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Synthesis and Transformations of 2-Deoxy-2-iodo-pyranosyl Isothiocyanates from Glycals

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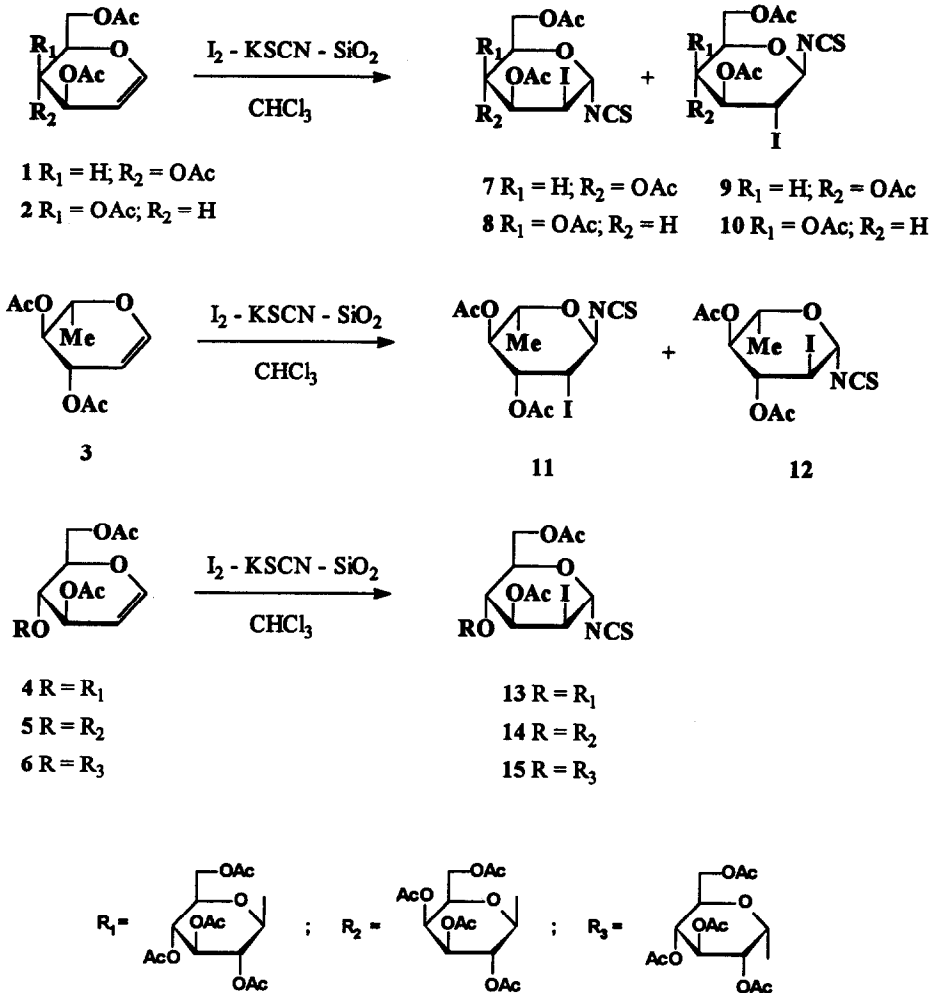
Abstract.: A convenient one-step synthesis of 2-deoxy-2-iodoglycosyl isothiocyanates from monosaccharidic and disaccharidic glycals is reported. Treatment of iodoisothiocyanates **7, 11, 13-15** with ammonia gives the corresponding 2-amino-thiazolines **16, 17, 23-25**, respectively. Under the same conditions, iodoisothiocyanate **8** affords the iodothiourea **18**. 2-Amino-2-thiazolines **23-25** can be readily transformed into thiazolidin-2-ones **26-28**. Reduction of compounds **7, 8, 13-15** by tributyltin hydride yields the corresponding N-(2'-deoxyglycosyl)thioureas **21, 22, 29-31**.

The growing significance of glycosides and oligosaccharides as constituents of biologically important compounds such as antibiotics, glycolipids, glycoproteins and bacterial lipopolysaccharides has caused considerable interest in expeditious methods for the stereocontrolled construction of the glycosyl linkage[1]. In spite of the progress made in this field, the highly stereoselective synthesis of 1,2-*cis*-glycoside linkage is still difficult and a satisfactory solution remains a problem in the synthetic chemistry of carbohydrates. Recently, N. K. Kochetkov *et al*[2] reported a new approach to specific 1,2-*cis*-glycosylations by using 1,2-*trans*-glycosyl thiocyanates with a non-participanting substituent at C-2 as glycosyl donors.

Continuing our efforts in the synthesis of new glycosyl donors[3], we thought that these types of glycosyl thiocyanates could be obtained from glycals. It is known that alkenes react with iodine (I) thiocyanate to give vicinal iodothiocyanates and iodoisothiocyanates[4]. The reagent is prepared *in situ* by treatment of ICl with potassium or thallium thiocyanate, or by heating iodine with potassium thiocyanate in chloroform or chloroform-sulfolane mixtures. The iodothiocyanate : iodoisothiocyanate ratio depends on the reagents used to generate the ISCN, the reaction conditions employed and the nature of the alkene[4]. Thus, T. Ando *et al*[5] found that the addition of iodine-thiocyanogen to alkenes using a solid-supported inorganic salt gave only *vic*-iodothiocyanates.

This last result encouraged us to apply the same reaction conditions to glycals hoping that 2-deoxy-2-



Scheme 1

iodoglycosyl thiocyanates can be obtained and used as glycosyl donors. However, the reactions of peracetylated monosaccharidic and disaccharidic glycals [D-glucal (**1**), D-galactal (**2**), L-rhamnal (**3**), celobial (**4**), lactal (**5**) and maltal (**6**)] with iodine-KSCN-SiO_2[5] gave exclusively the 2-deoxy-2-iodopyranosyl isothiocyanates (see Scheme 1). Isothiocyanates[6] are important reagents in heterocyclic chemistry and undergo several reactions such as nucleophylic additions and cycloadditions. Glycosyl isothiocyanates and glycosyl thioureas are valuable and versatile intermediates in the synthesis of various type of heterocycles derivatives of sugars[7]. Furthermore, glycosyl isothiocyanates have been used for coupling carbohydrate molecules with aspartic acid derivatives for the construction of asparagine glycosylated building blocks[8]. In spite of the recent

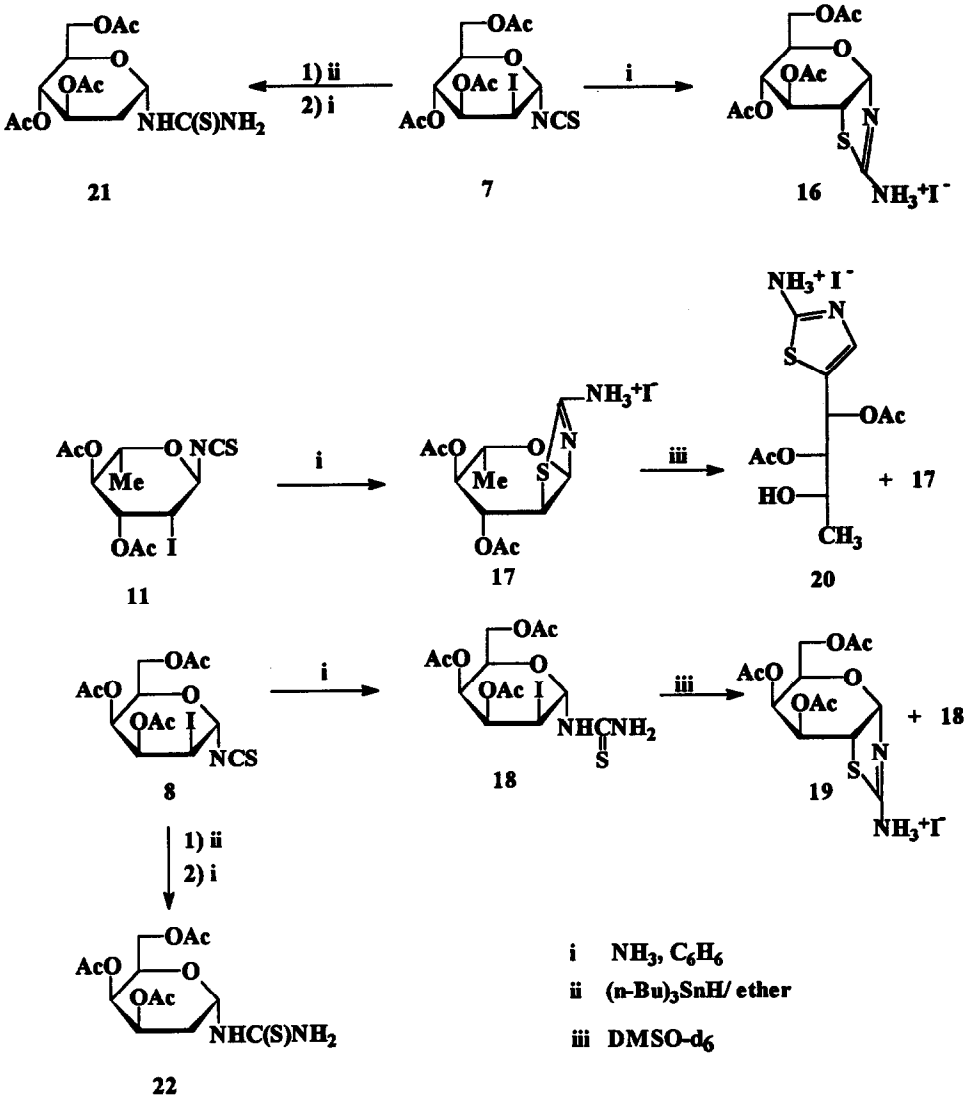
advances in this field, there are no precedented cases for the synthesis of 2-deoxy-2-iodoglycosyl isothiocyanates. In this paper we report the synthesis of such compounds as well as some of its transformations exploiting the functionality of both the anomeric and the C-2 positions.

RESULTS AND DISCUSSION

The reactions of the monosaccharidic glycals **1-3** with silica-supported potassium thiocyanate and iodine in ethanol-free chloroform solution at room temperature gave in all cases the *trans*-diaxial 2-deoxy-2-iodopyranosyl isothiocyanates **7**, **8**, and **11**, as major products, and the *trans*-diequatorial derivatives **9**, **10**, and **12**, as minor products, respectively, with high yields (see Scheme 1 and Experimental). The reaction of the peracetylated disaccharidic glycals **4**, **5** and **6** gave exclusively the *trans*-diaxial 2-deoxy-2-iodopyranosyl isothiocyanates **13-15**, respectively, with good yields (56-82 %) (see Scheme 1). These results show that the reaction of the disaccharidic glycals **4-6** with I_2-KSCN-SiO_2 is more stereoselective than in the case of the monosaccharidic glycals **1-3**.

The structures of **7-15** were assigned on the basis of the i.r., ^{1}H-n.m.r., ^{13}C-n.m.r., and m. s. data. All compounds have υ_{NCS} 2020 $\pm$ 30 cm^{-1} and δ 143.5 $\pm$ 1.0 ppm for the NCS group, δ 28.8 $\pm$ 1.4 ppm for C-2, and the mass spectra showed the loss of NCS form M^+ as it has been reported[7e,f] for other glycosyl isothiocyanates. Compounds **7**, **8**, **11** and **13-15** showed $^3J_{1,2}$ and $^3J_{2,3}$ values of 2.1 $\pm$ 0.5 Hz and 4.4 $\pm$ 0.3 Hz, respectively, in accordance with a H-1*eq*-H-2*eq*-H-3*ax* relationship which is in agreement with the proposed structures. The $^3J_{1,2}$ and $^3J_{2,3}$ values for **9**, **10**, and **12** (9.8 Hz and 11.3 $\pm$ 0.3 Hz, respectively) indicated a H-1*ax*-H-2*ax*-H-3*ax* relationship in these compounds.

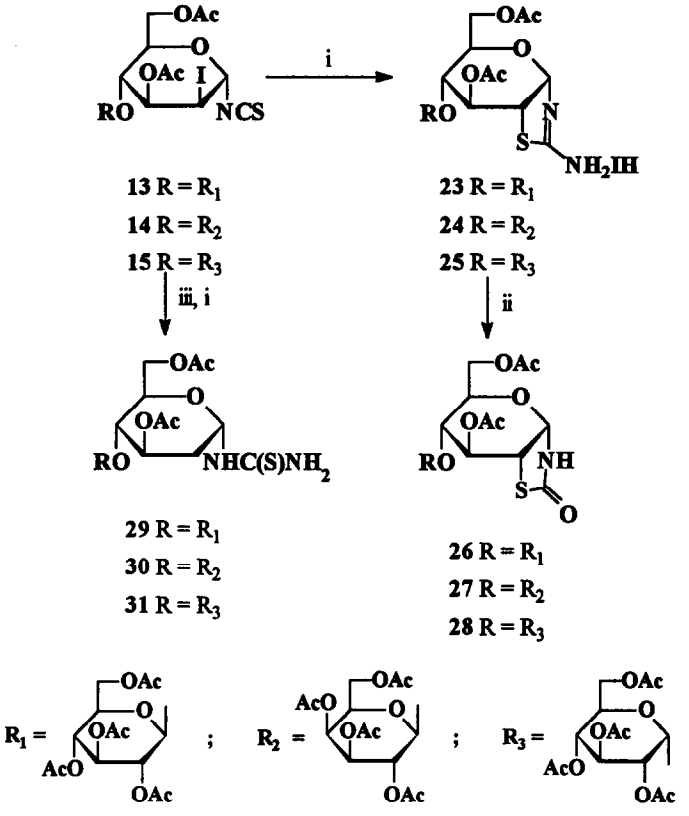
The transformation of the 2-deoxy-2-iodopyranosyl isothiocyanates was now considered because isothiocyanates are important reagents that can undergo several reactions such as nucleophylic additions[4,6]. Thus, the reaction between *vic*-iodoisothiocyanates and ammonia or aromatic amines is a general method for the synthesis of 2-amino-2-thiazolines or 2-arylamino-2-thiazolines *via vic*-iodothioureas[4,9]. As expected, the reaction of compounds **7** and **11** with an excess of anhydrous ammonia at 0° C gave the 2-amino-thiazolines **16** and **17**, respectively (see Scheme 2). However, when this reaction was applied to iodoisothiocyanate **8** the *vic*-iodothiourea **18** was isolated. This compound did not undergo spontaneous S_Ni reaction to give the corresponding 2-thiazolinyl ammonium iodide **19**, a fact that is in agreement with the $^1C_4$ (D) conformation found for **18** (*vide infra*). However, the formation of compound **19** was detected when a solution of **18** in dimethylsulfoxide was stored at room temperature for 12 h. Under these conditions a *ca.* 3:1 mixture (from ^{1}H-n.m.r.) of **18** and **19** was formed.



Scheme 2

The transformation of the disaccharidic isothiocyanates **13-15** into the corresponding 2-aminothiazoline iodides **23-25** was effected also by the reaction with anhydrous ammonia in similar conditions as described above (49-67 % yield) (see Scheme 3). During the isolation of compounds **23-25** by column chromatography was observed that the formation of a more polar by-product happens if this purification is not carried out in a short time. The spectroscopic and analytical data of these compounds allowed to identify them as the thiazolidin-2-one derivatives **26-28**. The complete conversion of **23-25** into **26-28** could be performed by

heating under reflux a solution of **23-25** and silica in ethyl acetate-water with good yields (60-69 %) (see Experimental).



(i) NH_3 - C_6H_6; (ii) AcOEt - H_2O - SiO_2 - reflux; (iii) $(n\text{-}Bu)_3SnH$ - ether

Scheme 3

The structures of **16-19** and **23-28** were established on the basis of the elemental analysis and/or spectroscopic data. Compounds **16**, **17** and **23-28** showed the i.r. bands[6] for NH (~ 3450-3330 cm^{-1}) and CO-ester (~ 1750 cm^{-1}), thiazoline group (~ 1640-1505 cm^{-1}, two bands) for **16**, **17**, **23-25**, and *CO*NH (~ 1641 cm^{-1}) for **26-28**. The significant deshielding of carbon C-2' in compounds **16**, **17**, **23-28** (40-53 ppm) respecting to the corresponding precursors is in good agreement with the replacement of the iodine atom by the sulfur of the thiourea group. The $^3J_{1',2'}$ and $^3J_{2',3'}$ values (6.5 ± 0.5 and 7.0 ± 0.3 Hz, respectively) for **16**, **17** were different from those for **7** and **11** in accordance with a conformation change in the formation of

the bicyclic system. In the disaccharidic derivatives **23-28** the $^3J_{1',2'}$ values were similar to those found in the corresponding 2-ammonium thiazoline iododides monosaccharidic derivatives. Therefore, $^{O,3}B$ (D) and a $^{O,3}B$ (L) conformation were show to predominate for **16** and **23-28**, and **17**, respectively. Compound **18** had ^{13}C-n.m.r. signals at 78.8 and 26.0 ppm corresponding to $NH_2C(S)NH$-**C**-1 and I-**C**-2, respectively. This compound adopts the $^1C_4$ (D) conformation as indicated by the $^3J_{1,2}$ value of 8.8 Hz (H-1,2 *trans*-diaxial). In support of this assignment is the fact that H-3 resonates at ~ 0.2 ppm higher field than H-4. Compound **19** showed characteristic signals at δ 6.02 (d, J 5.7 Hz) for H-1 and 4.07 (dd, J 9.4 and 5.7 Hz) for H-2, and δ 88.0 and 45.0 ppm for C-1 and C-2, respectively (see Scheme 2 and 3).

When a solution of **17** in DMSO-d_6 was left at room temperature for 12 h a *ca.* 1:1 mixture of **17** and the thiazol **20** was observed by ^1H- and ^{13}C-n.m.r. Compound **20** showed a singlet at δ 7.45 ppm corresponding to H-4 of the thiazol ring and a downfield doublet at δ 6.20 ppm attributed to the H-1'. In the ^{13}C-n.m.r. spectrum the resonance of C-4 appeared at δ 128.2 ppm.

The 2-deoxy-2-iodopyranosyl isothiocyanates also gave us access to 2-deoxyglycosyl thioureas. The reaction of alkyl iodides with tributyltin hydride afforded alkanes in high yields[11]. R. C. Cambie *et al.*[9] reported that the treatment of *vic*-iodoisothiocyanates with Bu_3SnH provides a selective reduction to the correponding isothiocyanates. To the best of our knowledge only an example of preparation of 2-deoxyglycosyl isothiocyanates from sugars has been reported[7e]. The procedure involves the reaction of 2-deoxy-hexopyranose with bromotrimethylsilane followed by treatment with silver isothiocianate. When compounds **7**, **8** and **13-15** were reacted with tributyltin hydride followed by the treatment of an excess of anhydrous ammonia at 0° C the 2-deoxy-glycosyl thioureas **21**, **22** and **29-31** were obtained in moderate or good yields (31-70 %), respectively.

Among the spectrocopic data for these compounds, the i.r. absorptions at 3580-3340 and 1620 cm^{-1} (NH), and the ^{13}C-n.m.r. signals at δ 184.5 ± 1 ppm (C=S) and 31.0 ± 2.5 ppm (C-2) are characteristic of its structure of 2-deoxyglycosyl thioureas. Significative changes were observed in the chemical shifts of the protons of the ring that contain the thiourea group when the spectra were recorded in $CDCl_3$ or DMSO-d_6 solution (see Experimental).

In summary, 2-deoxy-2-iodogycosyl isothiocyanates can be readily obtained in one-pot from monosaccharidic and disaccharidic glycals with good yields and a high stereselectivity. In addition, these compounds give an easy access to 2-amino-2-thiazolines, thiazolidin-2-ones and 2-deoxyglycosyl thioureas.

EXPERIMENTAL

General Methods.- Melting points were determined with a Reichter hotplate microscope and are uncorrected. Spectral measurements were recorded on Perkin-Elmer 983G (i.r.), Perkin-Elmer 141 ($[\alpha]_D$) and Bruker AM 300, 400 and 500 instruments (n.m.r.). G.I. (ether)-mass spectra were obtained with a Hewlett-Packard 5988A instrument. Elemental analyses were obtained with a Perkin-Elmer 240C instrument. Optical rotations were measured at room temperature. Column chromatography was performed on Silica Gel Merck (70-230 mesh, ASTM). Peracetylated glycals D-galactal (**2**), celobial (**4**), lactal (**5**) and maltal (**6**) were prepared according to the published procedure[12]. All the other reagents were purchased from Aldrich Chemical Co.

***General Procedure for Formation of 2-Deoxy-2-Iodo-Glycosyl Isothiocyanate* 7-15.**- A mixture of the corresponding glycals **1-6** (1mmol), KSCN (1.5mmol) supported on silica, [prepared by rotatory evaporation of an aqueous solution of KSCN (1.5 mmol) with silica (Merck 60) (3 $mmol.g^{-1}$), followed by drying] , iodine (1.5 mmol) in ethanol-free, chloroform (10 mL), was stirred at room temperature until t.l.c. (1:1 ether - hexane) showed complete dissappearence of the starting material (24-48 h). The mixture was filtered and the silica washed with chloroform. The chloroform was washed with aqueous $Na_2S_2O_3$ and water, dryed (Na_2SO_4), concentrated, and the residue was purified by column chromatography. The following amounts and conditions were used:

Glycal (g)	KSCN (g)	I_2 (g)	Time (h)	Product (g, %)
1(0.54)	0.85	0.76	24	**7** (0.68, 74) **9** (0.07, 7)
2 (0.50)	0.79	0.92	48	**8** (0.65, 77) **10** (0.03, 3)
3 (0.64)	0.97	1.14	24	**11** (0.58, 49) **12** (0.25, 21)
4 (0.56)	0.33	0.38	72	**13** (0.42, 56)
5 (1.02)	0.79	0.92	72	**14** (0.91, 67)
6 (1.10)	0.84	0.98	72	**15** (1.20, 82)

3,4,6-tri-O-Acetyl-2-deoxy-2-iodo-α-D-manno- (**7**) and *-β*-D-glucopyranosyl isothiocyanates (**9**).- Column chromatography (1:2 ether-hexane) of the crude product gave first **7**, isolated as syrup; $[\alpha]_D$ +59° (c 1, chloroform); υ_{max} 2006, and 1747 cm^{-1}. For ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 5.86 (d, 1 H, J 1.8 Hz, H-1), 5.37 (t, 1 H, J ~ 9.7 Hz, H-4), 4.68 (dd, 1 H, J 4.3 and 1.8 Hz, H-2), 4.54 (dd, 1 H, J 9.7 and 9.4 Hz, H-3), 4.23 (m, 1 H, H-6), 4.18 (m, 1 H, H-6'), 4.14 (m, 1 H, H-5), and 2.11, 2.09, 2.07 (3s, 9 H, 3 Ac). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 170.6, 169.7, 169.4 (3 CO), 144.2 (NCS), 86.0 (C-1), 72.3, 68.8, 66.8 (C-

3,4,5), 61.8 (C-6), and 20.9, 20.8, 20.7 (3 *Me*CO). Mass spectrum: *m/z*, 458 (M^+ + 1), 399 (M^+ - NCS), 339 (M^+ - NCS - AcOH), 279 (M^+ - NCS - 2AcOH), and 213 ((M^+ - NCS - I - AcOH). *Anal. Calcd for* $C_{13}H_{16}INO_7S$: C, 34.15; H, 3.53; N, 3.06. Found: C, 34.42; H, 3.20; N, 3.27.

Eluted second was **9**, m. p. 103-105 °C; $[\alpha]_D$ +4° (c 1, chloroform); υ_{max} 2030, 1749 cm^{-1}. For ^1H n.m.r. (300 MHz, $CDCl_3$): δ 5.13 (d, 1 H, J 9.8 Hz, H-1), 5.26 (dd, 1 H, J 11.0 and 9.1 Hz, H-3), 4.95 (dd, 1 H, J 10.1 and 9.1 Hz, H-4), 4.25 (dd, 1 H, J 12.5 and 2.3 Hz, H-6), 4.11 (dd, 1 H, J 12.5 and 4.8 Hz, H-6'), 3.99 (dd, 1 H, J 11.0 and 9.8 Hz, H-2), 3.79 (ddd, 1 H, J 10.1, 4.8 and 2.3 Hz, H-5), and 2.07, 2.06, 1.99 (3s, 9 H, 3 Ac). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 170.5, 169.4, 169.3 (3 CO), 144.1 (NCS), 86.9 (C-1), 75.0, 74.4, 68.3 (C-3,4,5), 61.6 (C-6), 28.4 (C-2), and 20.7, 20.7, 20.5 (3 *Me*CO). Mass spectrum: *m/z*, 399 (M^+ - NCS), 399 (M^+ - NCS - AcOH), 279 (M^+ - NCS - AcOH), and 213 (M^+ - NCS - I - AcOH). *Anal. Calcd for* $C_{13}H_{16}INO_7S$: C, 34.15; H, 3.53; N, 3.06. Found: C, 34.50; H, 3.95; N, 2.91.

3,4,6-tri-O-Acetyl-2-deoxy-2-iodo-α-D-talo- **(8)** *and -β-D-galactopyranosyl isothiocyanates* **(10)**.- Column chromatography (1:3 ether-hexane) of the crude product gave first **8**, m.p. 116-119 °C (from hexane-ether), $[\alpha]_D$ +110° (c 1, chloroform); υ_{max} 1997, and 1744 cm^{-1}. ^1H-n.m.r. (300 MHz, $CDCl_3$): δ 6.00 (d, 1 H, J 2.0 Hz, H-1), 5.39 (dd, 1 H, J 3.6 and 3.2 Hz, H-4), 4.89 (dd, 1 H, J 3.6 and 4.7 Hz, H-3), 4.40 (dt, 1 H, J 6.6, 6.2 and 2.2 Hz, H-5), 4.37 (ddd, 1 H, $J_{2,3}$ 4.7, $J_{1,2}$ 2.2 and $J_{2,4}$ 0.8 Hz, H-2), 4.22 (dd, 1 H, J 11.6 and 6.6 Hz, H-6), 4.16 (dd, 1 H, J 11.6 and 6.2 Hz, H-6'), and 2.15, 2.07, 2.05 (3s, 9 H, 3 Ac). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 170.5, 169.8, 169.4 (3 CO), 144.0 (NCS), 87.3 (C-1), 70.4, 65.1, 65.0 (C-3,4,5), 61.4 (C-6), 29.8 (C-2), and 21.0, 20.9, 20.8 (3 *Me*CO). Mass spectrum: m/z, 458 (M^+ + 1), 399 (M^+ - NCS), 279 (M^+ - NCS - 2AcOH), and 213 (M^+ - NCS - I -AcOH). *Anal.* Calcd *for* $C_{13}H_{16}INO_7S$: C, 34.15; H, 3.53; N, 3.06. Found: C, 34.47; H, 3.90; N, 3.41.

Eluted second was **10**, m.p. 145-150 °C, $[\alpha]_D$ +110° (c 1, chloroform); υ_{max} 2047, 1746 cm^{-1}. ^1H-n.m.r. (300 MHz, $CDCl_3$): δ 5.18 (bd, 1 H, $J_{3,4}$ 3.2 Hz, $J_{4,5}$ < 1.0 Hz, H-4), 5.16 (d, 1 H, J 9.8 Hz, H-1), 5.05 (dd, 1 H, J 11.6 and 3.2 Hz, H-3), 4.17 (dd, 1 H, J 11.5 and 5.7 Hz, H-6), 4.13-4.07 (m, 2 H, H-2,6'), 4.01 (t, 1 H, J ~ 6.3 Hz, H-5), and 2.12, 2.03, 2.02 (3s, 9 H, 3 Ac). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 170.3, 169.9, 169.3, (3 CO), 144.0 (NCS), 87.2 (C-1), 73.4, 73.3, 66.9 (C-3,4,5), 61.3 (C-6), 27.4 (C-2), and 20.7, 20.6, 20.5 (3 *Me*CO).

3,4-di-O-Acetyl-2-deoxy-2-iodo-α-L-manno- **(11)** *and -β-L-glucopyranosyl isothiocyanates* **(12)**.- Column chromatography (1:4 ether-hexane) of the crude product gave first **11** , isolated as syrup; $[\alpha_D]$ - 115° (c 1, chloroform); υ_{max} 2006, and 1750 cm^{-1}. ^1H-n.m.r. (300 MHz, $CDCl_3$): δ 5.76 (d, 1 H, J 1.7 Hz, H-1), 5.07 (t, 1 H, J 9.5 Hz, H-4), 4.61 (dd, 1 H, J 4.3 and 1.7 Hz, H-2), 4.41 (dd, 9.5 and 4.3 Hz, H-3), 4.0 (dq, 1 H, J 9.6 and 3.5 Hz, H-5), 2.03, 2.01, (2s, 6 H, 2 Ac), and 1.20 (d, 3 H, J 6.3 Hz, H-6). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 169.6, 169.5 (2 CO), 142.9 (NCS), 86.1 (C-1), 71.6, 70.3, 68.8 (C-3,4,5), 29.5 (C-2),

20.9, 20.6 (2 *Me*CO), and 17.4 (C-6). Mass spectrum: *m/z*, 400 (M^+ + 1), 341 (M^+ -NCS), 299 (M^+ - NCS - AcOH), 272 (M^+ - I), and 221 (M^+ - NCS - AcO). *Anal. Calcd for* $C_{11}H_{14}INO_5S$: C, 33.09; H, 3.54; N, 3.51. Found: C, 32.82; H, 3.61; N, 3.52.

Eluted second was **12**, m. p. 62-65 °C; $[\alpha]_D$ - 5° (c 1, chloroform); υ_{max} 2030, 1750 cm^{-1}. ^{1}H-n.m.r (300 MHz, $CDCl_3$): δ 5.17 (dd, 1 H, J 11.0 and 9.1 Hz, H-3), 5.07 (dd, 1 H, J 9.8 Hz, H-1), 4.66 (t, 1 H, J ~ 9.4 Hz, H-4), 3.93 (dd, 1 H, J 11.0 and 9.8 Hz, H-2), 3.63 (dq, 1 H, J 9.8 and 6.2 Hz, H-5), 2.01, 1.95 (2s, 6 H, 2 Ac), and 1.19 (d, 3 H, J 6.2 Hz, H-6). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 169.6, 169.5 (2 CO), 143.6 (NCS), 86.8 (C-1), 75.1, 73.5, 72.7 (C-3,4,5), 29.3 (C-2), 20.8, 20.7, (2 *Me*CO), and 17.4 (C-6) . Mass spectrum: *m/z*, 400 (M^+ + 1), 341 (M^+ - NCS), 299 (M^+ - NCS - AcOH), 281 (M^+ - NCS - AcOH), and 221 (M^+ - NCS - AcO). *Anal. Calcd for* $C_{11}H_{14}INO_5S$: C, 33.09; H, 3.54; N, 3.51. Found: C, 33.34; H, 3.70; N, 3.46.

3,6-di-O-Acetyl-2-deoxy-2-iodo-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-glucopyranosyl isothiocyanate (**13**).- Column chromatography (2:1 ether-hexane) of the crude product gave **13**, m.p. 127-129 °C; $[\alpha]_D$ +33° (c 1, methanol); υ_{max} 1991 and 1758 cm^{-1}; ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 5.79 (d, 1 H, J 2.3 Hz, H-1), 5.15 (*pseudo*-t, 1 H, $J_{2',3'}$ + $J_{3',4'}$ 18.6 Hz, H-3'), 5.03 (*pseudo*-t, 1 H, $J_{3',4'}$ + $J_{4',5'}$ 19.3 Hz, H-4'), 4.92 (dd, 1 H, J 9.4 and 7.8 Hz, H-2'), 4.62 (dd, 1 H, J 7.7 and 4.3 Hz, H-3), 4.60 (d, 1 H, J 8.1 Hz, H-1'), 4.57 (dd, 1 H, J 4.3 and 2.3 Hz, H-2), 4.49 (dd, 1 H, J 12.0 and 1.7 Hz, CH_2OAc), 4.28 (dd, 1 H, J 12.4 and 5.2 Hz, CH_2OAc), 4.10 (dd, 1 H, J 11.8 and 4.4 Hz, CH_2OAc), 4.06 (m, 1 H, CH_2OAc), 4.02 (m, 1 H, H-5), 3.94 (dd, 1 H, J 9.4 and 7.4 Hz, H-4), 3.71 (ddd, 1 H, J 10.5, 5.2 and 2.3 Hz, H-5'), and 2.12, 2.09, 2.07, 2.02, 1.99, 1.97 (6s, 18 H, 6 Ac). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 170.6, 170.2, 170.3, 169.4, 169.1 (6 CO), 144.2 (NCS), 100.9 (C-1'), 85.9 (C-1), 75.3, 72.9, 72.7, 72.0, 71.6, 69.0, 68.9 (C-2',3,3',4,4',5,5'), 62.0, 61.4 (C-6,6'), 29.2 (C-2), and 20.9, 20.8, 20.6 (6 *Me*CO). *Anal. Calcd for* $C_{25}H_{32}INO_{15}S$: C, 40.28; H, 4.33; N, 1.88. Found: C, 39.92; H, 4.56; N, 2.07.

3,6-di-O-Acetyl-2-deoxy-2-iodo-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranosyl isothiocyanate (**14**).- Column chromatography (4:1 ether-hexane) of the crude product gave **14**, m.p. 57-59 °C; $[\alpha]_D$ +47° (c 1, chloroform); υ_{max} 2009, and 1749 cm^{-1}. ^{1}H-n.m.r (300 MHz, $CDCl_3$): δ 5.78 (d, 1 H, J 2.6 Hz, H-1), 5.34 (dd, 1 H, J 3.4 and 1.1 Hz, H-4'), 5.13 (dd, 1 H, J 10.4 and 7.9 Hz, H-2'), 4.97 (dd, 1 H, J 10.4 and 3.4 Hz, H-3'), 4.63 (dd, 1 H, J 7.3 and 4.1 Hz, H-3), 4.60 (dd, 1 H, J 4.1 and 2.6 Hz, H-2), 4.57 (d, 1 H, J 7.9 Hz, H-1'), 4.46 (dd, 1 H, J 12.0 and 1.9 Hz, CH_2OAc), 4.17-3.90 (m, 6 H, H-4,5,5', CH_2OAc and 1 H of CH_2OAc), and 2.13, 2.12, 2.11, 2.04, 1.94 (5s, 18 H, 6 Ac). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 170.5, 170.4, 170.2, 169.3, 169.2 (6 CO), 144.1 (NCS), 101.3 (C-1'), 85.9 (C-1), 75.1, 72.6, 70.9, 70.8, 69.5, 69.2, 66.8 (C-2',3,3',4,4',5,5'), 61.5, 61.2 (C-6,6'), 28.9 (C-2), and 21.0, 20.9, 20.8, 20.6 (6 *Me*CO). Mass spectrum: *m/z*, 687 (M^+ - NCS), 627 (M^+ - NCS - $C_2H_4O_2$), 501 (M^+ - NCS -

I - $C_2H_3O_2$), and 331 (M^+ -$C_{11}H_{13}INO_6S$). *Anal. Calcd. for* $C_{25}H_{32}INO_{15}S$: C, 40.28; H, 4.33; N, 1.88. Found: C, 40.69; H, 4.52; N, 1.71.

3,6-di-O-Acetyl-2-deoxy-2-iodo-4-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-α-D-glucopyranosyl isothiocyanate (**15**).- Column chromatography (3:1 ether-hexane) of the crude product gave **15**, isolated as an amorphous solid m.p. 60-62 °C; $[\alpha_D]$ + 120° (c 0.5, chloroform); υ_{max} 1999, and 1747 cm^{-1}. ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 5.79 (d, 1 H, J 2.2 Hz, H-1), 5.51 (d, 1 H, J 4.1 Hz, H-1'), 5.35 (dd, 1 H, J 10.4 and 9.6 Hz, H-3'), 5.04 (*pseudo*-t, 1 H, $J_{3',4'}$ + $J_{4',5'}$ = 19.7 Hz, H-4'), 4.85 (dd, 1 H, J 10.4 and 4.1 Hz, H-2'), 4.60 (dd, 1 H, J 4.2 and 2.2 Hz, H-2), 4.48 (dd, 1 H, J 12.1 and 1.6 Hz, CH_2OAc), 4.45 (m, 1 H, H-5), 4.24 (dd, 1 H, J 12.5 and 3.8 Hz, CH_2OAc), 4.19 (dd, 1 H, J 12.3 and 4.1 Hz, CH_2OAc), 4.10 (m, 2 H, H-3,4), 4.04 (dd, 1 H, J 12.5 and 2.3 Hz, CH_2OAc), 3.97 (ddd, 1 H, J 10.3, 3.6 and 2.4 Hz, H-5), and 2.12, 2.09, 2.06, 2.01, 1.99, 1.97 (6s, 18 H, 6 Ac). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 170.5, 170.4, 170.2, 169.9, 169.7, 169.4 (6 CO), 144.5 (NCS), 95.9 (C-1'), 85.7 (C-1), 72.2, 71.8, 71.6, 70.2, 69.4, 68.8, 67.9 (C-2',3,3',4,4',5,5'), 62.2, 61.4 (C-6,6'), 28.5 (C-2), and 21.1, 20.8, 20.6 (6 *Me*CO). Mass spectrum: *m/z*, 687 (M^+ - NCS), 627 (M^+ - NCS - $C_2H_4O_2$), 501 (M^+ - NCS- I - $C_2H_3O_2$), and 331 (M^+ - $C_{11}H_{13}INO_6S$); *Anal. Calcd for* $C_{25}H_{32}INO_{15}S$: C, 40.28; H, 4.33; N, 1.88. Found: C, 39.80; H, 4.27; N, 1.74.

Reaction of 2-Deoxy-2-Iodoglycopyranosyl Isothiocyanates* 7, 8, 11 *and* 13-15 *with Ammonia. General Procedure.- Anhydrous ammonia was bubbled through a solution of the iodothiocyanate (**7, 8, 11, 13-15**) in anhydrous benzene (25 mL) in a water-ice bath until t.l.c. (ether) showed the complete disappearance of the starting material. The mixture was warmed at room temperature and the benzene was removed *in vacuo* to give a crude product that was purified by column chromatography. The following amounts and conditions were used:

Starting compound (g)	Benzene (mL)	Time (min)	Product (g, %)
7 (0.22)	20	20	**16** (0.20, 90)
8 (0.20)	20	40	**18** (0.14, 68)
11 (0.43)	40	30	**17** (0.43, ~100)
13 (0.20)	25	40	**23** (0.10, 49)
14 (0.20)	25	40	**24** (0.14, 67)
15 (0.20)	25	40	**25** (0.13, 64)

2-Ammonio-3',4',6'-tri-O-acetyl-α-D-glucopyrano[1',2':4,5]-2-thiazoline Iodide (16).- Column chromatography (ethyl acetate) yielded **16** as a pale yellow solid, m. p. 83-86 °C; $[\alpha]_D$ +64° (c 1, methanol); υ_{max} 3420, 1745, 1619 cm^{-1}. ^{1}H-n.m.r (300 MHz, DMSO-d_6): δ 9.75, 8.75 (2 bs, 3 H, NH_3), 5.97 (d, 1 H, J 6.3 Hz, H-1'), 5.23 (dd, 1 H, J 7.2 and 6.8 Hz, H-3'), 4.97 (dd, 1 H, J 8.8 and 7.2 Hz, H-4'), 4.33 (dd, 1 H, J 6.8 and 6.3 Hz, H-2'), 4.24 (dd, 1 H, J 12.0 and 4.9 Hz, CH_2OAc), 4.13 (m, 1 H, H-5'), 4.08 (dd, 1 H, J 12.0 and 2.4 Hz, CH_2OAc), and 2.07, 2.04, 2.03 (3s, 9 H, 3 Ac). ^{13}C-n.m.r. (75 MHz, DMSO-d_6): δ 170.8, 170.0, 169.5, 169.3 (C-2, 3 CO), 86.5 (C-1'), 71.8, 69.6, 66.9 (C-3',4'5'), 62.0 (C-6'), 46.9 (C-2'), 20.6 (3 *Me*CO). Mass spectrum: *m/z*, 329 (M^+ - HI - NH_3), 287 (M^+ - IH - 2AcOH), 227 (M^+ + 1 - HI - 2AcOH), *Anal. Calcd for* $C_{13}H_{19}IN_2O_7S$: C, 32.92; H, 4.04; N 5.91. Found: C; 33.69; H, 4.37; N, 5.85.

N-(3,4,6-tri-O-Acetyl-2-deoxy-2-iodo-α-D-talo-pyranosyl)thiourea (**18**) *and 2-Ammonio-3',4',6'-tri-O-Acetyl-5'-methyl-α-glucopyrano[1',2':4,5]-2-thiazoline Iodide* (**19**).- The crude product was crystallized from ether to give **18**, m. p. 109-110 °C; $[\alpha]_D$ +85° (c 1, chloroform); υ_{max} 3333, 1748, 1620 and 1552 cm^{-1}. ^{1}H-n.m.r. (300 MHz, DMSO-d_6) (The spectrum was registred inmediately after the sample was dissolved): δ 8.35 (d, 1 H, J 8.8 Hz, NH), 7.36 (bs, 2 H, NH_2), 6.00-5.84 (broad signal, H-1), 5.38 (t, 1 H, J 3.2 Hz, H-3), 5.18 (dd, 1 H, J 5.5 and 3.1 Hz, H-4), 4.61 (dd, 1 H, J 8.8 and 3.3 Hz, H-2), 4.49 (dd, 1 H, J 11.4 and 8.0 Hz, H-6), 4.28 (m, 1 H, H-5), 4.21 (dd, 1 H, J 11.4 and 3.3 Hz, H-6'), and 2.12, 1.99 (2s, 9 H, 3 Ac). ^{13}C-n.m.r. (75 MHz, DMSO-d_6): δ 170.0, 169.9, 169.7 (3 CO), 78.8 (C-1), 71.2 (C-5), 70.0 (C-3), 66.4 (C-4), 60.7 (C-6), 26.0 (C-2), and 20.9, 20.6 (3 *Me*CO). Mass spectrum: *m/z*, 475 (M^+ + 1), 347 (M^+ - I), and 287 (M^+ - I - AcOH), *Anal. Calcd for* $C_{13}H_{19}IN_2O_7S$: C, 32.92; H, 4.04; N 5.91. Found: C; 33.06; H, 4.27; N, 5.58. When a solution of **18** in dimetilsulfoxide was stored at room temperature for 12 h the formation of compound **19** was detected by n.m.r. The resonances corresponding to this product are: ^{1}H-n.m.r. (300 MHz, DMSO-d_6): δ 6.02 (d, J 5.7 Hz, H-1'), 5.29 (bs, H-4), 5.18 (dd, J 9.4 and 3.1 Hz, H-3'), 4.47 (m, H-5'), 4.30-4.10 (m, CH_2OAc), 4.07 (dd, J 9.4 and 5.7 Hz, H-2'), and 2.11, 2.01, 2.00 (3s, 3 Ac). ^{13}C-n.m.r. (75 MHz, DMSO-d_6): δ 175.9, 170.0, 169.9, 169.3 (C-2, 3 CO), 88.0 (C-1'), 72.2, 69.2, 66.1 (C-3',4',5'), 61.3 (C-6'), 45.0 (C-2'), and 20.5, 20.3 (3 *Me*CO).

2-Ammonio-3',4'-di-O-acetyl-5'-methyl-α-L-glucopyrano-[1',2':4,5]-2-thiazoline Iodide (**17**).- The crude product was crystallized from ether to give **17**, m.p. 111-113 °C; $[\alpha]_D$ - 56° (c 1, methanol); υ_{max} 3370, 3186, 1752, 1625 and 1505 cm^{-1} ^{1}H-n.m.r. (300 MHz, DMSO-d_6): δ 9.7-9.5 (bs, 3 H, NH_3), 5.94 (d, 1 H, J 6.3 Hz, H-1'), 5.19 (dd, 1 H, J 7.8 and 7.3 Hz, H-3'), 4.69 (dd, 1 H, J 9.1 and 7.8 Hz, H-4'), 4.27 (dd, 1 H, J 7.3 and 6.3 Hz, H-2'), 4.00, (dq, 1 H, J 9.1 and 6.2 Hz, H-5'), 2.03, 2.01 (2s, 6 H, 2 Ac), and 1.17 (d, 3 H, J 6.2 Hz, H-6'). ^{13}C-n.m.r (75 MHz, DMSO-d_6): δ 169.4, 169.3 (C-2, 2 CO), 87.2 (C-1'), 72.3 (C-3'), 71.8 (C-4'), 67.4 (C-5'), 46.7 (C-2'), 20.4 (2 *Me*CO), and 17.2 (C-6'). Mass spectrum: *m/z*, 417

(M^+ + 1), 289 (M^+ - I), 229 (M^+ - I - AcOH), and 169 (M^+ - I - 2AcOH). *Anal. Calcd for* $C_{11}H_{17}IN_2O_5S$: C, 31.74; H, 4.12; N, 6.73. Found: C, 31.54; H, 4.15; N, 7.05.

2-Ammonio-3',6'-di-O-acetyl-4'-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-glucopyrano[1',2':4,5]-2-thiazoline Iodide (**23**).- Column chromatography (ethyl acetate- hexane, 4:1) yielded **23** as a solid. m. p. 129-132 °C; $[\alpha]_D$ +11° (c 1, methanol); υ_{max} 3426, 1747, 1619 and 1551 cm^{-1}. ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 6.07 (d, 1 H, J 7.0 Hz, H-1'), 5.48 (*pseudo*-t, 1 H, $J_{3',2'}$ + $J_{3',4'}$ 10.2 Hz, H-3'), 5.16 (*pseudo*-t, 1 H, $J_{3'',2''}$ + $J_{3'',4''}$ = 18.6 Hz, H-3''), 5.10 (*pseudo*-t, 1 H, $J_{3'',4''}$ + $J_{4'',5''}$ = 19.2 Hz, H-4''), 4.91 (dd, 1 H, J 9.3 and 8.1 Hz, H-2''), 4.66 (d, 1 H, J 8.0 Hz, H-1''), 4.40-3.70 (several m, 8 H, H-2',4',5',5'', 2 CH_2OAc), and 2.14, 2.12, 2.08, 2.04, 1.99 and 1.97 (6s, 18 H, 6 Ac). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 183.8 (C-2), 172.3, 170.9, 170.8, 169.9, 169.7, 169.5 (6 CO), 101.6 (C-1''), 86.8 (C-1'), 76.2, 72.8, 72.2, 71.4, 70.8, 70.2, 67.9 (C-2'',3',3'',4',4'',5',5''), 62.3, 61.5 (C-6',6''), 46.1 (C-2'), and 21.3, 21.0, 20.8, 20.6 (6 *Me*CO). *Anal. Calcd for* $C_{25}H_{33}IN_2O_{15}S$: C, 39.38; H, 4.63; N 3.67. Found: C; 39.70; H, 4.82; N, 3.88.

2-Ammonio-3',6'-di-O-acetyl-4'-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyrano-[1',2':4,5]-2-thiazoline Iodide (**24**).- Column chromatography (ethyl acetate-hexane, 4:1) yielded **24** as a solid .m.p. 110-113 °C; $[\alpha]_D$ + 31° (c 1, methanol); υ_{max} 3347, 1748, and 1649 cm^{-1}. ^{1}H-n.m.r. (500 MHz, $CDCl_3$): δ 6.70 (bs, 3 H, NH_3), 6.03 (d, 1 H, J 6.9 Hz, H-1'), 5.42 (*pseudo*-t, 1 H, $J_{2',3'}$ + $J_{3',4'}$ = 10.5 Hz, H-3'), 5.39 (bd, 1 H, J ~ 3.4 Hz, H-4''), 5.10 (dd, 1 H, J 10.3 and 7.9 Hz, H-2''), 5.01 (dd, 1 H, J 10.4 and 3.4 Hz, H-3''), 4.61 (d, 1 H, J 7.9 Hz, H-1''), 4.43-3.77 (several m, 8 H, H-2',4',5',5'', 2 CH_2OAc), and 2.19, 2.18, 2.15, 2.09, 2.06, 1.98 (6 s, 18 H, 6 Ac). ^{13}C-n.m.r (125.75 MHz, $CDCl_3$): δ 184.0 (C-2), 170.7, 170.4, 170.1, 169.9, 169.6, 169.5 (6 CO), 101.8 (C-1''), 86.9 (C-1'), 75.8, 71.0, 70.9, 70.6, 69.9, 68.8, 66.7 (C-2'',3',3'',4',4'',5',5''), 62.2, 60.9 (C-6',6''), 46.1 (C-2'), and 21.1, 20.9, 20.8, 20.7, 20.6, 20.4 (6 *Me*CO). *Anal. Calcd for* $C_{25}H_{35}IN_2O_{15}S$: C, 39.38; H, 4.63; N, 3.67. Found: C, 40.02; H, 4.98; N, 3.53.

2-Ammonio-3',6'-di-O-acetyl-4'-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-α-D-glucopyrano-[1',2':4,5]-2-thiazoline Iodide (**25**).- Column chromatography (ethyl acetate- hexane, 4:1) yielded **25** as a solid. m. p. 114-117 °C; $[\alpha]_D$ +93° (c 1, chloroform); υ_{max} 3461, 1747, 1646, and 1564 cm^{-1}. ^{1}H-n.m.r. (500 MHz, $CDCl_3$): δ 6.38 (d, 1 H, J 7.1 Hz, H-1'), 5.53 (d, 1 H, J 4.0 Hz, H-1''), 5.40 (*pseudo*-t, 1 H, $J_{2'',3''}$ + $J_{3'',4''}$ = 19.7 Hz, H-3''), 5.12 (*pseudo*-t, 1 H, $J_{2',3'}$ + $J_{3',4'}$ = 5.1 Hz, H-3'), 5.04 (*pseudo*-t, 1 H, $J_{4'',3''}$ + $J_{4'',5''}$ = 19.7 Hz, H-4''), 4.88 (dd, 1 H, J 10.2 and 4.0 Hz, H-2''), 4.28 (dd, 1 H, J 12.1 and 6.4 Hz, CH_2OAc), 4.24 (dd, 1 H, J 12.1 and 3.0 Hz, CH_2OAc), 4.19 (dd, 1 H, J 12.4 and 4.8 Hz, CH_2OAc), 4.10 (m, 1 H, H-5'), 4.07 (dd, 1 H, J 12.4 and 2.2 Hz, CH_2OAc), 3.95 (ddd, 1 H, J 10.2, 4.7 and 2.2 Hz, H-5''), 3.88 (ddd, 1 H, J 7.1, 3.1 and 1.3 Hz, H-2'), 3.82 (dt, 1 H, J 7.9, 2.0 and 1.3 Hz, H-4'), and 2.17, 2.10, 2.09, 2.06,

2.00, 1.99 (6s, 18 H, 6 Ac). ^{13}C-n.m.r. (125.75 MHz, $CDCl_3$): δ 182.3 (C-2), 170.3, 170.3, 170.1, 169.3, 169.2 (6 CO), 94.6 (C-1''), 80.2 (C-1'), 72.4, 70.1, 70.0, 69.7, 68.9, 68.2, 68.0 (C-2'',3',3'',4',4'',5',5''), 62.9, 61.6 (C-6',6''), 40.7 (C-2') and 20.6, 20.5, 20.4 (6 *Me*CO). *Anal. Calcd for* $C_{25}H_{35}IN_2O_{15}S$: C, 39.28; H, 4.63 N 3.67. Found: C; 39.02; H, 4.37; N, 3.89.

Synthesis of Thiazolidin-2-one* (26-28). *General Procedure.- A mixture of the corresponding 2-amino-2-thiazoline iodide (**23-25**) (0.1 g) and silica (1.0 g) in ethyl acetate-H_2O (25 mL : 1 mL) was heated under reflux for 1 h. The silica was filtered and washed with ethyl acetate (15 mL). The organic solution was washed with water (5 mL), dried and concentrated. Column chromatography of the crude product (ethyl acetate-hexane 4:1) gave **26** (0.05 g, 60%), **27** (0.058 g, 69%) and **28** (0.055 g, 66%), respectively.

3',6'-di-O-Acetyl-4'-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-glucopyrano-[1',2':4,5]-thiazolidin-2-one (**26**).- m.p. 96-97 °C; $[\alpha]_D$ +52° (c 1, chloroform); υ_{max} 3465, 1748, and 1640 cm^{-1}. ^{1}H-n.m.r. (400 MHz, $CDCl_3$): δ 5.76 (d, 1 H, J 6.1 Hz, H-1'), 5.24 (*pseudo*-t, 1 H, $J_{3',2'} + J_{3',4'}$ = 15.7 Hz, H-3'), 5.13 (*pseudo*-t, 1 H, $J_{3'',4''} + J_{3'',2''}$ = 19.6 Hz, H-3''), 5.06 (*pseudo*-t, 1 H, $J_{4'',3''} + J_{4'',5''}$ = 19.1 Hz, H-4''), 4.90 (*pseudo*-t, 1 H, $J_{2'',3''} + J_{2'',1''}$ = 17.3 Hz, H-2''), 4.54 (d, 1 H, J 8.0 Hz, H-1''), 4.48 (bd, 1 H, J 10.6 Hz, CH_2OAc), 4.35 (dd, 1 H, J 12.5 and 4.3 Hz, CH_2OAc), 4.12 (dd, 1 H, J 12.1 and 4.9 Hz, CH_2OAc), 4.10-3.95 (m, 2 H, CH_2OAc, H-5' or H-5''), 3.80 (*pseudo*-t, 1 H, $J_{2',1'} + J_{2',3'}$ = 14.1 Hz, H-2'), 3.86 (dd, 1 H, J 9.5 and 7.6 Hz, H-4'), 3.85 (m, 1 H, H-5'' or H-5'), and 2.13, 2.07, 2.02, 1.99, 1.96 (6 s, 18 H, 6 Ac). ^{13}C-n.m.r (100 MHz, $CDCl_3$): δ 170.5, 170.2, 169.4, 169.3 (6 CO), 101.1 (C-1''), 76.5, 73.6, 72.9, 72.0, 71.4, 70.3, 67.9 (C-2'',3',3'',4',4'',5',5''), 62.5, 61.6 (C-6',6''), 51.5 (C-2'), and 20.7, 20.6, 20.5 (6 *Me*CO). *Anal. Calcd for* $C_{25}H_{33}NO_{16}S$: C, 47.24; H, 5.23; N, 2.20. Found: C, 46.87; H, 5.32; N, 2.46.

3',6'-di-O-Acetyl-4'-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyrano-[1',2':4,5]-thiazolidin-2-one (**27**).- m.p. 105-108 °C; $[\alpha]_D$ +43° (c 1, chloroform); υ_{max} 3462, 1748, and 1641 cm^{-1}. ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 5.69 (d, 1 H, J 6.0 Hz, H-1'), 5.34 (dd, 1 H, J 3.4 and 0.9 Hz, H-4''), 5.19 (*pseudo*-t, 1 H, $J_{2',3'} + J_{3',4'}$ = 16.4 Hz, H-3'), 5.05 (dd, 1 H, J 10.4 and 7.8 Hz, H-2''), 4.92 (dd, 1 H, J 10.4 and 3.4 Hz, H-3''), 4.46 (d, 1 H, J 7.8 Hz, H-1''), 4.42 (dd, 1 H, J 11.5 and 2.0 Hz, CH_2OAc), 4.20-4.00 (m, 5 H, H-4',5', CH_2OAc and 1 H of CH_2OAc), 3.85 (dt, 1 H, J ~ 7.2 and 0.9 Hz H-5''), 3.69 (dd, 1 H, J 8.4 and 6.0 Hz, H-2'), and 2.13, 2.11, 2.06, 2.03, 2.02, 1.93 (6 s, 18 H, 6 Ac). ^{13}C-n.m.r (75 MHz, $CDCl_3$): δ 170.5, 170.4, 170.2, 170.1, 169.7, 169.2, (6 CO), 161.2 (NHCO), 101.3 (C-1''), 97.1 (C-1'), 76.1, 74.4, 71.0, 70.8, 69.8, 69.0, 66.8 (C-2'',3',3'',4',4'',5',5''), 62.5, 60.9 (C-6',6''), 52.6 (C-2'), and 21.1, 21.0, 20.7, 20.5 (6 *Me*CO). *Anal. Calcd for* $C_{25}H_{33}NO_{16}S$: C, 47.24; H, 5.23; N, 2.20. Found: C, 47.56; H, 5.07; N, 1.93.

3',6'-di-O-acetyl-4'-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-α-D-glucopyrano-[1',2':4,5]-thiazolidin-2-one (**28**).- m.p. 83-86 °C; $[\alpha]_D$ +114° (c 1, chloroform) ; υ_{max} 3462, 1748, and 1641 cm^{-1}. ^{1}H-n.m.r. (400 MHz, $CDCl_3$): δ 5.75 (d, 1 H, J6.3 Hz, H-1'), 5.43 (*pseudo*-t, 1 H, $J_{3'',4''} + J_{3'',2''}$ = 19.9 Hz, H-3''), 5.28 (d, 1 H, J 3.8 Hz, H-1''), 5.20 (*pseudo*-t, 1 H, $J_{3',2'} + J_{3',4'}$ = 14.0 Hz, H-3'), 5.03 (*pseudo*-t, 1 H, $J_{4'',3''} + J_{4'',5''}$ = 19.6 Hz, H-4''), 4.84 (dd, 1 H, J 10.5 and 3.8 Hz, H-2''), 4.42 (dd, 1 H, J 12.2 and 3.0 Hz, CH_2OAc), 4.27 (dd, 1 H, J 12.1 and 4.7 Hz, CH_2OAc), 4.21 (dd, 1 H, J 12.4 and 4.2 Hz, CH_2OAc), 4.07-3.99 (m, 3 H, H-5',5'' and 1 H of CH_2OAc,), 3.80-3.75 (m, 2 H, H-2',4'), and 2.11, 2.07, 2.07, 2.05, 2.00, 1.97 (6 s, 18 H, 6 Ac). ^{13}C-n.m.r (100 MHz, $CDCl_3$): δ 170.7, 170.6, 170.5, 170.1, 170.0, 169.5 (6 CO), 161.6 (NHCO), 97.0, 96.1 (C-1',1''), 75.0, 73.9, 70.3, 69.5, 68.5, 68.1 (C-2'',3',3'',4',4'',5',5''), 63.4, 61.7 (C-6',6''), 52.8 (C-2'), and 20.8, 20.7, 20.6 (6 *Me*CO). *Anal. Calcd for* $C_{25}H_{33}NO_{16}S$: C, 47.24; H, 5.23; N, 2.20. Found: C, 46.78; H, 5.15; N, 2.46.

***Synthesis of 2'-Deoxy-glycosyl Thioureas* 21, 22, and 29-31. *General Procedure.*-** A solution of the corresponding 2-deoxy-2-iodoglycosyl isothiocyanate (**7**, **8**) (0.3 g), Bu_3SnH (1.2 equiv.) and α,α'-azobis(isobutyronitrile) (~ 10 mg) in dry ether (25 mL) was boiled under nitrogen atmosphere until reaction was complete (t.l.c), and the mixture was then concentred. Anhydrous ammonia was bubbled through a solution of the crude product in anhydrous bencene (10 mL) at 0 °C for 20 min. Processing (as described above for **16-18** and **23-25**) and column chromatography (ethyl acetate for **21**, **22**, and ethyl acetate-hexane 2:1) for **29-31**) of the product gave **21** (160 mg, 70%), **22** (70 mg, 31 %), **29** (0.12 g, 47%), **30** (0.10 g, 39%), and **31** (0.17 g, 66%), respectively.

N-(3',4',6'-tri-O-Acetyl-2-deoxy-α-D-arabinohexopyranosyl) thiourea (**21**).- m.p. 209-210 °C; $[\alpha]_D$ +56° (c 1, chloroformm); υ_{max} 3385, 3279, 3173, 1742, 1628 and 1513 cm^{-1}. ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 6.8, 6.5 (2 bs, 3 H, NH, NH_2), 5.34 (m, 1 H, H-1), 5.13 (ddd, 1 H, J 11.4, 9.2 and 5.1 Hz, H-3), 5.00 (t, 1 H, J ~ 9.3 H, H-4), 4.25 (dd, 1 H, J 12.4 and 5.4 Hz, H-6), 4.10 (dd, 1 H, J 12.4 and 2.2 Hz, H-6'), 4.03 (ddd, 1 H, J 9.5, 5.4 and 2.2 Hz, H-5), 2.29 (ddd, 1 H, J 14.0, 5.1 and 1.4 Hz, H-2), 2.07, 2.06, 2.04 (3s, 9 H, 3 Ac), and 2.01 (ddd, 1 H, J 14.0, 11.4 and 5.3 Hz, H-2'). (300 MHz, DMSO-d_6): 8.72 (d, 1H, J 8.3 Hz, NH), 7.90, 6.90 (2bs, 2 H, NH_2), 5.85 (bs, 1 H, H-1), 5.32 (m, 1 H, H-3), 4.79 (t, 1 H, J ~ 9.3 Hz, H-4), 4.18 (dd, 1 H, J 12.2 and 4.4 Hz, H-6), 3.92 (dd, 1 H, J 12.2 and 2.7 Hz, H-6'), 3.78 (ddd, 1 H, J 9.6, 4.4 and 2.7 Hz, H-5), 2.05-1.80 (m, 2 H, H-2,2'), and 1.99, 1.98, 1.97 (3s, 9 H, 3 Ac). ^{13}C-n.m.r. ($CDCl_3$): δ 78.9 (C-1), 69.3, 68.4, 68.3 (C-3,4,5), 62.0 (C-6), 33.2 (C-2), and 21.0, 20.8, 20.7 (3 *Me*CO). ^{13}C-n.m.r. (DMSO-d_6): δ 183.6 (CS)), 170.3, 169.9, 169.6 (3 CO), 77.4 (C-1), 69.4, 68.6, 68.5 (C-3,4,5), 62.3 (C-6), 33.4 (C-2), and 20.9, 20.8, 20.7 (3 *Me*CO) . Mass spectrum: *m/z*, 349 (M^+ + 1), 289 (M^+ - AcO), and 213 (M^+ - AcOH - $NHCSNH_2$), *Anal. Calcd for* $C_{13}H_{20}N_2O_7S$: C, 44.82; H, 5.78; N 8.04. Found: C; 44.78; H, 5.69; N, 8.03.

N-(3',4',6'-tri-O-Acetyl-2-deoxy-α-D-lyxohexopyranosyl) thiourea (**22**).- m.p. 178-180 °C; $[\alpha]_D$ +90° (c 1, chloroform); υ_{max} 3372, 3262, 3159, 1750, 1735, 1629 and 1510 cm^{-1}. ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 7.1, 6.5 (2 bs, 3 H, NH, NH_2), 5.44 (bs, 1 H, H-1), 5.33 (bs, 1 H, H-4), 5.22 (ddd, 1 H, J 12.6, 4.9 and 2.6 Hz, H-3), 4.20 (m, 1 H, H-5), 4.14 (dd, 1 H, J 11.5 and 7.4 Hz, H-6), 4.06 (dd, 1 H, J 11.5 and 5.8 Hz, H-6'), 2.26 (ddd, 1 H, J 13.6, 12.6 and 4.9, H-2), 2.13, 2.04, 2.00 (3 s, 9 H, 3 Ac), and 1.93 (bdd, 1 H, J 13.6 and 5.2 Hz, H-2'). (300 MHz, DMSO-d_6): 8.70 (d, 1 H, J 8.5 Hz, NH), 7.90, 6.90 (2 bs, 2 H, NH_2), 5.80 (bs, 1 H, H-1), 5.20 (m, 1 H, H-3), 5.32 (bs, H-4), 4.10-3.90 (m, 3 H, H-5,6,6'), 2.10, 1.98, 1.95 (3 s, 9 H, 3 Ac) and 2.10-1.65 (m, 2 H, H-2,2'). ^{13}C-n.m.r. ($CDCl_3$): δ 185.5 (CS), 170.5, 170.1, 170.0 (3 CO), 79.7 (C-1), 68.3, 66.2, 65.4 (C-3,4,5), 62.5 (C-6), 28.7 (C-2), and 20.8, 20.7, 20.6 (3 *Me*CO). ^{13}C-n.m.r. (DMSO-d_6): δ 183.3 (CS), 170.1, 170.0, 169.5 (3 CO), 77.9 (C-1), 67.0, 65.9, 65.8 (C-3,4,5), 61.9 (C-6), 28.5, (C-2), and 20.6, 20.5 (3 *Me*CO). Mass spectrum: *m/z*, 349 (M^+ + 1), 289 (M^+ - AcO), and 213 (M^+- AcOH - $NHCSNH_2$), *Anal. Calcd for* $C_{13}H_{20}N_2O_7S$: C, 44.82; H, 5.78; N 8.04. Found: C; 45.18; H, 5.78; N, 8.04.

N-[3',6'-di-O-Acetyl-2-deoxy-4'-O-(2,3,4,6-tetra-O-acetyl--β-D-glucopyranosyl)-α-D-arabinohexopyranosyl] thiourea (**29**).- m.p. 108-110 °C; $[\alpha]_D$ +15° (c 1, chloroform); υ_{max} 3581, 3406, 3338, 1747, 1619 and 1511 cm^{-1}. ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 6.90 (bs, 1 H, NH), 6.50 (bs, 2 H, NH_2), 5.33 (m, 1 H, H-1'), 5.20-5.13 (m, 1 H, H-3'), 5.17 (t, 1 H, J ~ 9.3 Hz, H-3''), 5.08 (*pseudo*-t, 1 H, J ~ 9.5 Hz, H-4''), 4.93 (dd, 1 H, J 9.3 and 7.9 Hz, H-2''), 4.58 (d, 1 H, J 8.0 Hz, H-1''), 4.41 (dd, 1 H, J 12.1 and 2.3 Hz, CH_2OAc), 4.33 (dd, 1 H, J 12.4 and 4.4 Hz, CH_2OAc), 4.16 (dd, 1 H, J 12.0 and 5.7 Hz, CH_2OAc), 4.07 (dd, 1 H, J 12.4 and 2.3 Hz, CH_2OAc), 3.92 (ddd, 1 H, J ~ 9.0, 5.7 and 2.3 Hz, H-5'), 3.70-3.63 (m, 2 H, H-4',5''), 2.25-2.18 (m, 1 H, H-2'), 2.10, 2.08, 2.05, 2.04, 2.01, 1.99 (6s, 18 H, 6 Ac), and 1.98-1.88 (m, 1 H, H-2'); (300 MHz, DMSO-d_6): δ 8.68 (d, 1 H, J 8.6 Hz, NH), 7.80 (bs, 1 H, NH_2), 6.90 (bs, 1 H, NH_2), 5.58 (m, 1 H, H-1'), 5.30 (*pseudo*-t, 1 H, J ~ 9.5 Hz, H-3''), 5.20 (m, 1 H, H-3'), 4.88 (*pseudo*-t, 1 H, J ~ 9.7 Hz, H-4''), 4.86 (d, 1 H, J 8.0 Hz, H-1''), 4.66 (dd, 1 H, J 9.7 and 8.1 Hz, H-2''), 4.26-3.56 (several m, 7 H, H-4',5',5'', 2 CH_2OAc), 2.10-1.80 (m, 2 H, H-2',2'), and 2.05-1.91 (6 s, 18 H, 6 Ac). ^{13}C-n.m.r. (75 MHz, DMSO-d_6): δ 185.0 (CS), 170.2, 170.0, 169.5, 169.4, 169.1, 169.0 (6 CO), 99.3 (C-1''), 76.8 (C-1'), 72.0, 71.1, 70.2, 69.0, 68.5, 67.7 (C-2'',3',3'',4',4'',5',5''), 62.3, 61.6 (C-6',6''), 32.8 (C-2'), and 20.9-20.5 (6 peak, 6 *Me*CO). Mass spectrum: *m/z*, 637 (M^+ + 1), 501 (M^+ - $NHCSNH_2$ - $C_2H_4O_2$), 441 (M^+ - $NHCSNH_2$ - $2C_2H_4O_2$), 381 (M^+ - $NHCSNH_2$ - $2C_2H_4O_2$), and 331 (M^+ - $C_{11}H_{17}N_2O_6S$).

N-[3',6'-di-O-Acetyl-2-deoxy-4'-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-arabinohexopyranosyl] thiourea (**30**).- m.p. 106-109 °C; $[\alpha]_D$ +40° (c 1, chloroform); υ_{max} 3580, 3334, 1747, and 1619 cm^{-1}. ^{1}H-n.m.r. (300 MHz, $CDCl_3$): δ 6.75 (bs, 3 H, NH_2, NH), 5.32 (bd, 1 H, J ~ 2.6 Hz, H-4''), 5.30 (m, 1 H, H-1'), 5.22 (m, 1 H, H-3'), 5.07 (dd, 1 H, J 10.4 and 7.8 Hz, H-2''), 4.96 (dd, 1 H, J 10.4 and 3.3 Hz,

H-3''), 4.52 (d, 1 H, J 7.8 Hz, H-1''), 4.35 (dd, 1 H, J 12.0 and 2.2 Hz, CH_2OAc), 4.18-1.08 (m, 2 H, CH_2OAc), 4.03 (dd, 1 H, J 11.1 and 7.2 Hz, CH_2OAc), 3.90-3.82 (m, 2 H, H-5',5''), 3.65 (*pseudo*-t, 1 H, J ~ 8.5 Hz, H-4'), 2.28-2.18 (m, 1 H, H-2'), 2.12, 2.07, 2.04, 2.03, 2.02, 1.93 (6 s, 18 H, 6 Ac), and 2.00-1.85 (m, 1 H, H-2'). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 184.5 (CS), 170.6-169.4 (6 peak, 6 CO), 100.9 (C-1''), 78.1, 76.2, 70.8, 70.6, 69.8, 69.0, 68.7, 66.7 (C-1',2'',3',3'',4',4'',5',5''), 62.1, 60.9 (C-6',6''), 32.6 (C-2'), and 21.1, 20.9, 20.7, 20.6, 20.5 (6 *Me*CO). Mass spectrum: *m/z*, 637 (M^+ + 1), 501 (M^+ - $NHCSNH_2$ - $C_2H_4O_2$), 441 (M^+ - $NHCSNH_2$ - $2C_2H_4O_2$), 381 (M^+ - $NHCSNH_2$ - $3C_2H_4O_2$), and 331 (M^+ - $C_{11}H_{17}N_2O_6S$).

N-[3',6'-di-O-Acetyl-2-deoxy-4'-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl)-α-D-arabinohexopyranosyl] thiourea (**31**).- m.p. 105-107 °C; $[\alpha]_D$ +95° (c 1, chloroform); υ_{max} 3445, 1746, and 1620 cm^{-1}. ^{1}H-n.m.r. (300 MHz, DMSO-d_6): δ 8.70 (d, 1 H, J 8.9 Hz, NH), 7.65 (bs, 1 H, NH_2), 6.70 (bs, 1 H, NH_2), 5.65 (m, 1 H, H-1'), 5.39 (d, 1 H, J 3.9 Hz, H-1''), 5.26 (*pseudo*-t, 1 H, J ~ 10.0 Hz, H-3''), 5.13 (m, 1 H, H-3'), 4.99 (*pseudo*-t, 1 H, J ~ 9.8 Hz, H-4''), 4.87 (dd, 1 H, J 10.5 and 3.9 Hz, H-2''), 4.30-3.70 (several m, 7 H, H-4',5',5'', and 2 CH_2OAc), 2.10-1.93 (m, 2 H, H-2',2'), and 2.04-1.95 (5s, 18 H, 6 Ac); (300 MHz, $CDCl_3$): δ 7.00 (bs, NH), 6.60 (bs, 2 H, NH_2), 5.54 (d, 1 H, H-1''), 5.35 (*pseudo*-t, 1 H, J ~ 10 Hz, H-3''), 5.32 (m, 1 H, H-1'), 5.07 (m, 1 H, H-3'), 5.05 (*pseudo*-t, 1 H, J ~ 9.9 Hz, H-4''), 4.84 (dd, 1 H, J 10.4 and 4.0 Hz, H-2''), 4.44-4.00 (several m, 6 H, H-5',5'', 2 CH_2OAc), 3.85 (*pseudo*-t, 1 H, J ~ 8.5 Hz, H-4'), 2.26 (ddd, 1 H, J 14.0, 5.0 and 2.1 Hz, H-2'), 2.11-2.00 (6 s, 18 H, 6 Ac), and 1.86 (m, 1 H, H-2'). ^{13}C-n.m.r. (75 MHz, $CDCl_3$): δ 185.0 (CS), 170.4-169.4 (6 peak, 6 CO), 95.6 (C-1''), 78.2 (C-1'), 72.7, 71.4, 70.3, 69.6, 69.4, 68.6, 68.1 (C-2'',3',3'',4',4'',5',5''), 62.5, 61.4 (C-6',6''), 32.6 (C-2'), 21.0-20.4 (6 peak, 6 *Me*CO). Mass spectrum: *m/z*, 637 (M^+ + 1), 501 (M^+ - $NHCSNH_2$ - $C_2H_4O_2$), 441 (M^+ - $NHCSNH_2$ - $2C_2H_4O_2$), and 331 (M^+ - $C_{11}H_{17}N_2O_6S$).

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REFERENCES

1. For recent reviews see (a) Paulsen, H. *Angew. Chem. Int.. Ed. Engl.*, **1982**, *21*, 155. (b) *Ibid. Chem.*

Soc. Rev. **1984**, *15*, 15. (c) Schmidt, R. R. *ibid.*, **1986**, *25* , 212. (d) Fügedi, P.; Gareg, P. J.; Lönn, H.; Norberg, T. *Glycoconjugate J.*, **1987**,*4*, 97; (e) Okamoto, K.; Goto, T. Tetrahedron, **1990**, *46*, 5835. (f) Paulsen, H. *Angew. Chem. Int. Ed. Engl.*, **1990**, *29*, 823. (g) Kunz, H. *Ibid.*, **1987**, *26*, 294. (h) Sinaÿ, P. *Pure Appl. Chem.* **1991**, *63*, 519. (i) Banoub, J; Boullanger,; Lafont, D. *Chem. Rev.* **1992**, *34*, 243. (j) Toshima, K. and Tatsuta, K. *Chem. Rev.* **1993**, *93*, 1503 .

2. (a) Kochetkov, N. K.; Klimov E. M.; Malysheva, N. N. *Tetrahedron Lett.*, **1989**, *30*, 5459. (b) Kochetkov, N. K.; Klimov E. M.; Malysheva, N. N.; Demchenko, A. V.; *Carbohydr. Res.*, **1991**, *212*, 77. (c) *Idem, ibid*, **1993**, *242*, C7-C10.
3. Santoyo-González, F., Calvo-Flores, F. G., García-Mendoza, P., Hernández-Mateo, F., Isac-García, J. and Robles-Díaz, R. *J. Org. Chem.* **1993**, *58*, 6122
4. For a recent review see: Avalos, M.; Babiano, R.; Cintas, P.; Jiménez J. L.; Palacios, *L.; Heterocycles*, **1990**, *30*, 463 and references cited therein.
5. Ando, T.; Clark ,J. H.; Cork, D. G; Fujita , M; Kimura, T. *J. Chem. Soc. Chem Commun.*, **1987**, 1301.
6. (a) Drobnica, L.; Kristian, P.; Augustin, J. *The Chemistry of Cyanates and their Thioderivatives*, **1987** Wiley-Interscience, New York,. (b) Mukerjee, A. K.; Ashare, R. *Chem Rev.* **1991**, *91*, 1.
7. Fuentes Mota, J.; Pradera Adrian, M. A.; Ortiz Mellet, C.; García Fernández, J. M.; Babiano Caballero, R.; Galbis Pérez, J. A. *Carbohydr. Res.* **1988**, *173*, 1. (b) Avalos González, M.; Babiano Caballero, R.; Cintas Moreno, P.; Fuentes Mota, J.; Jiménez Requejo, J. L.; Palacios Albarán. *Heterocycles*. **1989**, *29*, 1. (c) Ogura, H.; Takeda, K.; Takayanagui. *Heterocycles*. **1989** *29*, 1171. (d) Fuentes Mota, J.; García Fernández, J. M.; Ortiz Mellet, C.; Pradera Adrian, M. A.; Babiano Caballero, R. *Carbohydr. Res.* **1989**, *193*, 314. (e) Fuentes Mota, J.; Pradera Adrian, M. A.; Robina, I. *Tetrahedron*. **1991**, *47*, 5794. (f) Fuentes, J.; Moreda, W.; Ortiz, C.; Robina, I.; Welsh, C. *Ibid.* **1992**, *48*, 6413. (g) Fuentes, J.; García, J. M.; Ortiz, C.; Pradera, M. A.; Cuevas; T. *J. Carbohydr. Chem.* **1990**, *9*, 837. (h) For a review on monosaccharide isothiocyanates see Witczak, Z. J. *Adv. Carbohydr. Chem. Biochem.* **1986**, *44*, 91.
8. (a) Fischer, E. *Ber.* **1914**, *47*, 1377. (b) Günther, W.; Kunz, H. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1050. (c) Khordin, A. Y.; Zurabyan, S. E.; Macharadze, R. G. *Carbohydr. Res.* **1980**, *85*, 201. (d) Lee, H. H.; Baptista, J. A. B.; Krepinsky, J. J. *Can . J. Chem.* **1990**, *68*, 953.
9. Cambie, R.C.; Lee, H. H.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc. Perkin Trans I.* **1979**, 765 and references cited therein
10. (a) Bellamy, L. J. *The Infrared Spectrum of Complex Molecules*. **1954** Methuen , London. (b) Baker, B. R.; Neilson, T. *J. Org. Chem.* **1964**, *29*, 1051
11. Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*. **1987**, Butterworths, London, pp 35-68.

12. (a) Shafizadeh, F. *Methods Carbohydr. Chem,*, **1963**, *2*, 409.8. (b) Bergman, M.; Schotte, H. *Ber.* **1921**, *54*, 1564. (c) Harworth, W. N.; Hirst, E. L.; Streight, H. R.; Thomas, H. A.; Webb, I. J. *J. Chem. Soc.* **1939**, 2639. (d) Harworth, W. N.; Hirst, E. L.; Plant, M. M. T.; Reinolds, R. J. W. *Ibid.* **1930**, 2644. (e) Harworth, W. N.; Hirst, E. L.; Reinolds, R. J. *Ibid.* **1934**, 302.

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