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Convenient syntheses of symmetrical and unsymmetrical glycosyl carbodiimides and *N*,*N*-bis(glycosyl)cyanamides

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Abstract

Reaction of glycosyl trimethylphosphinimides with carbon disulfide under mild conditions (room temperature, short reaction time) leads to symmetrical glycosyl carbodiimides. Addition of bis(trimethylsilyl)carbodiimide to peracetylated aldoses under the influence of $SnCl_4$ afforded *N*,*N*-bis(glycosyl)cyanamides for the first time. Readily accessible unsymmetrical *N*,*N*′-bis(glycosyl)thioureas can be desulfurated and transformed into the corresponding carbodiimides using HgO in $CHCl_3$/water at room temperature. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Glycosyl azides; Glycosyl carbodiimides; Glycosyl cyanamides; Staudinger reaction

1. Introduction

Sugar carbodiimides are key intermediates in syntheses of various glycoconjugates (trehazolin-type glycosidase inhibitors,[1,2] glucocinnamoyl spermidine antibiotics,[3,4] etc.), which play an important role in biological systems.[5] These examples of synthetic compounds with two monosaccharide moieties bound by a (thio)urea bridge are limited to symmetrical and unsymmetrical *N*,*N*-bis(glycosyl) derivatives.[6] Glycosyl carbodiimides are precursors of urea-, thiourea-, and guanidine-type sugar derivatives, that can be easily synthesized from the corresponding glycosyl carbodiimides by nucleophilic addition of water or hydrogen sulfide, respectively.[7] Another possible application of carbodiimides is the synthesis of carbohydrate derivatives that could be utilised as core structures for the construction of dendrimers.[8] The use of sugar cores should lead to potentially biodegradable, non-toxic and chiral dendrimers. Two general methods are known for the synthesis of glycosyl carbodiimides: (i) from glycosyl thioureas[9] by elimination of hydrogen sulfide; (ii) from glycosyl phosphinimides which could be easily prepared from the glycosyl azides by Staudinger reaction.[10,11] Thiourea-linked pseudooligosaccharides both symmetrical and unsymmetrical, have been synthesized by the reaction of sugar isothiocyanates and amino sugars[9] (or glycosyl iminophosphorane).[12,13]

2. Results and discussion

Reaction of peracetylated glycopyranosyl azides[14] (β-D-*gluco* **1**, α-D-*gluco* **2**, β-D-*galacto* **3**, α-D-*galacto* **4**, 2-amino-2-deoxy-β-D-*gluco* **5**, β-D-*manno* **6**, β-D-*xylo* **7**, α-D-*arabino* **8**, β-D-*arabino* **9**) (Scheme 1) with 1 equivalent of trimethylphosphine in dry dichloromethane at room temperature led to the corresponding glycosyl trimethylphosphinimides.[15] The in situ reaction of these compounds with carbon disulfide under mild conditions led to the symmetrical glycosyl carbodiimides **10**–**14** (Scheme 2). In the case of the 1,2-trans azides **1**, **3**, **5**, **7**, **8**, the expected products were obtained in good yields as stable crystalline solids. The hexopyranosyl carbodiimides of D-*gluco* and D-*galacto* configuration **10** and **11** were obtained in about 10 min, while formation of the pentopyranosyl carbodiimides **13** and **14** took about 12 h. From the 1,2-cis azides **2**, **4**, **6**, **9**, complex

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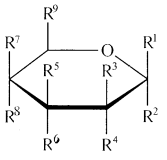


	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9
1	N_3	H	H	OAc	OAc	H	H	OAc	CH_2OAc
2	H	N_3	H	OAc	OAc	H	H	OAc	CH_2OAc
3	N_3	H	H	OAc	OAc	H	OAc	H	CH_2OAc
4	H	N_3	H	OAc	OAc	H	OAc	H	CH_2OAc
5	N_3	H	H	NHAc	OAc	H	H	OAc	CH_2OAc
6	N_3	H	OAc	H	OAc	H	H	OAc	CH_2OAc
7	N_3	H	H	OAc	OAc	H	H	OAc	H
8	H	N_3	OAc	H	H	OAc	H	OAc	H
9	N_3	H	OAc	H	H	OAc	H	OAc	H

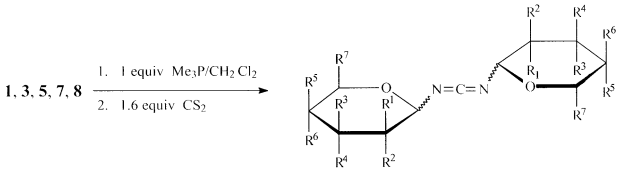
Scheme 1.

reaction mixtures were formed, and the expected products could not be isolated but were identified by NMR spectroscopy. According to Pintér and co-workers, the separation of these mixtures by chromatography is not possible because the carbodiimides react with traces of water to give the corresponding glycosyl ureas.[16]

Peracetylated glycoses can react with trimethylsilylated nucleophiles[17–19] (azide, cyanide, etc.) in the presence of a Lewis acid catalyst ($SnCl_4$, $BF_3{\cdot}Et_2O$, etc.) and the expected, nucleophile containing derivatives are formed. In order to obtain the symmetric *N*,*N*′-bis(glycosyl)carbodiimides, peracetylated glycopyranoses (β-D-*gluco* **15**, β-D-*galacto* **16**, β-D-*xylo* **17**, β-D-*ribo* **18**, α-D-*arabino* **19** and α-D-*lyxo* **20**, Scheme 3) were treated with 1.2 equivalents of freshly prepared bis(trimethylsilyl)carbodiimide.[20] Unexpectedly, the reaction of the aldose derivatives **15**–**20** furnished complex reaction mixtures from which the *N*,*N*-bis(glycopyranosyl) cyanamides **21**, **23**, **25**, **27**, **30**, **31**) and *N*,*N*-bis(glycopyranosyl) cyanoguanidines **22**, **24**, **26**, **28** could be isolated by column chromatography in convenient yields (Scheme 4). As Lewis acids tin tetrachloride, trimethylsilyl triflate and $BF_3{\cdot}Et_2O$ were tried. However, in the case of $BF_3{\cdot}Et_2O$ the starting material was recovered unchanged even after 7 days of continuous stirring at room temperature. The pentopyranosyl cyanamide derivatives **25**, **27**, **30**, **31** were obtained more rapidly than the hexopyranosyl compounds **21** and **23**. Starting from **19**, we isolated the monosubstituted cyanamide derivative **29**, too (Scheme 5). Further experiments showed that the pure symmetrical glycosyl carbodiimides were transformed into the corresponding cyanamides under the influence of the Lewis acid. Similar carbodiimide–cyanamide isomerization have been observed recently in the case of an aromatic carbodiimide in the presence of 2.5 mol % of $Pd_2(dba)_3{\cdot}CHCl_3$ and 10 mol % of 1,2-bis(diphenylphosphino)ethane.[21]

In order to obtain the unsymmetrical carbodiimides, methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside[22] (**32**) was reacted with methylisothiocyanate and 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl isothiocyanate[9] (**33**) in dry ethylacetate to give the corresponding *N*-methyl-*N*′-glycosyl thiourea **34** and *N*,*N*′-bis(glycosyl) thiourea derivative (**35**), respectively (Scheme 6). These compounds can be desulfurated in excellent yields using HgO in $CHCl_3$–water at room temperature. The synthesized products **36** and **37** are crystalline solids.

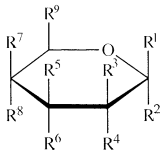
The structure elucidation of the newly prepared compounds was based mainly on IR and NMR measurements. We have found strong absorptions around 2150 and 2230 cm^{-1} in the infrared spectra corresponding to the carbodiimide and cyanamide groups. The presence of one series of sugar signals in the ^1H as well as ^{13}C NMR spectra of these compounds indicates symmetrical bis(glycosyl) structures. The proton assignments were based on ^1H–^1H COSY experiments. The ^{13}C NMR spectra revealed signals characteristic for the carbodiimide (137–140 ppm) and for the cyanamide (108–111 ppm) type carbons. ^{15}N NMR spectra of compounds **13** and **25** indicated the presence of one (77.2 ppm) versus two nitrogen resonances (45.8 and 196.3 ppm) characteristic for the carbodiimides and



10-14

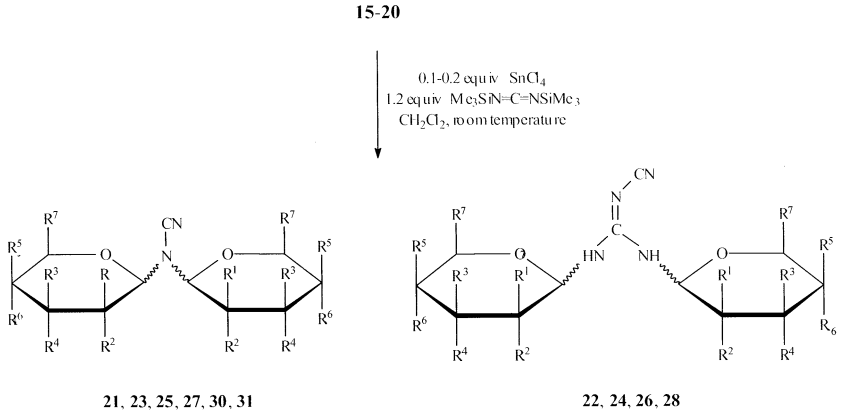
Educt	Product	R^1	R^2	R^3	R^4	R^5	R^6	R^7
1	**10**	H	OAc	OAc	H	H	OAc	CH_2OAc
3	**11**	H	OAc	OAc	H	OAc	H	CH_2OAc
5	**12**	H	NHAc	OAc	H	H	OAc	CH_2OAc
7	**13**	H	OAc	OAc	H	H	OAc	H
8	**14**	OAc	H	H	OAc	H	OAc	H

Scheme 2.



	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9
15	OAc	H	H	OAc	OAc	H	H	OAc	CH_2OAc
16	OAc	H	H	OAc	OAc	H	OAc	H	CH_2OAc
17	OAc	H	H	OAc	OAc	H	H	OAc	H
18	OAc	H	H	OAc	H	OAc	H	OAc	H
19	H	OAc	OAc	H	H	OAc	H	OAc	H
20	H	OAc	OAc	H	OAc	H	H	OAc	H

Scheme 3.

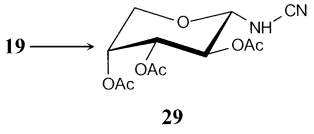


Educt	Product	R^1	R^2	R^3	R^4	R^5	R^6	R^7
15	**21**	H	OAc	OAc	H	H	OAc	CH_2OAc
15	**22**	H	OAc	OAc	H	H	OAc	CH_2OAc
16	**23**	H	OAc	OAc	H	OAc	H	CH_2OAc
16	**24**	H	OAc	OAc	H	OAc	H	CH_2OAc
17	**25**	H	OAc	OAc	H	H	OAc	H
17	**26**	H	OAc	OAc	H	H	OAc	H
18	**27**	H	OAc	H	OAc	H	OAc	H
18	**28**	H	OAc	H	OAc	H	OAc	H
19	**30**	OAc	H	H	OAc	H	OAc	H
20	**31**	OAc	H	OAc	H	H	OAc	H

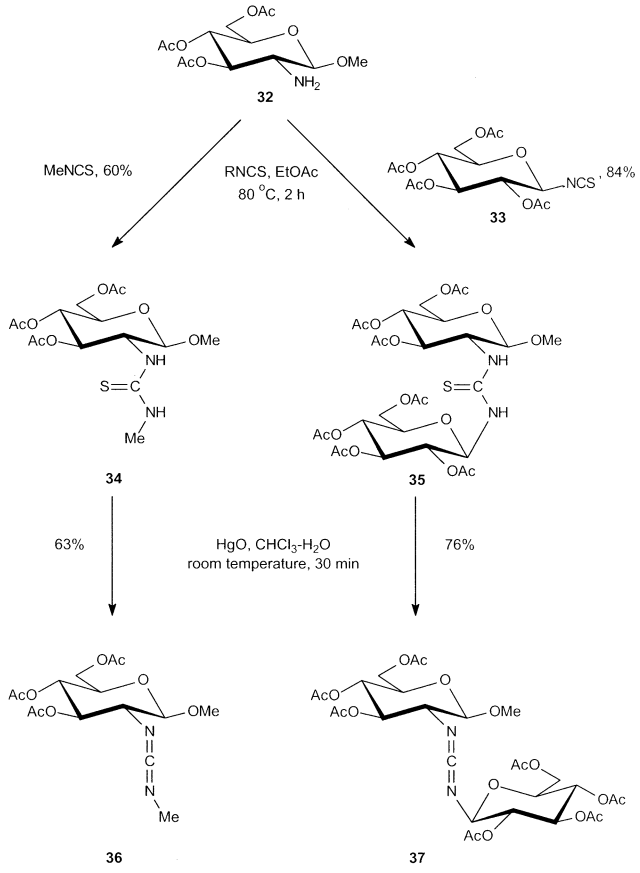
Scheme 4.

cyanamides, respectively.[23] The conformations of the sugar moieties ($^4C_1$ for **10**–**13**, **21**–**28**, **31**, **34**–**37** and $^1C_4$ for **14**, **29**, **30**) are evident from the vicinal ^1H–^1H coupling constants determined from the ^1H NMR spectra (see Section 3). In the case of pentopyranose derivatives the conformer ratio (Table 1) was calculated by using $J_{4a,5a}$ 11.6 Hz and $J_{4e,5e}$ 1.5 Hz as limiting values for the $^4C_1$ and $^1C_4$ conformers, respectively taken from the literature.[24] The configurations of the anomeric carbons could be deduced by relying on the $^3J_{H\text{-}1,H\text{-}2}$ values (see Section 3).

In summary, symmetrical and unsymmetrical glycosyl carbodiimides, *N*,*N*-bis(glycosyl)cyanamides could be obtained under mild conditions. To the best of our knowledge, glycosyl cyanamides are not known in the literature. We have found that pure symmetrical glycosyl carbodiimides were transformed into the corresponding cyanamides under the influence of Lewis acid.



Scheme 5.



Scheme 6.

Table 1
Conformational equilibria of D-pentopyranosyl carbodiimides, cyanamides and cyanoguanidines[a] in $CDCl_3$

Compound	$^4C_1$	$^1C_4$
13	84	16
14	5	95
25	82	18
26	84	16
27	89	11
29	7	93
30	11	89
31	89	11

[a] Calculated on the basis of $J_{4,5}$ couplings using $J_{4a,5a}$ 11.6 Hz and $J_{4e,5e}$ 1.5 Hz as limiting values for the $^4C_1$ and $^1C_4$ conformers, respectively as taken from Ref. 24.

3. Experimental

Distilled dichloromethane was dried by storage over 4 Å molecular sieves. Melting points were measured on a Kofler hot-stage and are uncorrected. Optical rotations were recorded in chloroform solution on a Perkin–Elmer 241 polarimeter in a 1 dm cell at room temperature (22 ± 2 °C). IR spectra were taken with a Perkin–Elmer 16 PC FT-IR spectrometer. NMR spectra were recorded with Bruker WP 360 SY (360/90 MHz for $^1H/^{13}C$) and Varian ^{UNITY}INOVA 400 WB (400/100/40 MHz for $^1H/^{13}C/^{15}N$) spectrometers. Chemical shifts are referenced to Me_4Si (^1H), to the residual solvent signal (^{13}C: 77.00 ppm for $CDCl_3$) or to NH_4Cl (50 mg/700 μL $H_2O/D_2O = 9:1$) as an external standard (^{15}N). Measurements were run at 298 K probe temperature. The ^1H and ^{13}C assignments were based on $^1H-^1H$ COSY, gradient enhanced $^{13}C-^1H$ HSQC, $^{15}N-^1H$ HSQC, $^{13}C-^1H$ HMBC and $^{15}N-^1H$ HMBC experiments measured using standard Varian software. The designation of peak multiplicities follows the general use (s: singlet, d: doublet, t: triplet, Ψt: pseudo triplet, q: quartet, m: multiplet). MALDI-TOF measurements were performed with a Bruker BIFLEX III mass spectrometer. TLC was performed on DC-Alurolle, Kieselgel 60 F_{25} (E. Merck); the plates were visualized by gentle heating. For column chromatography, Kieselgel 60 (E. Merck) was used. Organic solutions were concentrated under diminished pressure at 40–50 °C (water bath). Glycosyl azides (**1**–**9**), peracetylated aldoses (**15**–**20**) were prepared as described in the literature.[18,25,26] Me_3P solution (1 M in toluene), methylisothiocyanate and bis(trimethylsilyl)carbodiimide are commercial products of Fluka AG, Buchs, Switzerland.

*General Procedure A for the preparation of symmetric glycopyranosyl carbodiimides (**10**–**14**).*—To a solution of glycosyl azide (**1**–**9**) (0.20 g, 0.54 mmol) in dry CH_2Cl_2 (2 mL) 1 equiv of trimethylphosphine was added. The mixture was stirred at room temperature until the N_2 evolution ceased. Then 1.6 equiv of CS_2 was added and the resulting mixture was stirred at room temperature temperature for 12 h (pentopyranosyl derivatives) and 1 h (hexopyranosyl derivatives). Finally, the solution was evaporated and the crude product was purified by crystallisation.

*Bis(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)carbodiimide (**10**).* Prepared from **1** (0.20 g, 0.53 mmol) according to General Procedure A; Yield: 0.15 g (80%), colourless crystalline product; mp 177–179 °C (CH_2Cl_2–Et_2O), lit.[11] mp 178 °C; $[\alpha]_D$ −42.5° (*c* 1.0, $CHCl_3$); lit.[11] $[\alpha]_D$ −43.0° (*c* 1.0, $CHCl_3$); *ν* (KBr): 2154 (N=C=N) and 1746 (OAc) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.12 (Ψt, 1H, $J_{3,4}$ 9.5 Hz, H-3), 5.05 (Ψt, 1H, $J_{4,5}$ 10.0 Hz, H-4), 4.90 (Ψt, 1H, $J_{2,3}$ 8.9 Hz, H-2), 4.68 (d, 1H, $J_{1,2}$ 9.0 Hz, H-1), 4.22 (dd, 1H, $J_{5,6a}$ 4.8 Hz, $J_{6a,6b}$ 12.1 Hz, H-6a), 4.10 (m, 1H, H-6b), 3.71 (ddd, 1H, $J_{5,6b}$ 2.1 Hz, H-5), 2.05, 1.99, 1.96, 1.93 (s, 12H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 170.5, 170.0, 169.2, 169.0 (acetyl *C*O), 137.9 (N=*C*=N), 84.0 (C-1), 73.8, 72.8, 72.4, 67.9 (C-2, C-3, C-4, C-5), 61.6 (C-6), 20.4 (acetyl CH_3).

*Bis(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)carbodiimide (**11**).* Prepared from **3** (0.20 g, 0.53 mmol) according to General Procedure A; Yield: 0.18 g (95%), mp 89–91 °C (CH_2Cl_2–Et_2O), lit.[11] syrup; $[\alpha]_D$ −9.4° (*c* 1.0, $CHCl_3$); *ν* (KBr): 2156 (N=C=N) and 1750 (OAc) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 5.39 (dd, 1H, $J_{4,5}$ 1.1 Hz, H-4), 5.15 (dd, 1H, $J_{2,3}$ 9.9 Hz, H-2), 5.00 (dd, 1H, $J_{3,4}$ 2.6 Hz, H-3), 4.74 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.25–3.90 (m, 3H, H-5, H-6a, H-6b), 2.18, 2.09, 2.06, 1.99 (s, 12H, acetyl C*H*$_3$); ^{13}C NMR ($CDCl_3$): *δ* 169.9, 169.8, 169.0, 168.9 (acetyl *C*O), 137.3 (N=*C*=N), 84.4 (C-1), 72.5, 70.7, 69.7, 66.8 (C-2, C-3, C-4, C-5), 60.9 (C-6), 20.5 (acetyl *C*H$_3$).

*Bis(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)carbodiimide (**12**).* (a) Prepared from **5** (0.20 g, 0.53 mmol) according to General Procedure A; Yield: 0.14 g (71%), colourless crystalline product; mp 212–214 °C (CH_2Cl_2–Et_2O), lit.[10] mp 205–210 °C; $[\alpha]_D$ −27.2° (*c* 1.0, $CHCl_3$); lit.[10] $[\alpha]_D$ −27.0° (*c* 1.0, $CHCl_3$).

(b) Prepared from **5** (0.38 g, 1.00 mmol) with triphenylphosphine according to General Procedure A; Yield: 0.20 g (54%), colourless crystalline product; mp 205–206 °C (EtOAc–Et_2O). This compound was identified using the ^1H and ^{13}C NMR chemical shift values known from the literature.[10]

*Bis(2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl)carbodiimide (**13**).* Prepared from **7** (0.30 g, 1.00 mmol) according to General Procedure A; Yield: 0.18 g (65%), colourless crystalline product; mp 133–134 °C (*i*Pr$_2$O), lit.[11] mp 139 °C; $[\alpha]_D$ −69.9° (*c* 1.0, $CHCl_3$); lit.[11] $[\alpha]_D$ −116.9° (*c* 1.0, $CHCl_3$); *ν* (KBr): 2153 (N=C=N) and 1760 (OAc) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 5.10 (dd, 1H, $J_{3,4}$ 9.5 Hz, H-3), 4.93 (ddd, 1H, $J_{4,5}$ 5.1 Hz, H-4), 4.82 (dd, 1H, $J_{2,3}$ 9.0 Hz, H-2), 4.65 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.10 (dd, 1H, $J_{5,5a}$ 11.5 Hz, H-5a), 3.33 (dd, 1H, $J_{4,5b}$ 10.0 Hz, H-5b), 2.00, 1.98, 1.97 (s, 9H, acetyl C*H*$_3$); ^{13}C NMR ($CDCl_3$): *δ* 169.8, 169.5, 169.1 (acetyl *C*O), 137.2 (N=*C*=N), 84.4 (C-1), 72.0, 71.8, 68.3 (C-2, C-3, C-4), 64.1 (C-5), 20.4 (acetyl *C*H$_3$); ^{15}N NMR ($CDCl_3$): *δ* 77.2 (*N*=C=*N*).

*Bis(2,3,4-tri-*O*-acetyl-α-*D*-arabinopyranosyl)carbodiimide (**14**).* Prepared from **8** (0.30 g, 1.00 mmol) according to General Procedure A; Yield: 0.21 g (76%), colourless crystalline product; mp 162–163 °C (EtOH–*i*Pr$_2$O), $[\alpha]_D$ −35.8° (*c* 1.1, $CHCl_3$); *ν* (KBr): 2151 (N=C=N) and 1748 (OAc) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 5.88 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 5.33 (ddd, 1H, $J_{4,5b}$ 1.5 Hz, H-4), 5.14 (dd, 1H, $J_{3,4}$ 3.2 Hz, H-3), 5.10 (dd, 1H, $J_{2,3}$ 10.0 Hz, H-2), 3.97 (dd, 1H, $J_{4,5a}$ 2.0 Hz, H-5a), 3.80 (dd, 1H, $J_{5,5b}$ 13.2 Hz, H-5b), 2.15, 2.08, 2.02 (s, 9H, acetyl C*H*$_3$); ^{13}C NMR ($CDCl_3$): *δ* 170.9, 170.2, 169.9 (acetyl *C*O), 140.7 (N=*C*=N), 79.8 (C-1), 70.9, 68.2, 68.1 (C-2, C-3, C-4), 65.3 (C-5), 20.5, 20.4, 20.2 (acetyl *C*H$_3$). Anal. Calcd for $C_{23}H_{30}N_2O_{14}$ (558.50): C, 49.46; H, 5.41; N, 5.02. Found: C, 49.55; H, 5.30; N, 4.92.

General Procedure B for the preparation of N,N′-*bis(glycopyranosyl)cyanamides (**21**, **23**, **25**, **27**, **30**, **31**).*—To a solution of peracetylated aldoses (**15**–**20**) (2 mmol) in dry CH_2Cl_2 (10 mL) 0.24 mL (0.2 mmol) of $SnCl_4$ and 0.54 mL (2.4 mmol) of bis(trimethylsilyl)carbodiimide were added and stirred at room temperature for 12 h (pentopyranosyl derivatives) and 48 h (hexopyranosyl derivatives). Then the reaction mixture was diluted with 18 mL of CH_2Cl_2, washed with cold saturated $NaHCO_3$ solution and water. After drying of the CH_2Cl_2 layer and evaporation of the solvent the crude product was separated by column chromatography using 1:1 EtOAc–hexane as eluent. The fractions were monitored by TLC (2:1 EtOAc–hexane).

N,N-*Bis(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-cyanamide (**21**) and* N^1,N^3-*bis(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-*N^2*-cyanoguanidine (**22**).* Prepared from **15** (0.78 g, 2.00 mmol) according to General Procedure B; The first fraction (R_f 0.56) gave 0.12 g (20%) of cyanamide **21** (with 90% conversion) as colourless crystalline product. Mp 187–190 °C, $[\alpha]_D$ −47.4° (*c* 1.0, $CHCl_3$); *ν* (KBr): 2230 (N-C=N) and 1752 (OAc) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 5.30 (dd, 1H, $J_{3,4}$ 9.5 Hz, H-3), 5.11 (dd, 1H, $J_{4,5}$ 10.0 Hz, H-4), 5.09 (dd, 1H, $J_{2,3}$ 8.9 Hz, H-2), 4.64 (d, 1H, $J_{1,2}$ 9.5 Hz, H-1), 4.24–4.15 (m, 2H, H-6a, H-6b), 3.76 (ddd, 1H, $J_{5,6a}$ 3.1 Hz, $J_{5,6b}$ 3.6 Hz, H-5), 2.11, 2.06, 2.04, 2.02 (s, 12H, acetyl C*H*$_3$); ^{13}C NMR ($CDCl_3$): *δ* 170.3, 170.0, 169.0, 168.8 (acetyl *C*O), 108.3 (*C*N), 88.6 (C-1), 73.9, 72.6, 69.7, 67.3 (C-2, C-3, C-4, C-5), 61.4 (C-6), 20.5, 20.3, 20.2 (acetyl *C*H$_3$). Anal. Calcd for $C_{29}H_{38}N_2O_{13}$ (702.63): C, 49.57; H, 5.45; N, 3.99. Found: C, 49.52; H, 5.49; N, 3.84.

The second fraction (R_f 0.41) gave 0.17 g (26%) of cyanoguanidine **22**. Mp 240–242 °C, $[\alpha]_D$ −19.8° (*c* 1.1, $CHCl_3$); *ν* (KBr): 3409 (NH), 2195 (CN), 1749 (OAc) and 1610 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 6.68 (m, 1H, N*H*), 5.33 (Ψt, 1H, $J_{4,5}$ 9.5 Hz, H-4), 5.06 (Ψt, 1H, $J_{2,3}$ 9.5 Hz, H-2), 4.92 (Ψt, 1H, $J_{3,4}$ 8.9 Hz, H-3), 4.80 (dd, 1H, $J_{1,2}$ 10.0 Hz, $J_{NH,1}$ 6.8 Hz, H-1), 4.30 (dd, 1H, $J_{6a,6b}$ 12.6 Hz, H-6a), 4.17 (m, 1H, H-6b), 3.76 (ddd, 1H, $J_{5,6a}$ 4.7 Hz, $J_{5,6b}$ 2.6 Hz, H-5), 2.14, 2.12, 2.05, 2.04 (s, 12H, acetyl C*H*$_3$); ^{13}C NMR ($CDCl_3$): *δ* 171.1, 170.3, 169.7, 169.3 (acetyl *C*O), 159.4 (guanidine), 115.0 (*C*N), 80.5 (C-1), 73.0, 72.2, 70.5, 67.4 (C-2, C-3, C-4, C-5), 61.5 (C-6), 20.5, 20.4 (acetyl *C*H$_3$). Anal. Calcd for $C_{30}H_{40}N_4O_{18}$ (744.67): C, 48.39; H, 5.41; N, 7.52. Found: C, 48.23; H, 5.49; N, 7.44.

N,N-*Bis(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-cyanamide (**23**) and* N^1,N^3-*bis(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-*N^2*-cyanoguanidine (**24**).* Prepared from **16** (0.78 g, 2.00 mmol) according to General Procedure B; the first fraction (R_f 0.30) gave 0.29 g (42%) of cyanamide **23** as colourless crystalline product; mp 156–157 °C, $[\alpha]_D$ +18.0° (*c* 1.0, $CHCl_3$); *ν* (KBr): 2232 (N-C=N) and 1748 (OAc) cm^{-1}. ^1H NMR

($CDCl_3$): δ 5.41 (m, 1H, H-4), 5.37 (dd, 1H, $J_{2,3}$ 10.0 Hz, H-2), 5.12 (dd, 1H, $J_{3,4}$ 2.7 Hz, H-3), 4.54 (d, 1H, $J_{1,2}$ 9.5 Hz, H-1), 4.15 (dd, 1H, $J_{5,6a}$ 6.3 Hz, $J_{6a,6b}$ 11.6 Hz, H-6a), 4.09 (dd, 1H, $J_{5,6b}$ 6.8 Hz, H-6b), 3.95 (ddd, 1H, $J_{4,5}$ 1.6 Hz, H-5), 2.21, 2.08, 2.06, 2.00 (s, 12H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 169.9, 169.8, 169.6, 168.5 (acetyl *C*O), 108.7 (*C*N), 88.7 (C-1), 72.5, 70.8, 66.9, 66.6 (C-2, C-3, C-4, C-5), 61.0 (C-6), 20.2 (acetyl *C*H_3). Anal. Calcd for $C_{29}H_{38}N_2O_{13}$ (702.63): C, 49.57; H, 5.45; N, 3.99. Found: C, 49.62; H, 5.58; N, 3.87.

The second fraction (R_f 0.20) gave 0.14 g (20%) of cyanoguanidine **24**. Mp 168–170 °C, $[\alpha]_D$ −32.5° (*c* 1.0, $CHCl_3$); *v* (KBr): 3411 (NH), 2186 (CN), 1749 (OAc) and 1615 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.74 (m, 1H, N*H*), 5.42 (dd, 1H, $J_{4,5}$ 1.0 Hz, H-4), 5.13 (dd, 1H, $J_{3,4}$ 3.2 Hz, H-3), 5.07 (dd, 1H, $J_{1,2}$ 8.9 Hz, $J_{2,3}$ 10.0 Hz, H-3), 4.75 (m, 1H, H-1), 4.20–4.05 (m, 3H, H-5, H-6a, H-6b), 2.11, 2.09, 2.04, 1.97 (s, 12H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 171.3, 170.2, 169.7, 169.5 (acetyl *C*O), 159.8 (guanidine), 115.2 (*C*N), 81.0 (C-1), 72.2, 70.2, 67.9, 66.9 (C-2, C-3, C-4, C-5), 61.0 (C-6), 20.6, 20.5, 20.4, 20.3 (acetyl *C*H_3). Anal. Calcd for $C_{30}H_{40}N_4O_{18}$ (744.67): C, 48.39; H, 5.41; N, 7.52. Found: C, 49.46; H, 5.33; N, 7.60.

N,N-*Bis(2,3,4-tri*-O-*acetyl-β*-D-*xylopyranosyl)cyanamide* ***(25)*** *and* N^1,N^3-*bis(2,3,4-tri*-O-*acetyl-β*-D-*xylopyranosyl)*-N^2-*cyanoguanidine* ***(26)***. Prepared from **17** (0.64 g, 2.00 mmol) according to General Procedure B; The first fraction (R_f 0.67)gave 0.24 g (43%) of cyanamide **25** as colourless crystalline product. Mp: 170–172 °C, $[\alpha]_D$ −62.8° (*c* 1.1, $CHCl_3$); *v* (KBr): 2232 (N-C=N) and 1758 (OAc) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.24 (t, 1H, $J_{3,4}$ 9.0 Hz, H-3 or H-2), 5.06 (t, 1H, $J_{2,3}$ 9.0 Hz, H-2 or H-3), 4.96 (ddd, 1H, H-4), 4.51 (d, 1H, $J_{1,2}$ 9.0 Hz, H-1), 4.15 (dd, 1H, $J_{4,5a}$ 5.3 Hz, H-5a), 3.35 (dd, 1H, $J_{5,5b}$ 11.6 Hz, $J_{4,5b}$ 9.7 Hz, H-5b), 2.04, 2.03 (s, 9H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 169.8, 169.4, 168.7 (acetyl *C*O), 108.4 (*C*N), 87.7 (C-1), 71.7, 69.1, 67.9 (C-2, C-3, C-4), 64.0 (C-5), 20.3, 20.2 (acetyl *C*H_3); ^{15}N NMR ($CDCl_3$): δ 196.3, 45.8 (*N*-C*N*). MALDI-TOF MS (558.50): 597.07 $[M+K]^+$, 581.10 $[M+Na]^+$. Anal. Calcd for $C_{23}H_{30}N_2O_{14}$ (558.50): C, 49.46; H, 5.41; N, 5.02. Found: C, 49.35; H, 5.35; N, 4.87.

The second fraction (R_f 0.51) gave 0.17 g (29%) of cyanoguanidine **26**. Mp: 122–123 °C, $[\alpha]_D$ −40.6° (*c* 1.0, $CHCl_3$); *v* (KBr): 3406 (NH), 2190 (CN), 1756 (OAc) and 1614 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.73 (d, 1H, $J_{NH,1}$ 8.2 Hz, NH), 5.24 (Ψt, 1H, $J_{2,3}$ 9.2, Hz $J_{3,4}$ 9.7 Hz, H-3), 4.92 (ddd, 1H, $J_{4,5ab}$ 5.5 Hz, $J_{4,5b}$ 10.0 Hz, H-4), 4.88 (t, 1H, $J_{1,2}$ 9.0 Hz, H-2), 4.80 (t, 1H, H-1), 4.05 (dd, 1H, $J_{5,5b}$ 11.7 Hz, H-5a), 3.46 (Ψt, 1H, H-5b), 2.04, 2.00, 1.99 (s, 9H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 171.0, 169.7 (acetyl *C*O), 159.5 (guanidine), 115.2 (*C*N), 80.8 (C-1), 71.5 (C-3), 70.3 (C-2), 68.3 (C-4), 63.7 (C-5), 20.6, 20.5, 20.5 (acetyl *C*H_3). MALDI-TOF MS (600.54): 623.05 $[M+Na]^+$. Anal. Calcd for $C_{24}H_{32}N_4O_{14}$ (600.54): C, 48.00; H, 5.37; N, 9.33. Found: C, 48.15; H, 5.43; N, 9.21.

N,N-*Bis(2,3,4-tri*-O-*acetyl-β*-D-*ribopyranosyl)cyanamide* ***(27)*** *and* N^1,N^3-*bis(2,3,4-tri*-O-*acetyl-β*-D-*ribopyranosyl)*-N^2-*cyanoguanidine* ***(28)***. Prepared from **18** (0.64 g, 2.00 mmol) according to General Procedure B; The first fraction (R_f 0.60) gave 0.28 g (51%) of cyanamide **27** as colourless crystalline product. Mp: 175–177 °C, $[\alpha]_D$ −35.1° (*c* 1.0, $CHCl_3$); *v* (KBr): 2228 (N-C=N) and 1752 (OAc) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.73 (m, 1H, H-3), 5.46 (m, 1H, H-4), 5.03 (dd, 1H, $J_{2,3}$ 2.4 Hz, H-2), 4.50 (d, 1H, $J_{1,2}$ 8.9 Hz, H-1), 3.99 (dd, 1H, $J_{4,5a}$ 5.3 Hz, $J_{5,5b}$ 11.0 Hz, H-5a), 3.80 (Ψt, 1H, $J_{4,5b}$ 10.5 Hz, H-5b), 2.21, 2.07, 2.03 (s, 9H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 169.5, 169.1, 168.6 (acetyl *C*O), 109.4 (*C*N), 84.3 (C-1), 67.8, 67.0, 65.3 (C-2, C-3, C-4), 62.8 (C-5), 20.5, 20.3, 20.2 (acetyl *C*H_3). Anal. Calcd for $C_{23}H_{30}N_2O_{14}$ (558.50): C, 49.46; H, 5.41; N, 5.02. Found: C, 49.33; H, 5.52; N, 4.89.

The second fraction (R_f 0.46) was 0.06 g (11%) of cyanoguanidine **28**. Mp: 215–217 °C, $[\alpha]_D$ −16.6° (*c* 1.0, $CHCl_3$); *v* (KBr): 3400 (NH), 2188 (CN), 1759 (OAc) and 1616 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.71 (bs, 1H, NH), 5.68 (Ψt, 1H, $J_{2,3}$ 2.8 Hz, $J_{3,4}$ 2.7 Hz, H-3), 5.03 (m, 1H, H-1), 4.99 (m, 1H, H-4), 4.94 (dd, 1H, $J_{1,2}$ 9.2 Hz, H-1), 3.90–3.80 (m, 2H, H-5a, H-5b), 2.10, 2.05, 2.00 (s, 9H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 170.6, 169.7, 169.4 (acetyl *C*O), 160.5 (guanidine), 115.5 (*C*N), 78.3 (C-1), 68.1 (C-2), 68.0 (C-3), 66.0 (C-4), 62.3 (C-5), 20.8, 20.7, 20.5 (acetyl *C*H_3). Anal. Calcd for $C_{24}H_{32}N_4O_{14}$ (600.54): C, 48.00; H, 5.37; N, 9.33. Found: C, 47.88; H, 5.32; N, 9.21.

N-*(2,3,4-Tri*-O-*acetyl-α*-D-*arabinopyranosyl)cyanamide* ***(29)*** *and* N,N-*bis(2,3,4-tri*-O-*acetyl-α*-D-*arabinopyranosyl)cyanamide* ***(30)***. Prepared from **19** (0.64 g, 2.00 mmol) according to General Procedure B; The first fraction (R_f 0.63) gave 0.11 g (18%) of cyanamide **29** as colourless crystalline product. Mp 189–190 °C $[\alpha]_D$ +30.9° (*c* 1.1, $CHCl_3$); *v* (KBr): 3400 (NH), 2196 (CN) and 1749 (OAc) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.29 (bs, 1H, N*H*), 5.27 (m, 1H, H-4), 5.08 (dd, 1H, $J_{2,3}$ 10.0 Hz, $J_{3,4}$ 3.4 Hz, H-3), 5.04 (dd, 1H, $J_{1,2}$ 10.1 Hz, H-2), 4.40 (t, 1H, $J_{NH,1}$ 8.5 Hz, H-1), 4.03 (dd, 1H, $J_{4,5a}$ 2.2 Hz, $J_{5,5b}$ 13.5 Hz, H-5a), 3.72 (dd, 1H, $J_{4,5b}$ 1.3 Hz, H-5b), 2.12, 2.10, 1.99 (s, 9H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 170.8, 170.1, 169.8 (acetyl *C*O), 112.6 (*C*N), 85.9 (C-1), 70.1 (C-3), 68.2 (C-2), 67.6 (C-4), 65.7 (C-5), 20.7, 20.6, 20.5 (acetyl *C*H_3). Anal. Calcd for $C_{12}H_{16}N_2O_7$ (300.24): C, 48.00; H, 5.37; N, 9.33. Found: C, 48.12; H, 5.42; N, 9.27.

The second fraction (R_f 0.41) was 0.30 g (53%) of bis(glycosyl)cyanamide **30**, colourless crystalline product; mp 203–205 °C (EtOH–*i*Pr_2O), $[\alpha]_D$ +59.8° (*c* 1.1, $CHCl_3$); *v* (KBr): 2230 (N-C=N) and 1742 (OAc) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.46 (t, 1H, $J_{2,3}$ 8.9 Hz, H-2), 5.23 (m, 1H, H-4), 5.11 (dd, 1H, $J_{3,4}$ 3.2 Hz, H-3),

4.50 (d, 1H, $J_{1,2}$ 8.9 Hz, H-1), 4.06 (dd, 1H, $J_{4,5a}$ 2.6 Hz, $J_{5,5b}$ 13.2 Hz, H-5a), 3.67 (m, 1H, H-5b), 2.21, 2.07, 2.04 (s, 9H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 170.0, 169.7, 168.6 (acetyl *C*O), 109.6 (*C*N), 88.0 (C-1), 70.4, 67.5, 67.1 (C-2, C-3, C-4), 65.2 (C-5), 20.6, 20.3 (acetyl *C*H_3). Anal. Calcd for $C_{23}H_{30}N_2O_{14}$ (558.50): C, 49.46; H, 5.41; N, 5.02. Found: C, 49.68; H, 5.55; N, 4.96.

N,N-*Bis(2,3,4-tri*-O-*acetyl*-α-D-*lyxopyranosyl)cyanamide* (**31**).—Prepared from **20** (0.64 g, 2.00 mmol) according to General Procedure B; Yield: 0.32 g (58%), colourless crystalline product; mp 195–197 °C, $[\alpha]_D$ −51.5° (*c* 1.0, $CHCl_3$); *v* (KBr): 2228 (N-C=N) and 1752 (OAc) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.49 (t, 1H, $J_{2,3}$ 3.3 Hz, H-2), 5.35 (dd, 1H, $J_{3,4}$ 9.5 Hz, H-3), 4.82 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1), 4.79 (dd, 1H, $J_{4,5a}$ 5.0 Hz, $J_{5a,5b}$ 13.0 Hz, H-5a), 4.01 (dd, 1H, $J_{4,5b}$ 10.5 Hz, H-5b), 3.93 (m, 1H, H-4), 2.21, 2.16, 2.04 (s, 9H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 169.5, 168.8, 168.7 (acetyl *C*O), 110.7 (*C*N), 84.5 (C-1), 68.0, 67.4, 66.0 (C-2, C-3, C-4), 64.8 (C-5), 20.7, 20.5, 20.3 (acetyl *C*H_3). Anal. Calcd for $C_{23}H_{30}N_2O_{14}$ (558.50): C, 49.46; H, 5.41; N, 5.02. Found: C, 49.52; H, 5.31; N, 5.15.

Methyl 3,4,6-tri-O-*acetyl-2-deoxy-2-(*N′-*methylthioureido)*-β-D-*glucopyranoside* (**34**).—Methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside (**32**, 0.96 g, 3 mmol) and 0.22 g (3 mmol) of methylisothiocyanate were stirred at 80 °C in 6 mL EtOAc for 2 h. After evaporation of the solvent, the crude product (0.94 g) was purified by crystallisation (benzene–hexane). Yield: 0.70 g (60%), mp 157–158 °C, colourless crystalline product, $[\alpha]_D$ +43.7° (*c* 1.0, $CHCl_3$); *v* (KBr): 3358, 1504, 1372 (thiourea) and 1748 (OAc) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.86 (m, 1H, N*H*), 6.20 (m, 1H, N*H*), 5.15 (dd, 1H, $J_{3,4}$ 7.9 Hz, H-4), 5.11 (dd, 1H, $J_{2,3}$ 9.0 Hz, H-3), 4.36 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.31 (dd, 1H, $J_{5,6a}$ 4.7 Hz, $J_{6a,6b}$ 12.6 Hz, H-6a), 4.14 (dd, 1H, $J_{5,6b}$ 2.6 Hz, H-6b), 3.70 (ddd, 1H, $J_{4,5}$ 9.5 Hz, H-5), 3.67 (m, 1H, H-2), 3.57 (s, 3H, OCH_3), 3.07 (d, 3H, $J_{NH,Me}$ 3.3 Hz, N*H*Me), 2.10, 2.05 (s, 9H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 180.8 (thiourea), 170.9, 170.4, 169.1 (acetyl *C*O), 104.6 (C-1), 75.0, 71.4, 67.9 (C-3, C-4, C-5), 61.9 (C-6), 58.6 (C-2), 57.0 (O*C*H_3), 55.6 (N*C*H_3), 20.5, 20.4 20.3 (acetyl *C*H_3). Anal. Calcd for $C_{15}H_{24}N_2O_8S$ (392.43): C, 45.91; H, 6.16; N, 7.14. Found: C, 46.34; H, 6.14; N: 6.81.

Methyl 3,4,6-tri-O-*acetyl-2-deoxy-2-[*N′-*(2,3,4,6-tetra*-O-*acetyl*-β-D-*glucopyranosyl)thioureido]*-β-D-*glucopyranoside* (**35**).—Prepared from **32** (1.60 g, 5 mmol) and **33** (1.94 g, 5 mmol) according to the previous procedure. Yield: 2.96 g (84%), colourless crystalline product, mp 191–192 °C (dry EtOH), $[\alpha]_D$ +5.9° (*c* 1.0, $CHCl_3$); *v* (KBr): 3372, 1562, 1366 (thiourea) and 1754 (OAc) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.53 (m, 1H, N*H*), 5.81 (m, 1H, N*H*), 5.35 (dd, 1H, $J_{3',4'}$ 8.9 Hz, $J_{4',5'}$ 10.0 Hz, H-4′), 5.20–5.05 (m, 4H, H-3, H-4, H-2′, H-3′), 5.01 (t, 1H, $J_{1',2'}$ 9.5 Hz, H-1′), 4.45–4.25 (m, 3H, H-1, H-6a, H-6a′), 4.20–4.05 (m, 2H, H-6b, H-6b′), 3.84 (m, 2H, H-5, H-5′), 3.61 (m, 1H, H-2), 3.55 (s, 3H, OCH_3), 2.11, 2.08, 2.04, 2.03 (s, 21H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 184.6 (thiourea), 170.9, 170.6, 170.5, 169.7, 169.5 169.2 (acetyl *C*O), 101.9 (C-1), 82.9 (C-1′), 73.2, 72.7, 71.6, 70.5, 68.0, 67.8 (C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′), 61.7, 61.5 (C-6, C-6′), 58.2 (C-2), 57.9 (O*C*H_3), 20.5, 20.4 (acetyl *C*H_3). Anal. Calcd for $C_{28}H_{40}N_2O_{17}S$ (708.70): C, 47.45; H, 5.69; N, 3.95. Found: C, 47.52; H, 5.55; N, 3.89.

Methyl 3,4,6-tri-O-*acetyl-2-deoxy-2-(*N′-*methylcarbodiimido)*-β-D-*glucopyranoside* (**36**).—Compound **34** (1.99 g, 5.1 mmol) and 3.25 g (1.5 mmol) of HgO were stirred in a mixture of 69 mL of $CHCl_3$ and 69 mL of water for 30 min at room temperature. The organic layer was separated from the water, dried on $CaCl_2$ and filtrated. After evaporation of the solvent, the crude product was purified by crystallisation (EtOAc–hexane). Yield: 1.14 g (63%), colourless crystalline product, mp 72–73 °C, $[\alpha]_D$ +2.9° (*c* 1.0, $CHCl_3$); *v* (KBr): 2148 (N=C=N) and 1754 (OAc) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.97 (t, 1H, $J_{3,4}$ 9.5 Hz, H-3), 4.90 (t, 1H, $J_{4,5}$ 9.5 Hz, H-4), 4.22 (dd, 1H, $J_{5,6a}$ 4.7 Hz, H-6a), 4.17 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.04 (dd, 1H, $J_{5,6b}$ 1.6 Hz, $J_{6,6b}$ 12.1 Hz, H-6b), 3.62 (ddd, 1H, H-5), 3.50 (s, 3H, OCH_3), 3.36 (dd, 1H, $J_{2,3}$ 9.5 Hz, H-2), 2.88 (s, 3H, NCH_3), 1.99, 1.93 (s, 9H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 170.4, 169.9, 169.4 (acetyl *C*O), 139.8 (N=*C*=N), 103.0 (C-1), 73.9, 71.5, 68.3 (C-3, C-4, C-5), 62.0 (C-6), 60.0 (C-2), 57.3 (O*C*H_3), 32.1 (N*C*H_3), 20.5, 20.4 (acetyl *C*H_3). Anal. Calcd for $C_{15}H_{22}N_2O_8$ (358.35): C, 50.28; H, 6.19; N, 7.82. Found: C, 50.35; H, 6.05; N, 7.76.

Methyl 3,4,6-tri-O-*acetyl-2-deoxy-2-[*N′-*(2,3,4,6-tetra*-O-*acetyl*-β-D-*glucopyranosyl)carbodiimido]*-β-D-*glucopyranoside* (**37**).—Prepared from **35** (1.42 g, 2.0 mmol) according to the previous procedure. Yield: 1.02 g (76%), colourless crystalline product, mp 141–142 °C, $[\alpha]_D$ +6.1° (*c* 1.0, $CHCl_3$); *v* (KBr): 2148 (N=C=N) and 1750 (OAc) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.16 (Ψt, 1H, $J_{4',5'}$ 8.5 Hz, H-4′), 5.10 (t, 1H, $J_{4,5}$ 9.5 Hz, H-4), 5.06 (dd, 1H, $J_{3,4}$ 9.5 Hz, H-3), 4.96 (t, 1H, $J_{3',4'}$ 9.5 Hz, H-3′), 4.91 (Ψt, 1H, $J_{2',3'}$ 9.5 Hz, H-2′), 4.69 (d, 1H, $J_{1,2}$ 8.9 Hz, H-1′), 4.32 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.28 (dd, 1H, $J_{5,6}$ 4.5 Hz, $J_{6a,6b}$ 12.3 Hz, H-6a), 4.21 (dd, 1H, $J_{5',6a'}$ 2.1 Hz, $J_{6a',6b'}$ 12.1 Hz, H-6a′), 4.16 (dd, 1H, $J_{5',6b'}$ 4.5 Hz, H-6b′), 4.11 (dd, 1H, $J_{5,6b}$ 2.1 Hz, H-6b), 3.73 (ddd, 2H, H-5, H-5′), 3.57 (s, 3H, OCH_3), 3.50 (dd, 1H, $J_{2,3}$ 10.0 Hz, H-2), 2.09, 2.07, 2.06, 2.02, 2.00, 1.99 (s, 21H, acetyl CH_3); ^{13}C NMR ($CDCl_3$): δ 170.4, 169.9, 169.8, 169.4, 169.1 (acetyl *C*O), 137.6 (N=*C*=N), 102.4 (C-1), 84.2 (C-1′), 73.7, 71.5, 68.3 (C-3, C-4, C-5), 73.3, 72.7, 72.3, 67.8 (C-2′, C-3′, C-4′, C-5′), 61.7, 61.3 (C-6, C-6′), 59.8 (C-2), 57.1 (O*C*H_3), 20.5, 20.4 (acetyl *C*H_3). Anal. Calcd for $C_{28}H_{38}N_2O_{17}$ (674.62): C, 49.85; H, 5.68; N, 4.15. Found: C, 50.01; H, 5.52; N, 4.17.

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