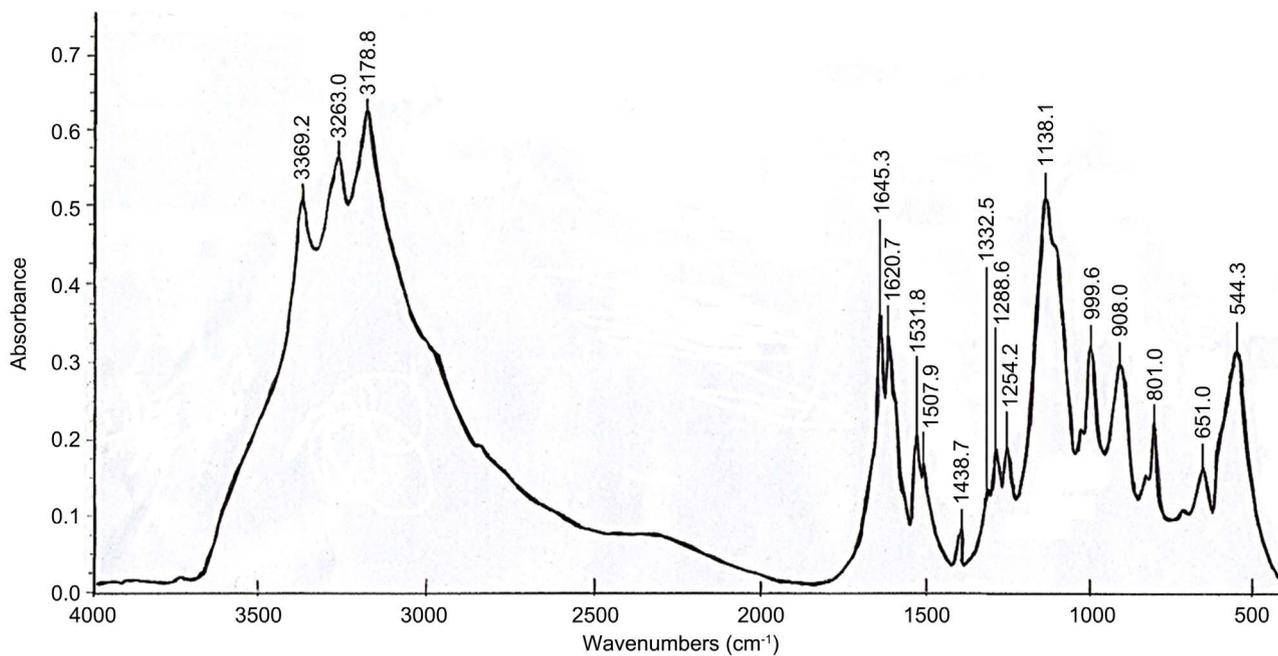


Figure 5. Characteristic maximums of sugar thiocarbamide 4-(N-β-D-galactopyranosyl) thiosemicarbazide in the IR spectrum absorption bands.

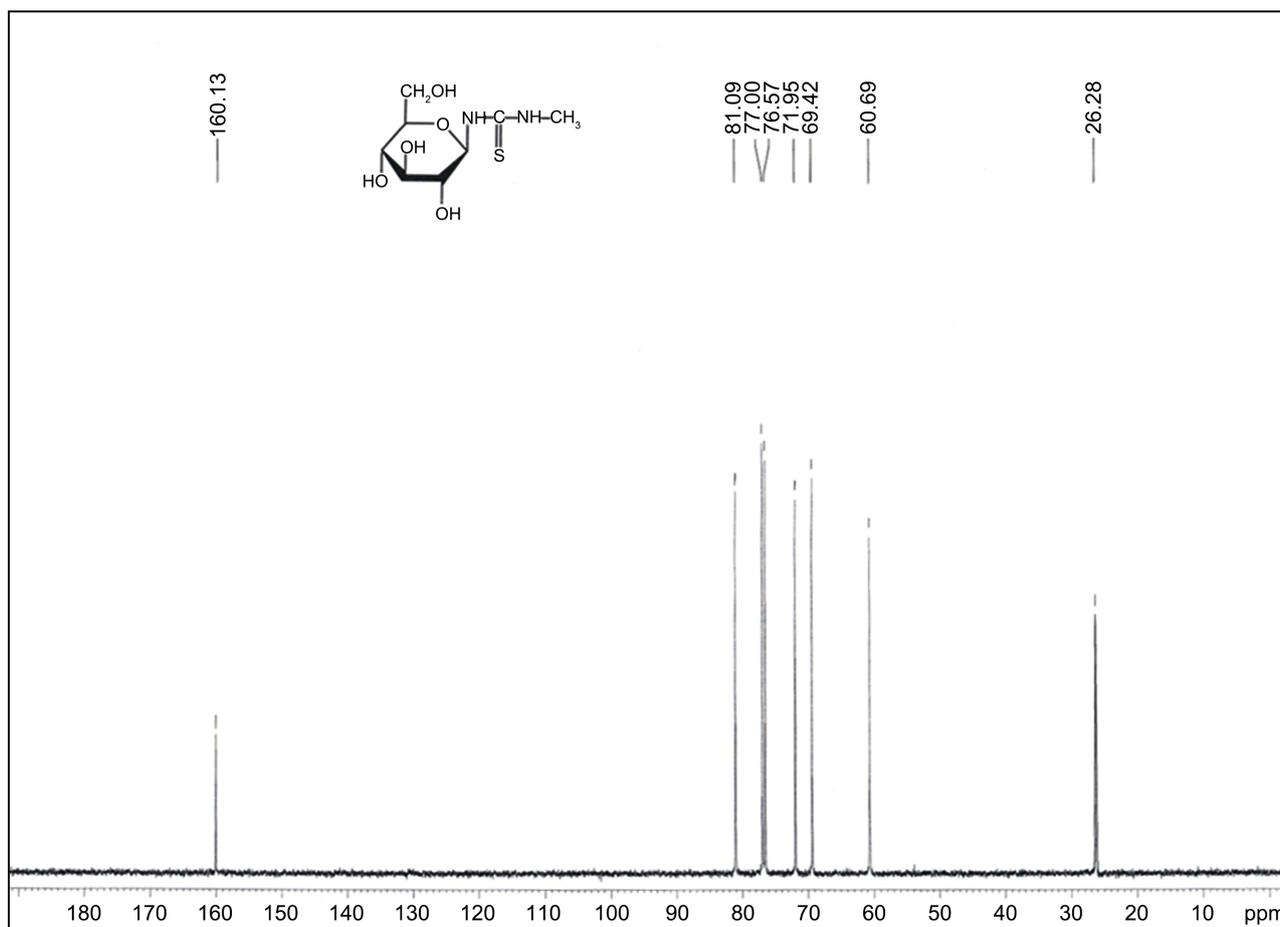


Figure 6. Pattern showing the chemical shifts for ¹³C NMR of sugar thiocarbamides (N-methyl-N¹-(β-D-glucopyranosyl)-thiourea).

Table 4. Chemical shifts for ^{13}C NMR of sugar thiocarbamides.

No.	Carbonaceous part					Aglycone part		
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C=S	Other signals
20	81.80	71.82	76.63	69.13	66.30	-	160.04	26.22 (CH ₃)
21	81.09	71.95	76.57	69.42	77.00	60.69	160.13	26.28 (CH ₃)
22	81.51	69.54	73.43	68.69	76.08	60.99	160.23	26.22 (CH ₃)
23	90.5	73.9	77.0	67.8	70.1	-	186.1	113.2; 129.2; 119.2; 151.0; 129.1 (CH-arom)
24	97.7	93.5	76.4	69.6	70.0	62.4	186.5	113.2; 118.2; 119.2; 129.3; 128 (CH-arom)
25	88.3	79.1	74.8	71.2	74.2	62.0	186.0	113.2; 118.2; 119.2; 129.2; 129 (CH-arom)
26	90.9	77.0	73.9	70.1	67.8	-	173.7	143.2; 144.32 (C-C); 105.0 (CH) 18.3; 11.3 (CH ₃)
27	88.7	79.0	74.8	71.0	74.0	62.2	173.8	143.2, 144.3 (C-C), 105.0 (CH) 18.3, 11.2 (CH ₃)
28	88.5	79.1	74.7	71.2	74.2	62.2	173.7	143.0; 144.1 (C-C); 105.2 (CH) 18.2; 11.2 (CH ₃)
29	90.5	73.9	77.0	70.1	67.8	-	183.6	-
30	88.3	74.2	74.8	71.2	79.1	62.0	183.5	-
31	88.3	74.0	74.5	71.0	78.8	61.3	183.4	-
32	87.8	32.9; 59.4; 170.3; 20.7 (4C)	19.9; 65.2; 170.8; 20.5 (4C)	35.5; 61.4; 170.2; 20.8 (4C)	20.7; 66.3; 170.0; 20.3 (4C)	-	183.7	56.9; 46.0; 56.9; 46.2 (C-amine)

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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