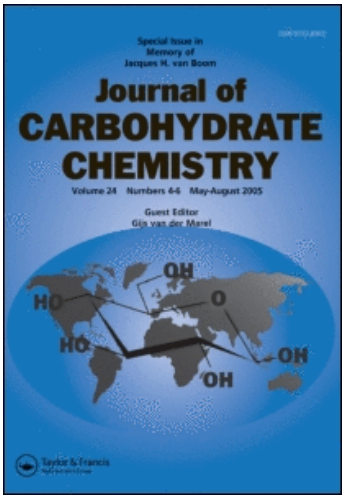

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Building Blocks for Glycopeptide Synthesis. Disaccharide Glycosyl Isothiocyanates

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BUILDING BLOCKS FOR GLYCOPEPTIDE SYNTHESIS. DISACCHARIDE GLYCOSYL ISOTHIOCYANATES[1]

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ABSTRACT

The reaction of aldose oligosaccharides with aqueous ammonium hydrogencarbonate was revised and optimized for gram scale preparation of glycosylamines, using lactose, cellobiose, maltose, and melibiose as model compounds. The unprotected glycosylamines **1b-4b** were transformed into the corresponding hepta-*O*-acetyl hydrochlorides **1e-4e** *via* diethyl *N*-glycosylaminomethylenemalonates (**1c-4c** and **1d-4d**). Reaction of **1e-3e** with thiophosgene in a three-phased system led to the target hepta-*O*-acetylglycosyl isothiocyanates **1f-3f** in excellent yields. Under the same conditions, the melibiosyl derivative **4e** underwent partial hydrolysis to give a mixture of melibiosyl isothiocyanate **4f** and the reducing sugar derivative **4h**. Treatment of **1f-4f** with ammonia resulted in the quantitative formation of *N*-glycosylthioureas (**1g-4g**).

INTRODUCTION

The reaction of glycosyl isothiocyanates with suitably protected aminoacid derivatives[2-7] is probably the most efficient method for the preparation of *N*- or *neo-N*-glycopeptides.[8] However, the formation of *N*-glycosidic linkages has been most often performed from glycosylamides or glycosylamines.[4,9] Although the synthesis of monosaccharide glycosyl isothiocyanates is now routine,[10-19] the procedures available are

not of general application for oligosaccharides, and only a few examples of *O*-protected di[20]- and trisaccharide glycosyl isothiocyanates[5,6] have been reported in the literature. The main problem is the use of acidic conditions in the preparation of suitable precursors, i.e., glycosyl halides[10,12,16,18] or oxazoline derivatives,[15] that may cause trouble in the case of acid-sensitive oligosaccharides such as α-L-fucoside or 2-deoxysugar derivatives.

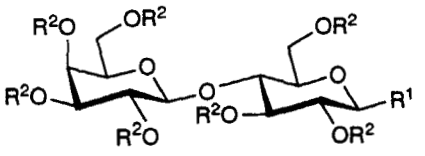
Some unstable, unprotected disaccharide glycosyl isothiocyanates have been obtained[21,22] by reaction of disaccharide glycosylamines with thiophosgene. Glycosylamines can be prepared from aldoses, under mild conditions, by reaction with aqueous ammonium hydrogencarbonate.[23] Recently, an improved modification of this method has been published.[24] In the framework of a program concerning *neo-N*-glycoconjugate synthesis, we have now explored the application of this reaction to the synthesis of the title compounds using diethyl *N*-glycosylaminomethylenemalonates as key intermediates, with the aim to develop a general route for the preparation of fully protected oligosaccharide glycosyl isothiocyanates.

Sugar isothiocyanates react with ammonia and amines to give thioureas with a variety of synthetic and pharmacological applications.[10,19] Interestingly, glycosyl residues can be attached in this way to peptide chains to give *N*-glycosylthiocarbamoyl peptides with immunoadjuvant activity.[3] In order to check the reactivity of the synthesized disaccharide glycosyl isothiocyanates against aminonucleophiles, we have regarded their reaction with ammonia and report on the preparation of the corresponding *N*-glycosylthioureas.

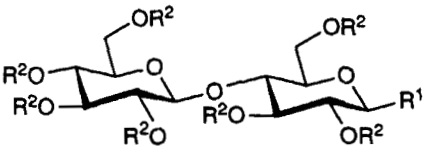
RESULTS AND DISCUSSION

The reaction of aldoses, 2-amino-2-deoxyaldoses, and oligosaccharides with saturated aqueous ammonium hydrogencarbonate leads to the formation of unstable *N*-glycosylcarbamates[25] (i.e., **1a-4a**) which, on treatment with strong acid resin[23,25] or by repeated evaporation of water from the reaction mixture,[24] give glycosylamines (i.e., **1b-4b**). In the first case, the yield of final product depends critically on the time of contact between the intermediate glycosylcarbamate and the resin.[25] The second procedure, although more tedious, provides higher yields and easier workup. Hitherto, this reaction has been applied to no more than 100 mg of starting material. During the course of our

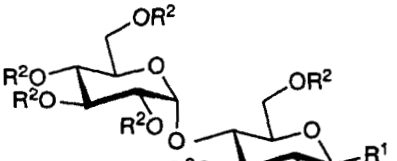
work, we have been interested in optimizing this method to a gram scale level using readily available disaccharides.



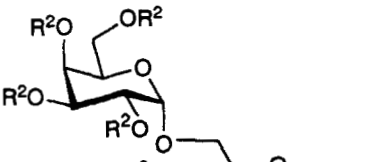
1a-1g



2a-2g



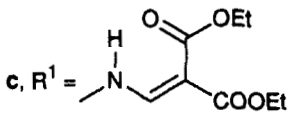
3a-3g



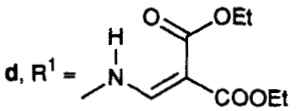
4a-4h

a, R^1 = NH-COO$^-$ NH_4^+; R^2 = H
b, R^1 = NH_2; R^2 = H

e, R^1 = NH_3^+ Cl^-; R^2 = Ac
f, R^1 = NCS ; R^2 = Ac
g, R^1 = NH-CS-NH_2; R^2 = Ac
h, R^1 = OH; R^2 = Ac



c, R^1 = ; R^2 = H



d, R^1 = ; R^2 = Ac

Reaction mixtures arising from the action of aqueous ammonium hydrogencarbonate on lactose, cellobiose, maltose, and melibiose (2 g) at room temperature for 5 days were diluted with water and concentrated. The composition of the mixtures was monitored by ^{13}C NMR (D_2O) spectroscopy and found to be highly dependent upon the nature of the sugar substrate and the volume of water evaporated. Thus, in the cases of lactose, cellobiose, and melibiose the ^{13}C NMR spectra of the crude products after evaporation of 4 x 500 mL of water showed, in the region of the resonances of the anomeric carbon atoms, signals at ~85 ppm for C-1 of the ß-glycosylamines[23,25] **1b**,[25,26] **2b**,[26] and **4b**, and at ~87 ppm for C-1 of the *N*-glycosylcarbamates **1a**, **2a**, and **4a**, respectively, in ~4:1 ratio (^{13}C integration). Only traces of the starting sugars were detected (96.8-95.8 and 93.0-91.9 for C-1ß and C-1α,

respectively).[27] Repetition of the treatment (see Experimental) resulted in the complete hydrolysis of the carbamates without any appreciable increase in the proportion of reducing sugar. No signals for α-glycosylamines were observed in agreement with reported results.[23-25]

In the case of maltose, the corresponding *N*-glycosylcarbamate **3a** showed higher resistence towards hydrolysis, and the subsequent hydrolysis of the maltosylamine[21,22,28] (**3b**) to give the starting sugar was an important side-reaction. After evaporation of 4 x 500 mL of water from the reaction mixture, the proportion of **4b** to **4a** was ~3:2 (^{13}C NMR). The treatment had to be repeated 4 times to get almost complete hydrolysis of **4a** into **4b**, but a gradual increase in the proportion of free sugar also occurred.

The amino group in crude **1b-4b** was protected by reaction with diethyl ethoxymethylenemalonate to give **1c-4c**, following the method described[13,29] for the preparation of other *N*-alkenylglycosylamines. The overall yields for this two-step conversion (sugar → compound **c**) were 67-75% except for maltose (50%). The ^1H (Experimental) and ^{13}C NMR data (Table 3) agreed with data reported for related diethyl *N*-glucopyranosylaminomethylenemalonates.[30] Compounds **1c-4c** presented two ^{13}C signals at δ 168.3-167.8 (C=O chelated) and 159.1-157.7 (C=O free). The former, together with δ_{NH} (9.27-9.15 ppm) and the $\nu_{C=O}$ (~1660 cm^{-1}) IR absorption are indicative of the hydrogen bond shown in the structure.[30]

Conventional acetylation of enamines **1c-4c** with Ac_2O-pyridine yielded the corresponding hepta-*O*-acetates **1d-4d**, whose structures were assigned on the basis of analytical, UV, IR, ^1H (Tables 1 and 2), ^{13}C (Table 3) NMR, and MS data. The assignments of ^{13}C resonances were supported by APT[31] spectra and bibliographic data for related compounds.[30-32] The $J_{1,2}$ values (9.3-8.9 Hz) were in the range for antiperiplanar protons and indicated that the glucosylamino moieties had the ß-configuration. The ß- (**1d, 2d**) and α-anomerism (**3d, 4d**) of the *O*-glycosidic linkages was evident from the $J_{1',2'}$ values (7.8 and 4.1-3.8 Hz, respectively). The $^3J_{H,H}$ values were indicative of $^4C_1$ (D) conformation for each sugar ring.

The EIMS spectra of **1d-4d** contained peaks for M^+ and the characteristic losses of $EtO^\cdot$ and the enamino group.[30,33]

The *N*-protecting groups in **1d-4d** were removed with Cl_2 in CH_2Cl_2 to give glycosylamine hydrochlorides[19,34] (**1e-4e**). The reaction was monitored by IR until

TABLE 1. ^{1}H NMR Spectral Data (δ values, $CDCl_3$) for Compounds 1d-4d, 4f, and 1g-4g.

Comp.	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	H-1'	H-2'	H-3'	H-4'	H-5'	H-6'a	H-6'b
1d[a]	4.51 t	4.97 t	5.27 dd	3.79 dd	3.69 ddd	4.45 dd	4.07 dd	4.47 d	5.10 dd	4.95 dd	5.35 dd	3.88 td	4.27 dd	4.13 dd
2d[a]	4.50 t	4.97 t	5.25 dd	3.77 dd	3.67 m	4.47 dd	4.08 dd	4.50 d	4.92 dd	5.14 t	5.06 t	3.67 m	4.38 dd	4.05 dd
3d[a]	4.58 t	4.89 t	5.32 t	3.99 t	3.78 ddd	4.45 dd	4.22 dd	5.41 d	4.86 dd	5.35 t	5.05 t	3.91 ddd	4.25 dd	4.04 dd
4d[a]	4.47 t	4.90 t	5.18 t	5.00 t	<------3.70-3.45-----> m			5.06 d	4.92 dd	5.20 dd	5.30 dd	4.08 t	<----3.92----> d	
4f[a]	5.03 d	5.28-4.89 m		5.08 t	<------3.80-3.54-----> m			5.14 d	5.10 m	5.36 dd	5.47 d	4.22 t	<----4.05----> d	
1g[b]	5.55 bs	4.97 t	5.27 t	3.90 t	3.78 m	4.44 dd	4.24 dd	4.50 d	5.12 dd	4.96 dd	5.35 d	3.88 dd	4.16 dd	4.06 dd
2g[a]	5.55 bs	5.02 t	5.22 t	3.97 t	3.80 m	4.47 dd	4.27 dd	4.56 d	4.96 dd	5.19 t	5.10 t	3.69 m	4.39 dd	4.00 dd
3g[b]	5.62 bs	4.93 t	5.38 t	4.06 t	3.87 ddd	4.45 dd	4.39 dd	5.39 d	4.87 dd	5.37 t	5.08 t	3.97 ddd	4.23 dd	4.11 dd
4g[b]	5.50 bs	4.95 t	5.35 t	5.00 t	3.84 ddd	3.71 dd	3.65 dd	5.22 d	5.08 dd	5.36 dd	5.43 dd	4.31 bt	4.17 dd	4.01 dd

a. At 200 MHz.
b. At 300 MHz.

TABLE 2. ^{1}H NMR Coupling Constants (Hz) of Compounds 1d-4d, 4f, and 1g-4g in $CDCl_3$.

Comp.	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$	$J_{1',2'}$	$J_{2',3'}$	$J_{3',4'}$	$J_{4',5'}$	$J_{5',6'a}$	$J_{5',6'b}$	$J_{6'a,6'b}$
1d	8.9	8.9	8.6	8.9	3.0	6.8	12.8	7.8	10.6	3.2	0.8	7.4	7.4	13.5
2d	9.3	9.3	8.4	9.3	1.6	4.8	12.6	7.8	9.0	9.0	9.0	4.3	2.1	12.8
3d	8.9	8.9	8.9	8.9	2.3	4.1	12.1	4.1	10.2	10.2	10.2	3.5	2.2	12.2
4d	8.9	8.9	8.9	8.9	--	--	--	3.8	10.5	3.1	0	6.4	6.4	--
4f	8.9	--	8.9	8.9	--	--	--	3.5	9.8	3.5	0	6.9	6.9	--
1g	9.2	9.2	9.2	9.2	1.1	5.8	12.4	7.8	10.2	3.2	0	6.4	7.1	10.7
2g	9.0	9.0	9.0	9.0	2.0	6.4	12.4	7.6	9.0	9.0	9.0	3.6	2.0	12.4
3g	9.4	9.4	9.4	9.4	2.8	5.6	12.5	3.8	9.7	9.7	9.7	3.4	2.2	12.6
4g	9.5	9.5	9.5	9.5	5.8	2.9	12.4	3.6	10.7	3.3	1.0	5.8	7.1	11.1

TABLE 3. ^{13}C NMR Spectral Data (δ values) for Compounds 1c-4c, 1d-4d, 4f, and 1g-4g.

Comp.	C-1	C-2	C-3	C-4	C-5	C-6	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'
1c[a,c]	88.3	73.1	75.5	80.2	76.2	60.5	104.2	71.2	73.6	68.8	77.4	61.2
2c[a,c]	87.7	73.4	75.3	80.1	76.6[e]	60.7	103.3	72.7	76.9[e]	70.1	76.9[e]	61.2
3c[a,c]	88.2	73.9	77.5	79.5	76.9	61.2	101.5	72.7	73.5	70.2	72.7	60.8
4c[a,c]	88.3	71.4	77.1	69.3	73.2	66.7	99.3	77.4	69.9	68.8	70.0	61.1
1d[b,c]	86.8	70.8	72.1	75.6	74.5	61.6	100.9	68.8	70.7	66.4	70.6	60.6
2d[b,c]	86.8	70.5	71.8	75.9	74.5	61.5[f]	100.7	71.4	72.5	67.5	71.8	61.4[f]
3d[b,c]	86.1	70.8	74.2	72.0	73.5	62.2	95.2	69.5	68.7	67.5	68.1	61.1
4d[b,c]	86.4	70.1	72.1	68.0	74.1	66.0	95.9	67.5	67.0	67.7	66.1	61.2
4f[b,c]	83.1	71.5	72.2	67.9	74.4	65.8	95.9	67.7	67.2	67.7	66.1	61.3
1g[b,d]	82.9	70.8	72.4	75.9	74.6	61.8	100.7	68.8	70.7	66.4	70.5	60.6
2g[b,c]	83.0	72.7[g]	70.3	76.0	75.2	61.7	100.5	71.3	72.8[g]	67.5	71.7	61.2
3g[b,d]	82.7	70.9	75.5	72.7	74.5	62.5	95.4	69.9	69.1	67.8	68.3	61.1
4g[b,d]	82.5	70.3	72.7	68.7	74.2	65.3	95.5	68.1[h]	67.2	68.2[h]	66.4	61.7

a. In DMSO-d_6.
b. In $CDCl_3$.
c. At 50.3 MHz.
d. At 75.5 MHz.
e, f, g, h. Assignments may have to be reversed.

disappearance of the characteristic[35] band for the enamino group at ~1600 cm^{-1}. A broad and strong IR absorption at 3020-2400 cm^{-1} for the ammonium group was clearly observed. This method avoids the problems of acetyl migrations to the amino group that may occur when the free bases are obtained.[36] Additionally, the use of the ammonium salts is also advantageous in the reaction with thiophosgene (see later) because it prevents undesired reactions of the synthesized isothiocyanates with their precursor amines, resulting in higher overall yields.[37] Compounds **1e-4e** were isolated as hygroscopic, amorphous solids which were immediately used in the next step.

Reactions of crude **1e-3e** with thiophosgene using a three-phased system, as reported for monosaccharide derivatives,[11,13,14,19] yielded the known[20] per-*O*-acetyl disaccharide glycosyl isothiocyanates **1f-3f** in 85-90% yield (two steps). Under the same conditions, the melibiosyl derivative **4e** underwent partial hydrolysis giving the target melibiosyl isothiocyanate **4f** together with the reducing heptaacetate **4h** in ~3:2 ratio.

The presence of the NCS group in **4f** was confirmed by IR (ν_{NCS} 2033 cm^{-1}) and ^{13}C NMR (δ_{NCS} 144.2). A ^{1}H signal (Tables 1 and 2) at 5.03 ppm ($J_{1,2}$ = 8.9 Hz, H-1) and a ^{13}C signal (Table 3) at 83.1 ppm (C-1) also agreed with a ß-D-glucopyranosyl isothiocyanate structure.[19,20]

The structure of compound **4h** was stablished on the basis of FABMS (pseudomolecular $[M+Na]^+$ ion at *m/z* 659), ^{1}H and ^{13}C NMR. Signals for both anomers were observed with an α:ß ratio 1:1.2 (H-1 integration).

Compounds **1f-4f** were converted into the corresponding *N*-glycosylthioureas **1g-4g** by reaction with ammonia. Quantitative transformations were achieved after 10 min in ether at 0 °C, and no ammonolysis of the acetyl groups was observed. Compounds **1g-4g** showed ^{13}C signals at ~185 ppm, characteristic[19] of the thiourea group. The ^{1}H (Tables 1 and 2) and ^{13}C NMR data (Table 3) agreed with the ß-configuration of the glucosylthiourea moieties and the $^{4}C_{1}$ (D) conformation for all glycosyl residues.

EXPERIMENTAL

General Procedures. Concentrations were performed at <40 °C (bath). Melting points were determined with a Gallenkamp MFB 595 apparatus and are uncorrected. Optical rotations were measured at 22 °C with a Perkin-Elmer 141 MC

polarimeter. UV spectra were recorded with a Philips PU 8710 spectrophotometer. Infrared spectra were recorded on a Bomen Michelson MB-120 FTIR spectrophotometer (KBr pellets). ^{1}H NMR (200 and 300 MHz) and ^{13}C NMR spectra (50.3 and 75.5 MHz) were obtained on Varian XL-200 and Bruker 300 AMX spectrometers. For spectra in $CDCl_3$ or DMSO-d_6 solutions, tetramethylsilane (Me_4Si) was used as internal reference; for ^{13}C spectra of solutions in D_2O, acetone (δ 31.1) was used as the internal standard. The spectra are reported as chemical shifts downfield from Me_4Si. Assigments of ^{1}H signals were confirmed by decoupling and H/D exchange experiments. Proton-decoupled APT[32] (attached proton test) spectra were used to assist in carbon signal assigments. Mass spectra were taken on a Kratos MS-80 RFA instrument. In the EI mode, operating conditions were: ionizing energy 35 eV, ionizing current 100 μA, accelerating voltage 4 kV, resolution 1000 (10% valley definition). In the FAB mode, the primary beam consisted of xenon atoms with a maximun energy of 8 keV. The samples were dissolved in thioglycerol (unprotected derivatives) or *m*-nitrobenzyl alcohol (hepta-acetates), and the positive ions were separated and accelerated over a potential of 7 kV. NaI was added as cationizing agent. TLC was performed on silica gel 30 F_{254} (Merck) plates with visualization by UV light or/and by charring with 10% sulphuric acid, and column chromatography was carried out with silica gel 60 (Merck, 70-230 mesh). Microanalyses were performed by the Analytical Chemistry Deparment in Sevilla and by the Instituto de Química Orgánica General (CSIC) in Madrid. For unprotected derivatives the samples were prepared in sealed tubes after drying over P_2O_5 at 80 °C for 6 h.

Preparation of Disaccharide Glycosylamines (1b-4b). The glycosylamines were prepared essentially as described.[23] Typically, solid ammonium hydrogencarbonate was added until saturation to a solution of disaccharide (2 g, 5.8 mmol) in water (100 mL). After reacting for 5 days at room temperature, the mixture was diluted with water (4 x 500 mL) and concentrated to half the volume. This treatment was repeated until no presence of the intermediate *N*-glycosylcarbamate was observed in ^{13}C NMR. The crude products were used directly in the next step.

Preparation of *N*-(2,2-Diethoxycarbonylvinyl) Disaccharide Glycosylamines (1c-4c). To a solution of crude glycosylamines (**1b-4b**, 2 g, 5.8 mmol) in dry methanol (16 mL), diethyl ethoxymethylenemalonate (1.75 mL, 8.7 mmol) was added. The

mixture was stirred at 40 °C for 36 h, and concentrated. Column chromatography ($CHCl_3$-MeOH 3:1) of the resulting syrupy residue yielded pure **1c-4c**.

***N*-(2,2-Diethoxycarbonylvinyl)-4-*O*-(ß-D-galactopyranosyl)-ß-D-glucopyranosylamine** (**1c**, 2.14 g, 72%) had mp 137-139 °C (from MeOH); $[\alpha]_D^{22}$ -1.1° (*c* 0.5, pyridine); UV (H_2O) 274 and 218 nm (ϵ_{mM} 16.7 and 7.6); IR 3398 (OH), 1697 (C=O free), 1663 (C=O chelated), 1607 (C=C and NH), and 1244 cm^{-1} (C-O-C);^{1}H NMR (200 MHz, DMSO-d_6) δ 9.27 (dd, 1H, $J_{NH,=CH}$ = 13.1 Hz, $J_{1,NH}$ = 8.5 Hz, NH), 8.19 (d, 1H, =CH), 5.74 (d, 1H, $J_{H,OH}$ = 4.2 Hz, OH), 5.25 (d, 1H, $J_{H,OH}$ = 3.0 Hz, OH), 4.95 (s, 2H, 2OH), 4.80 (t, 2H, $J_{H,OH}$ = 3.2 Hz, 2OH), 4.74 (t, 1H, $J_{1,2}$ = 8.5 Hz, H-1), 4.65 (d, 1H, $J_{H,OH}$ = 4.0 Hz, OH), 4.34 (d, 1H, $J_{1',2'}$ = 8.5 Hz, H-1'), 4.27, 4.19 (2q, each 2H, $^3J_{H,H}$ = 7.3 Hz, CH_2CH_3), 4.00-3.00 (m, 12H, H-2 to H-6b and H-2' to H-6'b), 1.35 and 1.32 (2t, each 3H, $2CH_3$); ^{13}C NMR (50.3 MHz, DMSO-d_6) Table 3 and δ 168.3 (C=O chelated), 166.1 (C=O free), 159.1 (=CH), 91.7 (=C), 60.4, 60.3 ($2CH_2$), 15.0 and 14.9 ($2CH_3$).

Anal. Calcd for $C_{20}H_{33}NO_{14}$: C, 46.96; H, 6.50; N, 2.74. Found: C, 46.87; H, 6.55; N, 2,77.

A FABMS spectrum showed a pseudomolecular $[M+Na]^+$ ion at *m/z* 534.

***N*-(2,2-Diethoxycarbonylvinyl)-4-*O*-(ß-D-glucopyranosyl)-ß-D-glucopyranosylamine** (**2c**, 1.99 g, 67%) had mp 182-184 °C (from MeOH); $[\alpha]_D^{22}$ -3.8° (*c* 0.5, pyridine); UV (H_2O) 273 and 218 nm (ϵ_{mM} 8.6 and 4.6); IR 3366 (OH), 1759 (C=O free), 1707 (C=O chelated), 1613 (C=C and NH), and 1312 cm^{-1} (C-O-C); ^{1}H NMR (200 MHz, DMSO-d_6) δ 9.19 (dd, 1H, $J_{NH,=CH}$ = 13.1 Hz, $J_{1,NH}$ = 8.5 Hz, NH), 8.09 (d, 1H, =CH), 5.61 (d, 1H, $J_{H,OH}$ = 5.6 Hz, OH), 5.27 (d, 1H, $J_{H,OH}$ = 4.8 Hz, OH), 5.06 (d, 1H, $J_{H,OH}$ = 4.5 Hz, OH), 4.82 (s, 1H, OH), 4.70 (t, 1H, $J_{H,OH}$ = 5.5 Hz, OH), 4.63 (t, 1H, $J_{H,OH}$ = 5.5 Hz, OH), 4.59 (t, 1H, $J_{1,2}$ = 8.5 Hz, H-1), 4.27 (d, 1H, $J_{1',2'}$ = 7.4 Hz, H-1'), 4.14, 4.04 (2q, each 2H, $^3J_{H,H}$ = 7.0 Hz, CH_2CH_3), 3.80-2.80 (m, 12H, H-2 to H-6b and H-2' to H-6'b), 1.22 and 1.21 (2t, each 3H, $2CH_3$); ^{13}C NMR (50.3 MHz, DMSO-d_6) Table 3 and δ 167.8 (C=O chelated), 165.0 (C=O free), 158.7 (=CH), 90.9 (=C), 59.5, 59.3 ($2CH_2$), 14.5 and 14.4 ($2CH_3$).

Anal. Calcd for $C_{20}H_{33}NO_{14}$: C, 46.96; H, 6.50; N, 2.74. Found: C, 46.72; H, 6.49; N, 2,54.

A FABMS spectrum showed a pseudomolecular $[M+Na]^+$ ion at *m/z* 534.

***N*-(2,2-Diethoxycarbonylvinyl)-4-*O*-(α-D-glucopyranosyl)-ß-D-glucopyranosylamine** (**3c**, 1.49 g, 50%) had mp 112-114 °C (from MeOH); $[\alpha]_D^{22}$ +49.8° (*c* 0.5, pyridine); UV (H_2O) 275 and 218 nm (ϵ_{mM} 23.8 and 10.9); IR 3370 (OH), 1686 (C=O free), 1666 (C=O chelated), 1600 (C=C and NH), and 1244 cm^{-1} (C-O-C); ^1H NMR (200 MHz, DMSO-d_6) δ 9.19 (dd, 1H, $J_{NH,=CH}$ = 13.2 Hz, $J_{1,NH}$ = 8.5 Hz, NH), 8.08 (d, 1H, =CH), 5.70 (bs, 1H, OH), 5.58 (m, 2H, 2OH), 5.05 (d, 1H, $J_{1',2'}$ = 3.2 Hz, H-1'), 4.98 (d, 2H, $J_{H,OH}$ = 5.5 Hz, 2OH), 4.66 (m, 1H, OH), 4.58 (m, 1H, OH), 4.56 (t, 1H, $J_{1,2}$ = 8.5 Hz, H-1), 4.15, 4.08 (2q, each 2H, $^3J_{H,H}$ = 7.1 Hz, CH_2CH_3), 3.80-2.90 (m, 12H, H-2 to H-6b and H-2' to H-6'b), 1.24 and 1.21 (2t, each 3H, $2CH_3$); ^{13}C NMR (50.3 MHz, DMSO-d_6) Table 3 and δ 168.1 (C=O chelated), 165.6 (C=O free), 158.8 (=CH), 91.4 (=C), 60.0, 59.9 ($2CH_2$), 14.8 and 14.7 ($2CH_3$).

Anal. Calcd for $C_{20}H_{33}NO_{14}$: C, 46.96; H, 6.50; N, 2.74. Found: C, 46.65; H, 6.51; N, 2,86.

A FABMS spectrum showed a pseudomolecular $[M+Na]^+$ ion at *m/z* 534.

***N*-(2,2-Diethoxycarbonylvinyl)-6-*O*-(α-D-galactopyranosyl)-ß-D-glucopyranosylamine** (**4c**, 2.24 g, 75%), isolated as a white foam after concentration from methanol, had $[\alpha]_D^{22}$ +49.5° (*c* 1, pyridine); UV (H_2O) 273 and 217 nm (ϵ_{mM} 21.2 and 10.3); IR 3404 (OH), 1688 (C=O free), 1649 (C=O chelated), 1619 (C=C and NH), and 1254 cm^{-1} (C-O-C); ^1H NMR (200 MHz, DMSO-d_6) δ 9.15 (dd, 1H, $J_{NH,=CH}$ = 13.6 Hz, $J_{1,NH}$ = 7.8 Hz, NH), 8.06 (d, 1H, =CH), 5.47 (d, 1H, $J_{H,OH}$ = 5.2 Hz, OH), 5.21 (d, 1H, $J_{H,OH}$ = 4.1 Hz, OH), 5.13 (d, 1H, $J_{H,OH}$ = 4.6 Hz, OH), 4.67 (d, 1H, $J_{1',2'}$ = 2.7 Hz, H-1'), 4.50 (t, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.45 (m, 3H, 3OH), 4.37 (d, 1H, $J_{H,OH}$ = 3.7 Hz, OH), 4.13, 4.06 (2q, each 2H, $^3J_{H,H}$ = 7.0 Hz, CH_2CH_3), 3.90-3.10 (m, 12H, H-2 to H-6b and H-2' to H-6'b), 1.22 and 1.21 (2t, each 3H, $2CH_3$); ^{13}C NMR (50.3 MHz, DMSO-d_6) Table 3 and δ 168.1 (C=O chelated), 165.7 (C=O free), 158.7 (=CH), 91.3 (=C), 60.1, 59.9 ($2CH_2$), 14.9 and 14.8 ($2CH_3$).

Anal. Calcd for $C_{20}H_{33}NO_{14}$: C, 46.96; H, 6.50; N, 2.74. Found: C, 46.87; H, 6.44; N, 2,56.

A FABMS spectrum showed a pseudomolecular $[M+Na]^+$ ion at *m/z* 534.

2,3,6-Tri-*O*-acetyl-*N*-(2,2-diethoxycarbonylvinyl)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-ß-D-galactopyranosyl)-ß-D-glucopyranosylamine (1d). Conventional acetylation of **1c** (2 g, 3.9 mmol) yielded **1d** (2.89 g, 92%); mp 88-90 °C (from EtOH); $[\alpha]_D^{22}$ -10.0° (*c* 0.7, CH_2Cl_2); UV (CH_2Cl_2) 274 and 216 nm (ϵ_{mM} 23.8 and 5.2); IR 3250 (NH), 1736 (C=O acetate), 1715 (C=O free), 1638 (CO chelated), 1600 (C=C and NH), 1289 and 1192 cm^{-1} (C-O-C); ^1H NMR (200 MHz, $CDCl_3$) Tables 1 and 2, and δ 9.23 (dd, 1H, $J_{NH,=CH}$ = 13.0 Hz, $J_{1,NH}$ = 8.9 Hz, NH), 7.92 (d, 1H, =CH), 4.27, 4.20 (2q, each 2H, $^3J_{H,H}$ = 7.1 Hz, CH_2CH_3), 2.16, 2.14, 2.07, 2.06, 2.05, 2.03, 1.97 (7s, each 3H, 7Ac), 1.32 and 1.29 (2t, each 3H, $2CH_3$); ^{13}C NMR (50.3 MHz, $CDCl_3$) Table 3 and δ 170.3, 170.2, 170.1, 169.9, 169.6, 169.4, 168.9 ($7COCH_3$), 167.7 (C=O chelated), 165.3 (C=O free), 157.2 (=CH), 94.5 (=C), 60.2, 60.0 ($2CH_2$), 20.7, 20.6, 20.5 (2C), 20.4 (3C) ($7COCH_3$), 14.2 and 14.1 ($2CH_3$). EIMS, *m/z* 805 (5%, M^+), 760 (5, M^+-EtO·), 619 [10, M^+-NHCH=C$(CO_2Et)_2$], 331 (100, $C_{14}H_{18}O_9^+$).

Anal. Calcd for $C_{34}H_{47}NO_{21}$: C, 50.68; H, 5.88; N, 1.74. Found: C, 50.51; H, 5.95; N, 1.49.

2,3,6-Tri-*O*-acetyl-*N*-(2,2-diethoxycarbonylvinyl)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-ß-D-glucopyranosyl)-ß-D-glucopyranosylamine (2d). Conventional acetylation of **2c** (1.8 g, 3.5 mmol) yielded **2d** (2.69 g, 95%); mp 207-209 °C (from EtOH); $[\alpha]_D^{22}$ -11.5° (*c* 0.6, CH_2Cl_2); UV (CH_2Cl_2) 273 and 205 nm (ϵ_{mM} 25.2 and 6.5); IR 3277 (NH), 1748 (C=O acetate), 1699 (C=O free), 1669 (CO chelated), 1616 (C=C and NH), and 1231 cm^{-1} (C-O-C); ^1H NMR (200 MHz, $CDCl_3$) Tables 1 and 2, and δ 9.23 (dd, 1H, $J_{NH,=CH}$ = 13.0 Hz, $J_{1,NH}$ = 9.3 Hz, NH), 7.91 (d, 1H, =CH), 4.27, 4.20 (2q, each 2H, $^3J_{H,H}$ = 7.1 Hz, CH_2CH_3), 2.14, 2.09, 2.04, 2.04, 2.02, 2.01, 1.98 (6s, 21H, 7Ac), 1.32 and 1.29 (2t, each 3H, $2CH_3$); ^{13}C NMR (50.3 MHz, $CDCl_3$) Table 3 and δ 170.4, 170.1 (2C), 169.6, 169.5, 169.2, 168.9 ($7COCH_3$), 167.7 (C=O chelated), 165.3 (C=O free), 157.2 (=CH), 94.5 (=C), 60.3, 60.1 ($2CH_2$), 20.8, 20.6, 20.4 (5C) ($7COCH_3$), 14.2 and 14.1 ($2CH_3$). EIMS, *m/z* 805 (2%, M^+), 760 (1, M^+-EtO·), 619 [2, M^+-NHCH=C$(CO_2Et)_2$], 331 (100, $C_{14}H_{18}O_9^+$).

Anal. Calcd for $C_{34}H_{47}NO_{21}$: C, 50.68; H, 5.88; N, 1.74. Found: C, 50.68; H, 5.79; N, 1.76.

2,3,6-Tri-*O*-acetyl-*N*-(2,2-diethoxycarbonylvinyl)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-ß-D-glucopyranosylamine (3d). Conventional acetylation of **3c** (1.3

g, 2.5 mmol) yielded **3d** (1.94 g, 95%); mp 72-74 °C (from EtOH); $[\alpha]_D^{22}$ +42.7° (*c* 0.7, CH_2Cl_2); UV (CH_2Cl_2) 273 and 210 nm (ϵ_{mM} 25.2 and 3.5); IR 3275 (NH), 1753 (C=O acetate), 1699 (C=O free), 1663 (CO chelated), 1613 (C=C and NH), and 1240 cm^{-1} (C-O-C); ^1H NMR (200 MHz, $CDCl_3$) Tables 1 and 2, and δ 9.23 (dd, 1H, $J_{NH,=CH}$ = 13.2 Hz, $J_{1,NH}$ = 8.9 Hz, NH), 7.94 (d, 1H, =CH), 4.24, 4.20 (2q, each 2H, $^3J_{H,H}$ = 7.0 Hz, CH_2CH_3), 2.15, 2.10, 2.05, 2.03, 2.02, 2.00, 2.00 (6s, 21H, 7Ac), 1.32 and 1.29 (2t, each 3H, $2CH_3$); ^{13}C NMR (50.3 MHz, $CDCl_3$) Table 3 and δ 170.0 (2C), 169.9, 169.5, 169.4, 169.2, 168.9 ($7COCH_3$), 167.4 (C=O chelated), 165.0 (C=O free), 156.2 (=CH), 93.9 (=C), 59.8, 59.6 ($2CH_2$), 20.4, 20.3, 20.2 (2C), 20.1 (2C), 19.9 ($7COCH_3$), 13.9 and 13.7 ($2CH_3$). EIMS, *m/z* 805 (4%, M^+), 760 (2, M^+-EtO·), 619 [12 M^+-NHCH=C(CO_2Et)$_2$], 331 (100, $C_{14}H_{18}O_9^+$).

Anal. Calcd for $C_{34}H_{47}NO_{21}$: C, 50.68; H, 5.88; N, 1.74. Found: C, 50.62; H, 5.80; N, 1.96.

2,3,4-Tri-*O*-acetyl-*N*-(2,2-diethoxycarbonylvinyl)-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-ß-D-glucopyranosylamine (4d). Conventional acetylation of **4c** (2 g, 3.9 mmol) yielded **4d** (3.02 g, 96%); mp 123-125 °C (from EtOH); $[\alpha]_D^{22}$ +77.7° (*c* 0.8, CH_2Cl_2); UV (CH_2Cl_2) 274 and 222 nm (ϵ_{mM} 17.5 and 3.2); IR 3277 (NH), 1755 (C=O acetate), 1701 (C=O free), 1667 (CO chelated), 1607 (C=C and NH), and 1239 cm^{-1} (C-O-C); ^1H NMR (200 MHz, $CDCl_3$) Tables 1 and 2, and δ 9.08 (dd, 1H, $J_{NH,=CH}$ = 13.2 Hz, $J_{1,NH}$ = 8.9 Hz, NH), 7.83 (d, 1H, =CH), 4.10, 4.06 (2q, each 2H, $^3J_{H,H}$ = 7.0 Hz, CH_2CH_3), 2.05, 1.98, 1.94, 1.94, 1.94, 1.92, 1.87 (5s, 21H, 7Ac), 1.21 and 1.17 (2t, each 3H, $2CH_3$); ^{13}C NMR (50.3 MHz, $CDCl_3$) Table 3 and δ 170.1, 169.9, 169.8, 169.6, 169.4, 169.2, 168.9 ($7COCH_3$), 167.2 (C=O chelated), 165.1 (C=O free), 156.8 (=CH), 94.3 (=C), 59.9, 59.7 ($2CH_2$), 20.4 (2C) 20.3 (2C), 20.2 (2C), 20.1 ($7COCH_3$), 14.0 and 13.8 ($2CH_3$). EIMS, *m/z* 805 (1%, M^+), 760 (2, M^+-EtO·), 619 [4, M^+-NHCH=C(CO_2Et)$_2$], 331 (100, $C_{14}H_{18}O_9^+$).

Anal. Calcd for $C_{34}H_{47}NO_{21}$: C, 50.68; H, 5.88; N, 1.74. Found: C, 50.84; H, 5.57; N, 1.88.

Preparation of Hepta-*O*-acetyl Disaccharide Glycosylamine Hydrochlorides (1e-4e). Cl_2 was bubbled through solutions of per-*O*-acetylglycosylenamines (**1d-4d**, 1 g, 1.24 mmol) in CH_2Cl_2 (15 mL) at 0 °C until saturation. The reaction mixtures were

kept overnight at 5 °C and then concentrated. Ether (4 x 25 mL) was added and evaporated under reduced pressure. IR spectra of the resulting amorphous solids showed strong absorptions at 3100-2700 (NH_3^+) and 1750 cm^{-1} (C=O). The crude products were used directly in the next step.

Preparation of Hepta-*O*-acetyl Disaccharide Glycosyl Isothiocyanates (1f-4f). To a heterogeneous mixture of crude **1e-4e** (0.83 g, 1.24 mmol) in $CHCl_3$ (10 mL), $CaCO_3$ (0.37 g, 3.72 mmol), and water (4 mL) was added thiophosgene (0.2 mL, 1.86 mmol). The mixture was vigorously stirred for 4 h in a round bottom flask provided with a system for evacuation of gases, and then filtered. The organic layer was separated, washed with water, dried ($CaCl_2$), and concentrated to dryness.

2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-ß-D-galactopyranosyl)-ß-D-glucopyranosyl Isothiocyanate (1f). Treatment of **1e** as described above and column chromatography (AcOEt-toluene 1:1) of the resulting syrupy residue yielded **1f** (0.73 g, 87%); mp 167-169 °C (from ether); $[\alpha]_D^{22}$ -18.5° (*c* 0.5, $CHCl_3$). Lit.[20] mp 157-159 °C (benzene). Compound **1f** had the IR, ^1H and ^{13}C NMR data reported in the literature.[20]

2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-ß-D-glucopyranosyl)-ß-D-glucopyranosyl Isothiocyanate (2f). Treatment of **2e** as described above and crystallisation from ether yielded **2f** (0.76 g, 90%); mp 186-188 °C; $[\alpha]_D^{22}$ -9.0° (*c* 0.8, CH_2Cl_2). Lit.[20] mp 191-195 °C (benzene). Compound **2f** had the IR, ^1H and ^{13}C NMR data reported in the literature.[20]

2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-ß-D-glucopyranosyl Isothiocyanate (3f). Treatment of **3e** as described above and column chromatography (AcOEt-toluene 1:1) of the residue yielded **3f** (0.71 g, 85%) as a syrup having $[\alpha]_D^{22}$ +57.7° (*c* 0.8, CH_2Cl_2). Lit.[20] mp 120-123 °C (benzene). Compound **3f** had the IR, ^1H and ^{13}C NMR data reported in the literature.[20]

2,3,4-Tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-ß-D-glucopyranosyl Isothiocyanate (4f). Treatment of **4e** as described above gave a syrup which showed two spots in TLC (AcOEt-hexane 3:2). Column chromatography with the above eluent yielded syrupy **4f** (R_F 0.6, 0.41 g, 50%); $[\alpha]_D^{22}$ +92.8° (*c* 0.9, CH_2Cl_2); IR 2033 (NCS), 1755 (C=O), and 1230 cm^{-1} (C-O-C); ^1H NMR (200 MHz, $CDCl_3$)

Tables 1 and 2, and δ 2.14, 2.13, 2.11, 2.06, 2.06, 2.05 and 2.04 (6s, 21H, 7Ac); ^{13}C NMR (50.3 MHz, $CDCl_3$) Table 3 and δ 170.2, 170.1, 169.9, 169.8, 169.6, 168.9, 168.8 (7C=O), 144.2 (NCS), 20.6, 20.5, 20.4, 20.3 and 20.2 (3C) ($7CH_3$); EIMS, *m/z* 619 (1%, M^+-NCS·), 559 (2, 619-AcOH), 517 (2, 619-Ac_2O), 499 (1, 559-AcOH), 475 (2, 517-CH_2CO), 457 (1, 517-AcOH), 397 (2, 457-AcOH), 331 (100, $C_{14}H_{18}O_9^+$).

Anal. Calcd for $C_{27}H_{35}NO_{17}S$: C, 47.86; H, 5.21; N, 2.07; S, 4.73. Found: C, 47.97; H, 4.95; N, 2.01; S, 4.71.

A FABMS spectrum showed a pseudomolecular $[M+Na]^+$ ion at *m/z* 700.

Further elution gave 2,3,4-Tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-D-glucopyranose (**4h**, R_F 0.52, 0.24 g, 31%); ^1H NMR (300 MHz, $CDCl_3$) δ 6.28 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1α), 5.67 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1ß); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 91.4 (C-1ß), 88.7 (C-1α).

A FABMS spectrum showed a pseudomolecular $[M+Na]^+$ ion at *m/z* 659.

Preparation of Hepta-*O*-acetyl Disaccharide Glycosylthioureas (1g-4g). Dry (KOH) ammonia was bubbled into solutions of glycosyl isothiocyanates (**1f-4f**, 0.3 g, 0.44 mmol) in ether (10 mL) at 0 °C for 10 min. A TLC (AcOEt-hexane 2:1) of the reaction mixture showed a single spot (R_F 0.5). Evaporation of the solvent yielded pure **1g-4g**.

***N*-[2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-ß-D-galactopyranosyl)-ß-D-glucopyranosyl]thiourea** (**1g**, 0.29 g, 95%), isolated as an amorphous solid, had $[\alpha]_D^{22}$ +2.0° (*c* 0.7, $CHCl_3$); UV (CH_2Cl_2) 251 nm (ϵ_{mM} 16.7); IR 3339 (NH), 1750 (C=O), and 1235 cm^{-1} (C=S and C-O-C); ^1H NMR (300 MHz, $CDCl_3$) Tables 1 and 2, and δ 7.21 (d, 1H, $J_{1,NH}$ = 9.2 Hz, NH), 6.57 (s, 2H, NH_2), 2.16, 2.12, 2.08, 2.07, 2.07, 2.07, and 2.06 (5s, 21H, 7Ac); ^{13}C NMR (75.5 MHz, $CDCl_3$) Table 3 and δ 185.0 (C=S), 171.4, 170.5, 170.2, 170.0, 169.9, 169.2, 168.8 (7C=O), 20.8, 20.7, 20.6 (2C), 20.5 (2C), and 20.4 ($7CH_3$).

Anal. Calcd for $C_{27}H_{38}N_2O_{17}S$: C, 46.68; H, 5.51; N, 4.03; S, 4.62. Found: C, 46.51; H, 5.36; N, 3.81; S, 4.31.

A FABMS spectrum showed a pseudomolecular $[M+Na]^+$ ion at *m/z* 717.

***N*-[2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-ß-D-glucopyranosyl)-ß-D-glucopyranosyl]thiourea** (**2g**, 0.30 g, 97%), had mp 217-219 °C (dec); $[\alpha]_D^{22}$ -14.0° (*c* 0.8, CH_2Cl_2); UV (CH_2Cl_2) 255 nm (ϵ_{mM} 16.0); IR 3339 (NH), 1751 (C=O), and

1225 cm^{-1} (C=S and C-O-C); ^1H NMR (200 MHz, $CDCl_3$) Tables 1 and 2, and δ 7.09 (d, 1H, $J_{1,NH}$ = 9.0 Hz, NH), 6.55 (s, 2H, NH_2), 2.10, 2.08, 2.08, 2.07, 2.03, 2.01, and 1.99 (6s, 21H, 7Ac); ^{13}C NMR (50.3 MHz, $CDCl_3$) Table 3 and δ 185.2 (C=S), 171.1, 170.8, 170.4, 170.2, 169.4, 169.1, 169.0 (7C=O), 20.9, 20.8, 20.7, 20.6, 20.5 and 20.4 (2C) ($7CH_3$).

Anal. Calcd for $C_{27}H_{38}N_2O_{17}S$: C, 46.68; H, 5.51; N, 4.03; S, 4.62. Found: C, 46.72; H, 5.88; N, 4.07; S, 4.58.

A FABMS spectrum showed a pseudomolecular $[M+Na]^+$ ion at *m/z* 717.

***N*-[2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-ß-D-glucopyranosyl]thiourea** (**3g**, 0.30 g, 97%), had mp 168-170 °C; $[\alpha]_D^{22}$ +76.1° (*c* 0.8, $CHCl_3$); UV (CH_2Cl_2) 256 nm (ϵ_{mM} 12.8); IR 3337 (NH), 1750 (C=O), and 1235 cm^{-1} (C=S and C-O-C); ^1H NMR (300 MHz, $CDCl_3$) Tables 1 and 2, and δ 7.10 (d, 1H, $J_{1,NH}$ = 8.8 Hz, NH), 6.70 (s, 2H, NH_2), 2.14, 2.09, 2.07, 2.05, 2.04, 2.04, and 2.01 (6s, 21H, 7Ac); ^{13}C NMR (75.5 MHz, $CDCl_3$) Table 3 and δ 185.2 (C=S), 171.1, 171.0, 170.5, 170.4, 169.7 (2C), 169.3 (7C=O), 20.9, 20.6, 20.5, 20.4, 20.3 (3C) ($7CH_3$).

Anal. Calcd for $C_{27}H_{38}N_2O_{17}S$: C, 46.68; H, 5.51; N, 4.03; S, 4.62. Found: C, 46.87; H, 5.44; N, 4.01; S, 4.71.

A FABMS spectrum showed a pseudomolecular $[M+Na]^+$ ion at *m/z* 717.

***N*-[2,3,4-Tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-ß-D-glucopyranosyl]thiourea** (**4g**, 0.31 g, 98%), isolated as an amorphous solid, had $[\alpha]_D^{22}$ +78.0° (*c* 0.8, $CHCl_3$); UV (CH_2Cl_2) 256 nm (ϵ_{mM} 10.5); IR 3362 (NH), 1750 (C=O), and 1225 cm^{-1} (C=S and C-O-C); ^1H NMR (300 MHz, $CDCl_3$) Tables 1 and 2, and δ 7.17 (d, 1H, $J_{1,NH}$ = 8.9 Hz, NH), 6.50 (s, 2H, NH_2), 2.15, 2.14, 2.09, 2.08, 2.06, 2.02 and 2.01 (7s, each 3H, 7OAc); ^{13}C NMR (75.5 MHz, $CDCl_3$) Table 2 and δ 185.0 (C=S), 170.7, 170.6, 170.5, 170.2, 170.0, 169.7, 169.5 (7C=O), 20.8, 20.7, 20.6, 20.5 (3C), and 20.4 ($7CH_3$).

Anal. Calcd for $C_{27}H_{38}N_2O_{17}S$: C, 46.68; H, 5.51; N, 4.03; S, 4.62. Found: C, 46.70; H, 5.65; N, 4.00; S, 4.56.

A FABMS spectrum showed a pseudomolecular $[M+Na]^+$ ion at *m/z* 717.

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