Pergamon

Tetrahedron Vol. 51, No. 3, pp. 923-934, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)00981-3

Synthesis of Diisothiocyanato Derivatives of Disaccharides

M. Angeles Pradera, José L. Molina, and José Fuentes*

Departamento de Química Orgánica, Facultad de Química. Universidad de Sevilla. 41071 Sevilla. Spain.

Abstract: The glycosylation of 6-*O*-trityl ethers of *N*-protected aminomonosaccharides (**2**, **3**, and **13**) with 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-**D**-galactopyranosyl bromide (**1**) gives disaccharide derivatives (**4-6**, **14** and **15**) with an *N*-protected amino group in a sugar ring and a latent amino group in the other one. These disaccharide derivatives are transformed into disaccharide diisothiocyanates with the NCS groups in the 2,2' (**10-12**) or in the 1, 2' (**20**, **21**) positions. ^{1}H and ^{13}C NMR data of prepared compounds are reported.

INTRODUCTION

The carbohydrates are a type of chiral natural products, which have many interesting advantages for organic synthesis. They are inexpensive, widespread natural compounds with numerous stereogenic centers, but the number of different functional groups in naturally occurring sugars is limited, however many synthetic carbohydrate derivatives are easy to prepare. At the same time isothiocyanates are important reagents in heterocyclic chemistry[1] and undergo several reactions such as nucleophilic additions and cycloadditions. The glycosyl isothiocyanates have been a target of study in recent years, because they are versatile intermediates in the syntheses of bicyclic glycopyranothiazolines[2], glycopyranosylthioureas[3-6], *N*-nucleosides[4-8], *N*-glycopeptides[9-11] and other types of glycoconjugates[8,12], and also because they have been used as enzymatic inhibitors[13,14].

There are bibliographic data on monosaccharides with the NCS functional group in a non glycosydic position. This compounds were used in stereocontrolled syntheses of pseudo-*C*-nucleosides and bicyclic 1,3-*O*,*N*-heterocycles[15,16]. Oligosaccharide monoisothiocyanato derivatives have been described bearing the isothiocyanato group only in the anomeric position[17] and in the position two of gentiobiosides which were used to prepare thioureyleneoligosaccharides[18].

In this paper we report on the preparation of disaccharide derivatives bearing two isothiocyanate groups. These compounds have the same synthetic uses as monoisothiocyanate sugars and additionally can be used as building blocks in the syntheses of linear polymers and macrocycles. To obtain disaccharide diisothiocyanates two different synthetic pathways can be followed: a) The introduction of two isothiocyanato groups in a disaccharide; this method gives high yields only for the introduction of two isothiocyanato groups in homologous positions of symmetric disaccharides[19]. b) The construction of the disaccharide molecule through glycosylation reactions using as glycosyl acceptors and donors compounds having protected or latent amino

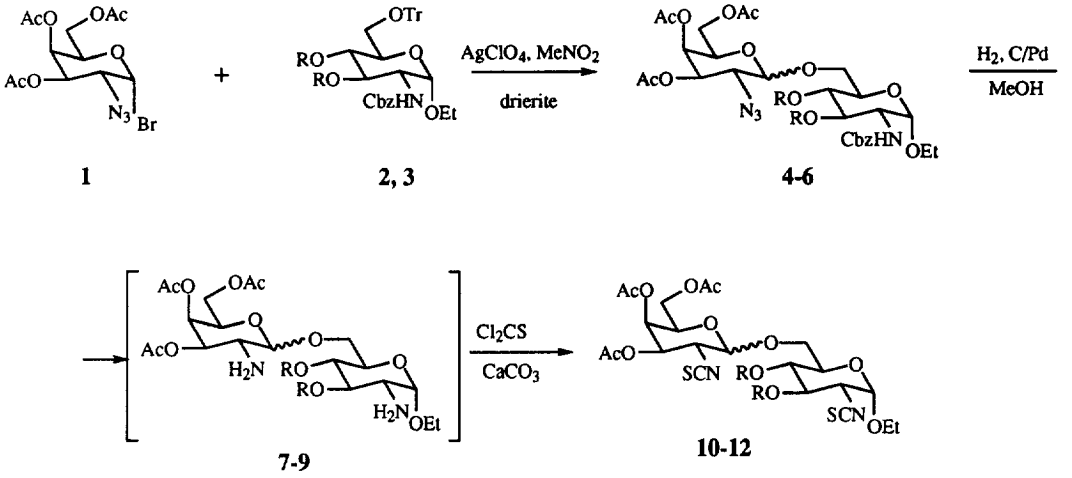
groups, which will afterwards be transformed into isothiocyanato groups by reaction with thiophosgene. This second and more versatile method is described in this paper.

RESULTS AND DISCUSSION

With the aim of obtaining disaccharide diisothiocyanates with α' and β' configurations[20] we have used as glycosyl donor the 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl bromide, which can originate mixtures of α and β galactosides either by a mechanism through an oxocarbenium ion or by direct anomerization[21]. The yields and stereochemistry of the glycosylation products obtained using this type of glycosyl halide have been shown to be strongly dependent on the acceptor (generally a partially protected sugar derivative) and the promoter, which often hinder any prediction on the stereoselectivity of the glycosylation reactions. In the described glycosylations[22,23] of D-*gluco* acceptors having the HO-6 free with 2-azido-2-deoxy-glycopyranosyl halides the 1',2'-*cis*-disaccharide derivative was the major product.

In this paper we have used as glycosyl acceptors 6-*O*-trityl ethers instead of partially protected sugar derivatives. 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl bromide **1**, prepared from D-galactal[24], was employed as glycosyl donor, and silver perchlorate as promoter. Thus the glycosylation of ethyl 3,4-di-*O*-acetyl(benzoyl)-2-benzyloxycarbonylamino-2-deoxy-6-*O*-trityl-α-D-glucopyranosides[25] (**2**, **3**, scheme 1) and 2,3,4-tri-*O*-acetyl-*N*-(2,2-diethoxycarbonylvinyl)-6-*O*-trityl-β-D-glucopyranosyl amine[26] (**13**, scheme 2) gave mixtures of the respective α' and β' disaccharide derivatives.

Scheme 1

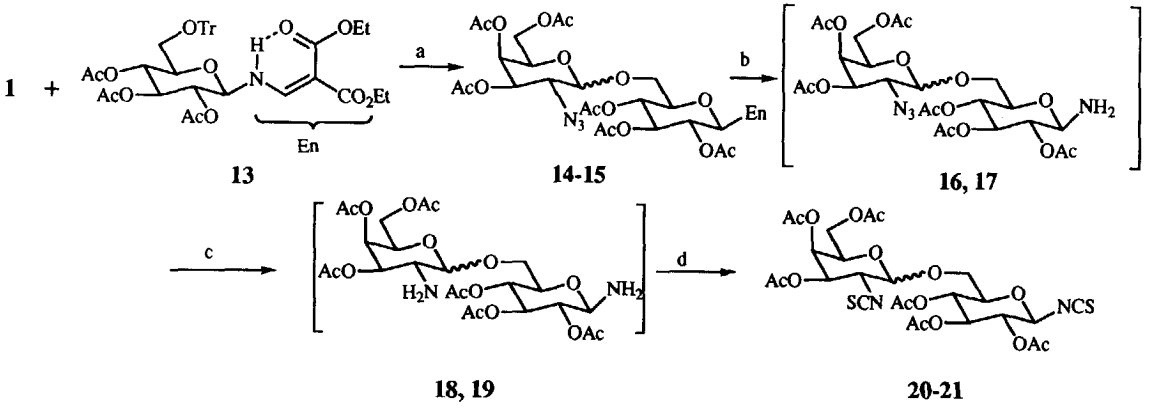


1 **2, 3** **4-6**

7-9 **10-12**

2, 4, 7, 10: R=Ac
3, 5, 6, 8, 9, 11, 12: R=Bz
4, 5, 7, 8, 10, 11: α-galactosides
6, 9, 12: β-galactosides

Scheme 2



14, 16, 18, 20: α-D-galactosides
15, 17, 19, 21: β-D-galactosides

(a) $AgClO_4$, $MeNO_2$ and drierite; (b) Cl_2/Cl_3CH; (c) H_2/Cat. Adams; (d) Cl_2CS, $CaCO_3$

These mixtures (except in the case of **2**) were directly subjected to further transformations for the synthesis of the isothiocyanates **10-12**, **20** and **21**. However a small part of each mixture was chromatographed and the products and yields shown in table 1 were obtained.

In the case of compound **2** (entry 1) the 1,2-*cis* galactoside (**4**) was the major product and the only one that could be isolated; column chromatography of the crude reaction product also gave a mixture of several compounds, with similar R_F values, whose NMR data showed the presence of β-galactosides and compounds coming from detritylation and acetyl migrations in **2**.

Table 1. Glycosylations of **2**, **3**, and **13**.

		Isolated product and yield	
Entry	Starting material	α anomer*	β anomer*
1	**2**	**4** (73)	-
2	**3**	**5** (24)	**6** (24)
3	**13**	**14** (68)	**15** (16)

*For D-galacto ring

The glycosylations on the acetyl derivatives **2** and **13** (entries 1 and 3) had a medium-high degree of 1,2-*cis*-stereoselectivity as has been mentioned for related glycosylations on D-*gluco* derivatives with the primary hydroxyl group free[22], whereas in the case of the benzoyl derivative **3** (entry 2) the ratio α':β' disaccharides was ≈1:1.

The structures of compounds **4-6**, **14** and **15** were based on analytical and spectroscopic data (Table 2). Every compound had the IR absorption at ≈ 2.115 cm^{-1} for the azido group and δ C-2' was in the range 57.2-60.8 ppm corresponding to a secondary C-N_3 group[27]. The resonance for C-6 (66.7-68.9 ppm) was indicative of a glycosylated position[28]. The anomeric configuration of the D-*galacto* ring was evident from $J_{1',2'}$, δ H-1', δ C-1' and δ C-2' values and was α for **4**, **5**, and **14** ($J_{1',2'}$ ≈ 3.5 Hz, δ H-1' ≈ 5.02 ppm, δ C-1' ≈ 98, δ C-2' ≈ 57.2 ppm), and β for **6** and **15** ($J_{1',2'}$ ≈ 8.0, δ H-1' = 4.5 ppm, δ C-1' ≈ 102.6, δ C-2' = 60.6 ppm). The chemical shifts for the resonance of N*H* (≈ 9.25 ppm) and one C=O group (≈ 169.0 ppm) and the high value for $J_{NH,=CH}$ (= 13.0 Hz), indicative of antiperiplanar protons, are in agreement[26] with a chelated structure for **14** and **15**. This hydrogen bond is also confirmed[29] by the low stretching frequencies for NH (≈ 3300 cm^{-1}) and C=O (≈ 1663 cm^{-1}) groups. The $^4C_1$ conformation for each sugar ring of **4-6**, **14**, and **15** was in agreement with the $^3J_{H,H}$ values (see experimental and Table 2). The assignments of ^1H and ^{13}C resonances were confirmed by $^1H,^1H$-COSY and $^1H,^{13}C$-HETCOR 2D correlated experiments.

The 2-*N*-benzyloxycarbonyl group of pure **4** and of the mixture **5-6**, were quantitatively removed by hydrogenolysis in the presence of C/Pd. FABMS of the resulting products were in agreement with structures **7-9**. In a similar way the mixture **14-15** was treated with chlorine in chloroform[25,30] to give the 2'-azido-glucosylamines **16-17**, whose molecular weights were measured by FABMS. Subsequent treatment of **16-17** with hydrogen in the presence of Adams catalyst quantitatively yielded the mixture of the diaminodisaccharides **18-19**, whose molecular weights also accorded with the FAB mass spectra.

Table 2. Selected spectroscopic data (IR, ^{1}H NMR, and ^{13}C NMR) for compounds **4-6**, **10-12**, **14**, **15**, **20**, and **21**.

Comp.	N_3	NCS		δ H-1	δ H-2	$J_{1,2}$	δ H-1'	δ H-2'	$J_{1',2'}$	δ C-1	δ C-2	δ C-6	δ C-1'	δ C-2'
	ν	ν	δ-C											
4	2110	-	-	4.86	3.98-4.03	3.5	5.01	3.65	3.5	97.6	53.6	66.7	96.8	57.2
5	2110	-	-	5.00	4.21-4.34	3.7	5.01	3.56-3.65	3.4	97.0	53.9	66.7	97.6	57.2
6	2116	-	-	5.00	4.29	3.5	4.46	3.69	8.0	97.0	53.8	68.7	102.4	60.8
10	-	2052	137.8 138.9	5.00	3.89	3.5	5.04	4.05-4.10	3.4	96.3	59.0	66.3	97.1	55.4
11	-	2047	138.0 138.9	5.13	4.08	3.5	5.05	4.07	3.4	96.7	59.3	66.3	97.1	55.4
12	-	2047	139.0 139.8	5.14	4.01	3.5	4.54	4.02-4.06	8.1	96.6	59.2	68.3	101.3	57.4
14	2112	-	-	4.58	5.04	9.3	5.03	3.62	3.6	86.8	70.4	66.7	98.5	57.3
15	2114	-	-	4.60	5.03	9.3	4.44	3.72	8.0	87.0	68.6	68.9	102.8	60.5
20	-	2108 2031	139.0 144.6	5.06	5.13	9.4	5.02	4.11	3.4	83.3	71.7	66.9	97.1	55.4
21	-	2108 2031	139.5 145.5	5.07	5.01	9.4	4.61	3.92	8.0	83.5	71.6	68.3	101.6	57.3

The reaction of **7**, and the mixtures of anomers **8, 9** and **18-19** with thiophosgene in a basic medium[3] yielded after chromatography the ethyl 2,2'-dideoxy-2',2'-diisothiocyanato glycosides **10-12** and the 2'-deoxy-2'-isothiocyanato-glycosyl isothiocyanates **20** and **21**. Compound **20** (56% yield) was also prepared from pure **14**.

In the synthesis of alkylene diisothiocyanates by reaction of the corresponding diamines with thiophosgene intermolecular polymeric thioureas and other intramolecular reaction compounds are frequently formed[31]. However such side-reactions have not been observed during the preparation of the diisothiocyanates **10-12, 20** and **21**. This is probably due to the conformational properties of the sugar molecules and also has been observed during the preparation of diisothiocyanatotrehalose and poliisothiocyanatocyclodextrines[19].

Compounds **10-12, 20** and **21** were amorphous and hygroscopic solids that could not be analyzed. The exact atomic composition of the molecular ions was determined by HRFABMS and the ^1H and ^{13}C NMR spectra of every compound showed no presence of any impurity. The presence of the NCS groups was confirmed (Table 2) by the IR band at 2050-2100 cm^{-1} (ν_{NCS}) and the δ values for the NCS carbon atoms (137.8-145.5 ppm). It is noteworthy that the ^{13}C resonances for the NCS groups joined to C-2 of the sugar rings appeared in the interval 137.8-139.5 ppm, whereas the resonance corresponding to the same group in the glycosidic position (**20, 21**) appeared at 144.6-145.5 ppm in agreement with reported data[3,17] for other glycosyl isothiocyanates. The resonances of C-2 in **10-12** showed a deshielding of $\approx$ 5.5 ppm when they were compared with the values of the same resonances in **4-6**, in accord with the introduction of an NCS group[18]. The atom C-2' which is joined to an NCS group, resonated at 55.4 ppm when a *cis*-relationship exists between the subtituents on C-1' and C-2' (α-D-*galacto* compounds **10, 11**, and **20**), whereas the same resonance appeared at 57.3-57.4 ppm in the compounds **12** and **21**, which have the *trans*-relationship between the same subtituents. The anomeric carbon atom (C-1) in the glucosyl isothiocyantes **20** and **21** resonated at 83.3-83.5 ppm as is described for related β-glycosyl isothiocyanates[3,4]. Also deshieldings, due to the introduction of NCS groups, in the chemical shifts values of the following pairs of resonances were observed: H-1 (**20, 21**) *vs.* H-1 (**14, 15**) and H-2' (**4-6, 14, 15**) *vs.* H-2' (**10-12, 20, 21**). The anomeric configuration of the D-*galacto* ring, as in the cases of **4-6, 14**, and **15** accorded with the values of δH-1', δ C-1', δ C-2' and $J_{1',2'}$ (Table 2). The $^3J_{H,H}$ values (see experimental) around the pyranose rings indicated that they adopt in chloroformic solution the expected $^4C_1$ conformation.

EXPERIMENTAL

General. Melting points are uncorrected. Optical rotations were measured at 21-25° for solutions in dichloromethane. FTIR spectra were recorded for KBr discs or thin film. ^1H NMR spectra (300, and 500 MHz) were obtained for solutions in $CDCl_3$. Assignments were confirmed by homonuclear 2D COSY correlated experiments. ^{13}C NMR spectra were recorded at 75.4, and 125.7 MHz. Heteronuclear 2D correlated spectra were obtained in order to assist in carbon resonance assignments. FAB-mass spectra were recorded with a Kratos MS-80RFA instrument with a resolution of 1000 (10% valley definition). The elemental composition of the ions was determined with a resolution of 10000 (10% valley definition). Ions were produced by a beam of xenon atoms (6-7 KeV) using a matrix consisting of glycerol, thioglycerol or 3-nitrobenzyl alcohol and NaI as salt, (CsI)37Cs was used as reference. TLC was performed on Silica Gel

HF_{254}, with detection by UV light or charring with H_2SO_4. Silica Gel 60 (Merck, 70-230 and 230-400 mesh) was used for preparative chromatography.

General procedure for the glycosylation of 2, 3 and 13. To a solution of silver perchlorate (0.49 g, 2.37 mmol) in freshly distilled nitromethane (5×7 mL) was added drierite (0.32 g, 2.37 mmol) and the mixture was kept under nitrogen for 5 min. Then the corresponding 6-*O*-trityl ether (**2**,**3**[25] or **13**[26], 2.37 mmol), and 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-**D**-galactopyranosyl bromide (**1**, 0.93g, 2.37 mmol) were added under nitrogen. The mixture was stirred for 10 min at r.t. under nitrogen, then diluted with dichloromethane (5 mL) and filtered through celite. The insoluble material was washed with nitromethane (5 mL) and the combined filtrate and washing were washed with water at 0 °C (5 mL), saturated aqueous sodium hydrogencarbonate (5 mL) and water (3-5 mL). The organic layer was dried ($MgSO_4$) and the solvent evaporated. This residue, except in the case of **4**, was directly used in the following reactions. The residue proceeding from **2**, and a part of that coming from **3** and **13** were purified as indicated. The following compounds were prepared in this manner.

*Ethyl 3,4-di-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-6-*O*-(3',4',6'-tri-*O*-acetyl-2'-azido-2'-deoxy-α-**D**-galactopyranosyl)-α-**D**-glucopyranoside* (**4**). From **2**. Column chromatography (ether:hexane 1:1, 3:1, 6:1) of the residue gave a white foam (1.28 g, 73%); $[\alpha]_D^{25}$ +114.0° (*c* 1.0); IR ν_{max} 3321, 3059, 2926, 2110 (N_3), 1755, 1726, 1693, 1582, 1514, 1443, 1371, 1236, 1032 cm^{-1}; ^1H NMR (500 MHz) δ 7.38-7.29 (m, 5 H, Ph), 5,46 (d, 1 H, $J_{3',4'}$ = 3.2, $J_{4',5'}$ = 0, H-4'), 5.37 (dd, 1 H, $J_{2',3'}$ = 10.8, H-3'), 5.23 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.9, H-3), 5.14 (d, 1 H, $^2J_{H,H}$ = 12.2, C*H*H of Cbz), 5.04 (d, 1 H, CH*H* of Cbz), 5.02 (m, 1 H, NH), 5.01 (d, 1 H, $J_{1',2'}$ = 3.5, H-1'), 4.98 (t, 1 H, $J_{4,5}$ = 9.9, H-4), 4.86 (d, 1 H, $J_{1,2}$ = 3.5, H-1), 4.30 (t, 1 H, $J_{5',6'a} = J_{5',6'b}$ = 6.4, H-5'), 4.14 (dd, 1 H, $J_{6'a,6'b}$ = 11.3, H-6'a), 4.03 (dd, 1 H, H-6'b), 4.03-3.98 (m, 2 H, H-2 and H-5), 3.80-3.73 (m, 1 H, C*H*HCH$_3$), 3.75 (dd, 1 H, $J_{5,6a}$ = 7.0, $J_{6a,6b}$ = 10.8, H-6a), 3.65 (dd, 1 H, H-2'), 3.55-3.48 (m, 1 H, CH*H*CH$_3$), 3.54 (dd, 1 H, $J_{5,6b}$ = 2.0, H-6b), 2.15 (s, 6 H, 2 Ac), 2.08, 2.06, 2.04, (each s, each 3 H, 3 Ac), 1.25 (t, 3 H, $^3J_{H,H}$ = 7.0, CH_2CH_3); ^{13}C NMR (125.7 MHz) δ 170.8, 170.3, 169.9, 169.8, 169.5, (each 1 C, 5 $COCH_3$), 155.6 (C=O of Cbz), 136.2-128.0 (6 C, Ph), 97.6 (C-1), 96.8 (C-1'), 71.3 (C-3), 68.9 (C-4), 68.3 (C-5), 67.9 (C-3'), 67.6 (C-4'), 66.8 (CH_2 of Cbz), 66.7 (C-6), 66.6 (C-5'), 63.8 (CH_2CH_3), 61.6 (C-6'), 57.2 (C-2'), 53.6 (C-2), 20.5 (3 C, 3 $COCH_3$), 20.4 (2 C, 2 $COCH_3$), 14.7 (CH_2CH_3); FABMS *m/z* 761 (100, $[M+Na]^+$). HRFABMS *m/z* obsd 823.1676 calcd for $C_{32}H_{42}O_{16}N_4$+Rb 823.1712, obsd 871.1658 calcd for $C_{32}H_{42}O_{16}N_4$+Cs 871.1649.

*Ethyl 3,4-di-*O*-benzoyl-2-benzyloxycarbonylamino-2-deoxy-6-*O*-(3',4',6'-tri-*O*-acetyl-2'-azido-2'-deoxy-α* (**5**) and β(**6**)-***D*-galactopyranosyl)-α-*D*-glucopyranosides*. Column chromatography (EtOAc:hexane 1:3, 1:2, 1:1) of the residue from **3** gave a white syrup (0.98 g, 48%); preparative layer chromatography (ether:hexane 1:1, -40 °C) of a part (30 mg) of the mixture gave **5** (15 mg) and **6** (15 mg). Compound **5** (24% from **3**) had $[\alpha]_D^{24}$ +87.9° (*c* 1.0); IR ν_{max} 3356, 3063, 2975, 2926, 2869, 2110 (N_3), 1740, 1518, 1595, 1451, 1371, 1269, 1028, 710 cm^{-1}; ^1H NMR (500 MHz) δ 8.00-7.10 (m, 15 H, 3 Ph), 5.71 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10.1, H-3), 5.48 (dd, 1 H, $J_{3',4'}$ =3.2, $J_{4',5'}$ = 1.1, H-4'), 5.45 (t, 1 H, $J_{4,5}$ = 10.1, H-4), 5.42 (dd, 1 H, $J_{2',3'}$ = 11.1, H-3'), 5.17 (d, 1 H, $J_{2,NH}$ = 10.0, NH), 5.01 (d, 1 H, $J_{1',2'}$ = 3.4, H-1'), 5.00 (d, 1 H, $J_{1,2}$ = 3.7, H-1), 4.97 (d, 1 H, $^2J_{H,H}$ = 12.5, C*H*H of Cbz), 4.94 (d, 1 H, CH*H* of Cbz), 4.34-4.21 (m, 4 H, H-2, 5, 5', C*H*HCH$_3$), 4.09 (dd, 1 H, $J_{5',6'a}$ = 5.7, $J_{6'a,6'b}$ = 11.3, H-6'a), 3.98 (dd, 1 H,

$J_{5',6'b}$ = 7.2, H-6'b), 3.90-3.84 (m, 2 H, H-6a and H-6b), 3.65-3.56 (m, 2 H, H-2' and CH*H*CH$_3$), 2.15, 2.08, 1.99 (each s, each 3 H, 3 Ac), 1.31 (t, 3 H, $^3J_{H,H}$ = 7.0, CH$_2$C*H*$_3$); ^{13}C NMR (125.7 MHz) δ 170.2, 169.9, 169.5 (3 *C*OCH$_3$), 166.4, 165.2 (2 *C*OPh), 155.6 (C=O of Cbz), 136.0-127.6 (18 C, 3 Ph), 97.6 (C-1'), 97.0 (C-1), 71.6 (C-3), 69.4 (C-4), 68.6 (C-5), 67.9 (C-3'), 67.6 (C-4'), 66.7 (C-6), 66.6 (2 C, C-5' and CH$_2$ of Cbz), 63.9 (*C*H$_2$CH$_3$), 61.7 (C-6'), 57.2 (C-2'), 53.9 (C-2), 20.5 (2 C, 2CO*C*H$_3$), 20.4 (2 C, 2 CO*C*H$_3$), 14.8 (CH$_2$*C*H$_3$); FABMS *m/z* 885 (100, [M+Na]$^+$). HRFABMS *m/z* obsd 995.1967 calcd for C$_{42}$H$_{46}$O$_{16}$N$_4$+Cs 995.1962. Anal. Calcd for C$_{42}$H$_{46}$O$_{16}$N$_4$: C, 58.46; H, 5.37; N, 6.49. Found: C, 58.86; H, 5.65; N, 6.58.

Compound **6** (24% from **3**) had $[\alpha]_D^{24}$ +7.1° (*c* 1.0); IR ν_{max} 3356, 3065, 2969, 2928, 2872, 2116 (N$_3$), 1742, 1595, 1520, 1451, 1371, 1273, 1032, 710 cm^{-1}; ^{1}H NMR (500 MHz) δ 7.96-7.10 (m, 15 H, 3 Ph), 5.72 (dd, 1 H, $J_{2,3}$= 10.4, $J_{3,4}$ = 9.8, H-3), 5.44 (t, 1 H, $J_{4,5}$ = 9.8, H-4), 5.32 (d, 1 H, $J_{3',4'}$ = 3.3, $J_{4',5'}$ = 0, H-4'), 5.17 (d, 1 H, $J_{2,NH}$ = 10.3, NH), 5.00 (d, 1 H, $J_{1,2}$ = 3.5, H-1), 4.96 (d, 1 H, $^2J_{H,H}$ = 12.4, CH$_2$ of Cbz), 4.93 (d, 1 H, CH$_2$ of Cbz), 4.78 (dd, 1 H, $J_{2',3'}$ = 10.9, H-3'), 4.46 (d, 1 H, $J_{1',2'}$ = 8.0, H-1'), 4.31-4.25 (m, 1 H, H-5), 4.29 (td, 1 H, H-2), 4.12-4.07 (m, 2 H, H-6'a,6'b), 4.07-4.05 (m, 1 H, H-6a), 3.91 (dq, 1 H, $^2J_{H,H}$ = 9.7, $^3J_{H,H}$ = 7.0, C*H*HCH3), 3.83 (t, 1 H, $J_{5',6'a}$ = $J_{5',6'b}$ = 6.7, H-5'), 3.77 (dd, 1 H, $J_{5,6a}$ = 7.0, $J_{6a,6b}$ = 11.25, H-6b), 3.69 (dd, 1 H, H-2'), 3.57 (dq, 1 H, CH*H*CH$_3$), 2.13, 2.06, 1.98 (each s, each 3 H, 3 Ac), 1.29 (t, 3 H, CH$_2$C*H*$_3$); ^{13}C NMR (125.7 MHz) δ 170.1, 169.8, 169.6 (3 *C*OCH$_3$), 166.4, 165.3 (2 *C*OPh), 155.6 (C=O of Cbz), 136.0-127.6 (18 C, 3 Ph), 102.4 (C-1'), 97.0 (C-1), 71.6 (C-3), 70.7 (C-3'), 70.5 (C-5'), 69.4 (C-4), 69.2 (C-5), 68.7 (C-6), 66.7 (CH$_2$ of Cbz), 66.1 (C-4'), 63.8 (*C*H$_2$CH$_3$), 61.0 (C-6'), 60.8 (C-2'), 53.8 (C-2), 20.4 (3 C, 3 CO*C*H$_3$), 14.8 (CH$_2$*C*H$_3$); FABMS *m/z* 885 (100, [M+Na]$^+$). HRFABMS *m/z* obsd 995.1897 calcd for C$_{42}$H$_{46}$O$_{16}$N$_4$+Cs 995.1962. Anal. Found: C, 58.80; H, 5.59; N, 6.60.

2,3,4-Tri-O-*acetyl-N-(2,2-diethoxycarbonylvinyl)-6*-O-*(3',4',6'-tri*-O-*acetyl-2'-azido-2'-deoxy-α* (**14**) and β (**15**)-***D*-*galactopyranosyl)-β-D-glucopyranosylamines***. Column chromatography (EtOAc:hexane 1:3, 1:1, 3:1) of the residue from **13** gave **14** (R_F minor) and **15** (R_F major) as white amorphous solids. Compound **14** crystallised from ether-hexane, (0.90 g, 50%) had mp 116-118 °C; $[\alpha]_D^{25}$ +70.1° (*c* 0.97); IR ν_{max} 3305, 2963, 2928, 2112 (N$_3$), 1753, 1692, 1663, 1609, 1443, 1375, 1260, 1032 cm^{-1}; ^{1}H NMR (500 MHz) δ 9.22 (dd, 1 H, $J_{NH,HC}$= 13.0, $J_{NH,H-1}$ = 9.3, NH), 7.96 (d, 1 H, HC=), 5.45 (dd, 1 H, $J_{3',4'}$ = 3.3, $J_{4',5'}$ = 1.0, H-4'), 5.40 (dd, 1 H, $J_{2',3'}$ = 11.1, H-3'), 5.32 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.3, H-3), 5.14 (t, 1 H, $J_{4,5}$ = 9.3, H-4), 5.04 (t, 1 H, $J_{1,2}$ = 9.3, H-2), 5.03 (d, 1 H, $J_{1',2'}$ = 3.6, H-1'), 4.58 (t, 1 H, H-1), 4.30-4.10 (m, 4 H, 2 C*H*$_2$CH$_3$), 4.22 (dd, 1 H, $J_{5',6'a}$ = 2.4, $J_{6'a,6'b}$ = 6.8, H-6'a), 4.20 (m, 1 H, H-5'), 4.06 (dd, 1 H, $J_{5',6'b}$ = 1.6, H-6'b), 3.80 (m, 1 H, H-5), 3.78 (dd, 1 H, $J_{5,6a}$ = 4.8, $J_{6a,6b}$ = 11.1, H-6a), 3.68 (dd, 1 H, $J_{5,6b}$ = 2.1, H-6b), 3.62 (dd, 1 H, H-2'), 2.16, 2.07, 2.06, 2.03 (each s, each 3 H, 4 Ac), 2.04 (s, 6 H, 2 Ac), 1.33, 1.31 (each t, each 3 H, $^3J_{H,H}$ = 7.0, CH$_2$C*H*$_3$); ^{13}C NMR (125.7 MHz) δ 170.2, 170.0, 169.8, 169.5, 169.3, 169.2 (6 *C*OCH$_3$), 167.5 (C=O chelated), 165.3 (C=O free), 157.0 (=CH), 98.5 (C-1'), 94.9 (=C), 86.8 (C-1), 74.6 (C-5), 72.3 (C-3), 70.4 (C-2), 68.3 (C-4), 67.8 (C-3'), 67.4 (C-4'), 66.8 (C-5'), 66.7 (C-6), 61.4 (C-6'), 60.2, 60.0 (2 *C*H$_2$CH$_3$), 57.3 (C-2'), 20.5 (4 C, 4 CO*C*H$_3$), 20.3 (2 C, 2 CO*C*H$_3$), 14.2, 14.1 (2 CH$_2$*C*H$_3$); FABMS *m/z* 811 (100, [M+Na]$^+$). Anal. Calcd for C$_{32}$H$_{44}$O$_{19}$N$_4$: C, 48.73; H, 5.62; N, 7.10. Found: C, 48.76; H, 5.72; N, 7.02.

Compound (**15**) had $[\alpha]_D^{23}$ +8.6° (*c* 0.7); IR ν_{max} 3300, 2978, 2942, 2114 (N_3), 1735, 1692, 1663, 1445, 1370, 1229, 1040 cm^{-1}; ^1H NMR (500 MHz) δ 9.26 (dd, 1 H, $J_{NH,HC=}$ = 13.1, $J_{NH,H-1}$ = 9.3, NH), 7.97 (d, 1 H, HC=), 5.36 (dd, 1 H, $J_{3',4'}$ = 3.3, $J_{4',5'}$ = 0.8, H-4'), 5.34 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.3, H-3), 5.08 (t, 1 H, $J_{4,5}$ = 9.3, H-4), 5.03 (t, 1 H, $J_{1,2}$ = 9.3, H-2), 4.76 (dd, 1 H, $J_{2',3'}$ = 11.0, H-3'), 4.60 (t, 1 H, H-1), 4.44 (d, 1 H, $J_{1',2'}$ = 8.0, H-1'), 4.34-4.23 (m, 4 H, 2 CH_2CH_3), 4.20 (dd, 1 H, $J_{5,6a}$ = 6.5, $J_{6a,6b}$ = 11.3, H-6a), 4.13 (dd, 1 H, $J_{5,6b}$ = 6.7, H-6b), 4.03 (dd, 1 H, $J_{5',6'a}$ = 1.9, $J_{6'a,6'b}$ = 11.5, H-6'a), 3.90-3.84 (m, 2 H, H-5, 5'), 3.66 (dd, 1 H, $J_{5',6'b}$ = 6.9, H-6'b), 3.72 (dd, 1 H, H-2'), 2.18, 2.09, 2.08, 2.07 (each s, each 3 H, 4 Ac), 2.06 (s, 6 H, 2 Ac), 1.36, 1.33 (each t, each 3 H, $^3J_{H,H}$ = 7.0, 2 CH_2CH_3); ^{13}C NMR (125.7 MHz) δ 170.2 ($COCH_3$), 169.9 (2 C, 2 $COCH_3$), 169.4 (3 C, 3 $COCH_3$), 167.6 (C=O chelated), 165.3 (C=O free), 157.4 (=CH), 102.8 (C-1'), 94.8 (=C), 87.0 (C-1), 77.1 (C-5), 72.3 (C-3), 70.7 (C-5'), 70.6 (C-3'), 70.5 (C-4), 68.9 (C-6'), 68.6 (C-2), 66.2 (C-4'), 61.0 (C-6), 60.5 (C-2'), 60.3, 60.0 (2 CH_2CH_3), 20.6 (2 C, 2 $COCH_3$), 20.5 (3 C, 3 $COCH_3$), 20.4 ($COCH_3$), 14.2, 14.1 (2 CH_2CH_3); FABMS *m/z* 811 (100, $[M+Na]^+$). HRFABMS *m/z* obsd 921.1718 calcd for $C_{32}H_{44}O_{19}N_4$+Cs 921.1653.

*Ethyl 3,4-di-*O*-acetyl-2-amino-2-deoxy-6-*O*-(3',4',6'-tri-*O*-acetyl-2'-amino-2'-deoxy-α-*D*-galactopyranosyl)-α-*D*-glucopyranoside* (**7**) and *ethyl 2-amino-3,4-di-*O*-benzoyl-2-deoxy-6-*O*-(3',4',6'-tri-*O*-acetyl-2'-amino-2'-deoxy-α* (**8**) *and-β* (**9**)*-D-galactopyranosyl)-α-D-glucopyranosides*. Compound **4** or the crude mixture of **5** and **6** (0.46 mmol) were dissolved in methanol (60 mL) and ethyl acetate (5 mL) and hydrogenated at 1 atm of pressure and room temperature for 4 h in the presence of C/Pd (0.3 g). The catalyst was filtered off, the solvent evaporated and the corresponding residue directly used in the following reaction. The molecular weights of **7**-**9** were checked by MS. Compound **7** had HRFABMS *m/z* obsd 579.2365 calcd for $C_{24}H_{38}O_{14}N_2$+H 579.2401; obsd 601.2237 calcd for $C_{24}H_{38}O_{14}N_2$+Na 601.2221.

The mixture of compounds **8** and **9** had FABMS *m/z* 703 (40, $[M+H]^+$), 725 (100, $[M+Na]^+$).

*2,3,4-Tri-*O*-acetyl-6-*O*-(3',4',6'-tri-*O*-acetyl-2'-azido-2'-deoxy-α* (**16**) and β (**17**)*-D-galactopyranosyl)-β-D-glucopyranosylamines*. Chlorine was bubbled through a solution of crude **14** and **15** (0.5 g, 0.63 mmol) in chloroform (60 mL) until total consumption of the starting material was observed by TLC (chloroform:EtOAc:MeOH 10:5:1). The solvent was evaporated and the residue directly used in the following reaction. This residue had IR ν_{max} 3500-3200, 2963, 2934, 2116 (N_3), 1753, 1526, 1443, 1371, 1244, 1036; FABMS *m/z* 619 (50, $[M+H]^+$), 641 (100, $[M+Na]^+$).

*2,3,4-Tri-*O*-acetyl-6-*O*-(3',4',6'-tri-*O*-acetyl-2'-amino-2'-deoxy-α*(**18**) and β(**19**)*-D-galactopyranosyl)-β-D-glucopyranosylamines*. The residue **16**+**17** (0.46 mmol) was dissolved in ethanol:EtOAc 2:1 (21 mL) and hydrogenated at 3 bar pressure, room temperature for 4 hours in the presence of Adams catalyst (204 mg). The catalyst was filtered off, the solvent evaporated and the residue directly used in the following reaction. The molecular weights of **18** and **19** were checked by FABMS *m/z* 615 (100, $[M+Na]^+$).

General procedure for the preparation of disaccharide diisithiocyanates **10**-**12**, **20**, and **21**. To a heterogeneous mixture of the corresponding diamino compound (0.46 mmol) in chloroform (5.4 mL) and calcium carbonate (0.28 g, 2.8 mmol) in water (5.4 mL), thiophosgene (0.13 mL) was added. The mixture was stirred vigorously (2 h) and then filtered; the organic layer was separated, washed with water (6 mL), dried

(MgSO4), and concentrated to dryness. The residue was purified as indicated. The following compounds were prepared in this manner.

*Ethyl 3,4-di-*O*-acetyl-2-deoxy-2-isothiocyanato-6-*O*-(3',4',6'-tri-*O*-acetyl-2'-deoxy-2'-isothiocyanato-α-D-galactopyranosyl)-α-D-glucopyranoside* (**10**). Prepared from **7**; column chromatography (ether:hexane 6:1) of the residue gave an amorphous and hygroscopic solid (0.036 g, 12% from **4**); IR ν_{max} 2963, 2924, 2859, 2052 (NCS), 1744, 1460, 1404, 1262, 1082, 1024 cm^{-1}; ^1H NMR (500 MHz) δ 5.51 (dd, 1 H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 9.3, H-3), 5.43 (dd, 1 H, $J_{3',4'}$ = 3.2, $J_{4',5'}$ = 1.2, H-4'), 5.33 (dd, 1 H, $J_{2',3'}$ = 10.9, H-3'), 5.04 (d, 1 H, $J_{1',2'}$ = 3.4, H-1'), 5.01 (dd, 1 H, $J_{4,5}$ = 10.2, H-4), 5.00 (d, 1 H, $J_{1,2}$ = 3.5, H-1), 4.33-4.13 (m, 3 H, H-5', 6'a, 6'b), 4.10-4.05 (m, 2 H, H-5, 2'), 3.89 (dd,1 H, H-2), 3.82 (dq, 1 H, $^2J_{H,H}$ = 9.6, $^3J_{H,H}$ = 7.1, C*H*HCH3), 3.73 (dd, 1 H, $J_{5,6a}$ = 5.2, $J_{6a,6b}$ = 11.3, H-6a), 3.63 (dq, 1 H, CH*H*CH3), 3.58 (dd, 1 H, $J_{5,6b}$ = 2.2, H-6b), 2.07, 2.04 (each s, each 3 H, 2 Ac), 2.00 (s, 6 H, 2 Ac), 1.99 (s, 3 H, Ac), 1.40 (t, 3 H, CH2C*H*3); ^{13}C NMR (125.7 MHz) δ 170.5, 170.1, 169.9, 169.6, 169.2 (5 *C*OCH3), 138.9 (C2'-N*C*S), 137.8 (C2-N*C*S), 97.1 (C-1'), 96.3 (C-1), 71.0 (C-3), 68.7 (C-4), 68.5 (C-3'), 68.4 (C-5), 67.0 (C-4'), 66.8 (C-5'), 66.3 (C-6), 64.7 (*C*H2CH3), 61.3 (C-6'), 59.0 (C-2), 55.4 (C-2'), 20.7, 20.6 (2 CO*C*H3), 20.5 (2 C, 2 CO*C*H3), 20.4 (CO*C*H3), 15.0 (CH2*C*H3); FABMS *m/z* 685 (100, $[M+Na]^{+\cdot}$). HRFABMS *m/z* obsd 795.0510 calcd for $C_{26}H_{34}O_{14}N_2S_2$+Cs 795.0505.

*Ethyl 3,4-di-*O*-benzoyl-2-deoxy-2-isothiocyanato-6-*O*-(3',4',6'-tri-*O*-acetyl-2'-deoxy-2'-isothiocyanato-α-D-galactopyranosyl)-α-D-glucopyranoside* (**11**). From **8**+**9**; column chromatography (ether:hexane 6:1) of the residue gave an amorphous and hygroscopic solid (0.083 g, 24% from **5**); $[\alpha]_D^{24}$ +149.0° (*c* 0.5); IR ν_{max} 3069, 2965, 2924, 2862, 2047 (NCS), 1740, 1597, 1452, 1353, 1263, 1084, 1034 cm^{-1}; ^1H NMR (500 MHz) δ 7.96-7.35 (m, 10 H, 2 Ph), 5.99 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 10.2, H-3), 5.47 (t, 1 H, $J_{4,5}$ = 10.2, H-4), 5.44 (d, 1 H, $J_{3',4'}$ = 3.2, $J_{4',5'}$ = 0, H-4'), 5.39 (dd, 1 H, $J_{2',3'}$ = 10.7, H-3'), 5.13 (d, 1 H, $J_{1,2}$ = 3.5, H-1), 5.05 (d, 1 H, $J_{1',2'}$ = 3.4, H-1'), 4.28 (ddd, 1 H, $J_{5,6a}$ = 5.2, $J_{5,6b}$ = 1.9, H-5), 4.26 (t, 1 H, $J_{5',6'a}$ = $J_{5',6'b}$ = 6.7, H-5'), 4.08 (dd, 1 H, H-2), 4.07 (dd, 1 H, H-2'), 4.01 (dd, 1 H, $J_{6'a,6'b}$ = 11.3, H-6'a), 3.98 (dd, 1 H, H-6'b), 3.92 (dq, 1 H, $^2J_{H,H}$ = 9.7, $^3J_{H,H}$ = 7.0, C*H*HCH3), 3.83 (dd, 1 H, $J_{6a,6b}$ = 11.3, H-6a), 3.71 (dq, 1 H, CH*H*CH3), 3.64 (dd,1 H, H-6b), 2.13, 2.08, 1.91 (each s, each 3 H, 3 Ac), 1.41 (t, 3 H, CH2C*H*3); ^{13}C NMR (125.7 MHz) δ 170.1, 169.7, 169.5 (3 *C*O2CH3), 165.3, 165.1 (2 *C*OPh), 138.9 (C2'-N*C*S), 138.0 (C2-N*C*S), 133.5-128.2 (12 C, 2 Ph), 97.1 (C-1'), 96.7 (C-1), 71.2 (C-3), 68.8 (3 C, C-3',4,5), 67.0 (C-4'), 66.8 (C-5'), 66.3 (C-6), 64.9 (*C*H2CH3), 61.5 (C-6'), 59.3 (C-2), 55.4 (C-2'), 20.6 (CO*C*H3), 20.4 (2 C, 2 CO*C*H3), 15.1 (CH2*C*H3); FABMS *m/z* 809 (100, $[M+Na]^{+\cdot}$). HRFABMS *m/z* obsd 919.0765 calcd for $C_{36}H_{38}O_{14}N_2S_2$+Cs 919.0818.

*Ethyl 3,4-di-*O*-benzoyl-2-deoxy-2-isothiocyanato-6-*O*-(3',4',6'-tri-*O*-acetyl-2'-deoxy-2'-isothiocyanato-β-D-galactopyranosyl)-α-D-glucopyranoside* (**12**). From **8**+**9**; column chromatography (ether:hexane 6:1) of the residue gave an amorphous solid (0.094 g, 26% from **6**); $[\alpha]_D^{24}$ +42.9° (*c* 0.6); IR vmax 3069, 2957, 2926, 2859, 2047, 1744, 1597, 1451, 1373, 1265, 1082, 1044 cm^{-1}; ^1H NMR (500 MHz) δ 7.95-7.34 (m, 10 H, 2 Ph), 6.00 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 10.0, H-3), 5.41 (t, 1 H, $J_{4,5}$ = 10.0, H-4), 5.34 (d, 1 H, $J_{3',4'}$ = 11.2, $J_{4',5'}$ = 0, H-4'), 5.14 (d, 1 H, $J_{1,2}$ = 3.5, H-1), 4.98 (dd, 1 H, $J_{2',3'}$ = 3.2, H-3'), 4.54 (d, 1 H, $J_{1',2'}$ = 8.1, H-1'), 4.27 (ddd, 1 H, $J_{5,6a}$ = 2.1, $J_{5,6b}$ = 6.0, H-5), 4.09 (dd, 1 H, $J_{5',6'a}$ = 6.8, $J_{6'a,6'b}$ = 11.4, H-6'a), 4.06-4.02 (m, 2 H, H-6a, 2'), 4.04 (dd, 1 H, $J_{5',6'b}$ = 5.0, H-6'b), 4.01 (dd,

1 H, H-2), 3.95 (dq, 1 H, $^2J_{H,H}$ = 9.6, $^3J_{H,H}$ = 7.0, *CH*HCH3), 3.86 (dd, 1 H, H-5'), 3.71 (dq, 1 H, CH*H*CH3), 3.69 (dd, 1 H, $J_{6a,6b}$ = 11.4, H-6b), 2.11, 2.08, 1.99 (each s, each 3 H, 3 Ac), 1.39 (t, 3 H, CH_2CH_3); ^{13}C NMR (125.7 MHz) δ 170.2, 169.7, 169.6 (3 *C*OCH3), 165.3, 165.2 (2 *C*OPh), 139.8 (C2-N*C*S), 139.0 (C2'-N*C*S), 133.5-128.2 (12 C, 2 Ph), 101.3 (C-1'), 96.6 (C-1), 71.1 (C-3), 71.0 (C-3'), 70.7 (C-5'), 69.2 (C-4), 69.1 (C-5), 68.3 (C-6), 65.8 (C-4'), 64.8 (*C*H2CH3), 60.8 (C-6'), 59.2 (C-2), 57.4 (C-2'), 20.5 (2 C, 2 CO*C*H3), 20.4 (CO*C*H3), 15.0 (CH2*C*H3); FABMS *m/z* 809 (100, [M+Na]$^{+\cdot}$). HRFABMS *m/z* obsd 919.0811 calcd for $C_{36}H_{38}O_{14}N_2S_2$+Cs 919.0818.

2,3,4-Tri-O-*acetyl-6*-O-*(3',4',6'-tri*-O-*acetyl-2'-deoxy-2'-isothiocyanato-α-D-galactopyranosyl)-β-D-glucopyranosyl isothiocyanate* (**20**). Prepared from **18+19**; column chromatography (ether:hexane 6:1) of the residue gave an amorphous and hygroscopic solid (0.190 g, 60% from **14**); $[\alpha]_D^{21}$ +60.0° (*c* 1.0); IR νmax 2963, 2930, 2857, 2108 (NCS), 2031 (NCS) 1753, 1373, 1260, 1082, 1030 cm^{-1}; ^{1}H NMR (500 MHz) δ 5.45 (d, 1 H, $J_{3',4'}$ = 3.2, $J_{4',5'}$ =0, H-4'), 5.30 (dd, 1 H, $J_{2',3'}$ = 11.0, H-3'), 5.24 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.4, H-3), 5.13 (t, 1 H, $J_{1,2}$ = 9.4, H-2), 5.06 (d, 1 H, H-1), 5.05 (t, 1 H, $J_{4,5}$ = 9.4, H-4), 5.02 (d, 1 H, $J_{1',2'}$ = 3.4, H-1'), 4.29 (t, 1 H, $J_{5',6'a}$ = $J_{5',6'b}$= 6.8, H-5'), 4.11 (dd, 1 H, H-2'), 4.03 (dd, 1 H, $J_{6'a,6'b}$ = 11.2, H-6'a), 3.99 (dd, 1 H, H-6'b), 3.83-3.74 (m, 2 H, H-5,6a), 3.60 (d, 1 H, $J_{6a,6b}$ = 9.8, H-6b), 2.14, 2.11, 2.06, 2.03 (each s, each 3 H, 4 Ac), 2.07 (s, 6 H, 2 Ac); ^{13}C NMR (125.7 MHz) δ 170.2, 170.0, 169.7, 169.5, 169.3, 168.9 (6 *C*OCH3), 144.6 (C-1-N*C*S), 139.0 (C-2'-N*C*S), 97.1 (C-1'), 83.3 (C-1), 74.9 (C-5), 72.3 (C-3), 71.7 (C-2), 68.6 (C-3'), 68.2 (C-4), 66.9 (3C, C-6,4',5'), 61.2 (C-6'), 55.4 (C-2'), 20.6 (CO*C*H3), 20.5 (2 C, 2 CO*C*H3), 20.4 (3 C, 3 CO*C*H3); FABMS *m/z* 699 (100, [M+Na]$^{+\cdot}$). HRFABMS *m/z* obsd 676.1208 calcd for $C_{26}H_{32}O_{15}N_2S_2$ 676.1244; obsd 677.1363 calcd for $C_{26}H_{32}O_{15}N_2S_2$+H 677.1322.

2,3,4-Tri-O-*acetyl-6*-O-*(3',4',6'-tri*-O-*acetyl-2'-deoxy-2'-isothiocyanate-β-D-galactopyranosyl)-β-D-glucopyranosyl isothiocyanate* (**21**). Prepared from **18+19**; column chromatography (ether:hexane 6:1) of the residue gave an amorphous and hygroscopic solid (0.062 g, 58% from **15**); $[\alpha]_D^{21}$ +0.0° (*c* 0.9); IR νmax 2963, 2108 (NCS), 2031 (NCS), 1753, 1373, 1260, 1080, 1036 cm^{-1}; ^{1}H NMR (500 MHz) δ 5.29 (d, 1 H, $J_{3',4'}$ = 2.8, $J_{4',5'}$ = 0, H-4'), 5.15 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.4, H-3), 5.07 (d, 1 H, $J_{1,2}$ = 9.4, H-1), 5.01 (t, 1 H, H-2), 4.91 (dd, 1 H, $J_{2',3'}$ = 11.0, H-3'), 4.90 (t, 1 H, $J_{4,5}$ = 9.4, H-4), 4.61 (d, 1 H, $J_{1',2'}$ = 8.0, H-1'), 4.09 (dd, 1 H, $J_{5',6'a}$ = 6.6, $J_{6'a,6'b}$ = 11.3, H-6'a), 4.05 (dd, 1 H, $J_{5',6'b}$ = 6.6, H-6'b), 3.92 (dd, 1 H, H-2'), 3.86-3.80 (m, 3 H, H-5, 5', 6a), 3.72 (dd, 1 H, $J_{5,6b}$ = 7.7, $J_{6a,6b}$ = 12.6, H-6b), 2.07, 2.04, 2.01, 2.00, 1.99, 1.96 (each s, each 3 H, 6 Ac); ^{13}C NMR (125.7 MHz) δ 170.2, 169.9, 169.7, 169.5, 169.3, 169.0 (6 *C*OCH3), 145.5 (C1-N*C*S), 139.5 (C2'-N*C*S), 101.6 (C-1'), 83.5 (C-1), 76.1 (C-5), 72.2 (C-3), 71.6 (C-2), 70.9 (C-5'), 70.8 (C-3'), 68.3 (C-6), 68.2 (C-4), 65.9 (C-4'), 60.9 (C-6'), 57.3 (C-2'), 20.5 (2 C, 2 CO*C*H3), 20.4 (4 C, 4 CO*C*H3); FABMS *m/z* 699 (100, [M+Na]$^{+\cdot}$). HRFABMS *m/z* obsd 677.1348 calcd for $C_{26}H_{32}O_{15}N_2S_2$+H 677.1322.

ACKNOWLEDGMENTS

We thank the Dirección General de Investigación Científica y Técnica for the financial support (grant number PB 91/0617)

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(*Received in UK* 20 *September* 1994; *revised* 1 *November* 1994; *accepted* 4 *November* 1994)