Carbohydrate Research xxx (2009) xxx–xxx

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Note

Synthesis of some O-, S- and N-glycosides of hept-2-ulopyranosonamides

Veronika Nagy [a], Katalin Czifrák [a], Attila Bényei [b], László Somsák [a,*]

[a] Department of Organic Chemistry (POB 20), University of Debrecen, H-4010 Debrecen, Hungary
[b] Department of Physical Chemistry (POB 7), University of Debrecen, H-4010 Debrecen, Hungary

ARTICLE INFO

Article history:
Received 30 December 2008
Received in revised form 6 February 2009
Accepted 7 February 2009
Available online xxxx

Keywords:
Hept-2-ulopyranosonamides
O-glycoside
S-glycoside
N-glycoside

ABSTRACT

(O-Peracylated α-D-*gluco*- and -*galacto*-hept-2-ulopyranosylbromide)onamides gave the corresponding (alkyl β-D-*glyco*-hept-2-ulopyranoside)onamides under Koenigs–Knorr conditions, and similar aryl glycosides were obtained with sodium phenolates; (aryl and hetaryl 2-thio-β-D-*gluco*-hept-2-ulopyranoside)onamides were formed with thiophenols in the presence of K_2CO_3 in acetone, and reactions with aniline in CH_2Cl_2 furnished (*N*-phenyl β-D-*glyco*-hept-2-ulopyranosylamine)onamides. Some deprotected derivatives of D-*gluco* configuration obtained by the Zemplén protocol showed no significant inhibition against rabbit muscle glycogen phosphorylase b.

C-(2,3,4,6-Tetra-*O*-acyl-1-bromo-1-deoxy-β-D-glycopyranosyl)formamides (3,4,5,7-tetra-*O*-acyl-α-D-*glyco*-hept-2-ulopyranosylbromide)onamides)[1–5] (e.g., **1**[1,2] and **2**[5]) proved versatile starting materials for the syntheses of diverse monosaccharide derivatives. Thus, their reactions with nucleophiles such as H_2O,[6] azide ion,[7,8] nitriles,[9] acetone and DMSO,[10] cyanate and thiocyanate ions,[2,3,6] the latter two resulting in cyclisations to give glycopyranosylidene-spiro-(thio)hydantoins efficient glucose analogue glycogen phosphorylase inhibitors (GPIs),[11–15] as well as eliminations to substituted glycals[1] were reported. Several derivatives of D-glucose with a $CONH_2$ moiety in the α-anomeric position were shown to be GPIs,[16–18] although a clearcut conclusion for the role of this group could not yet be drawn.[8] In order to produce new compounds of this type, and to study the reactivity of hept-2-ulopyranosylonamide bromides towards further nucleophiles, we have investigated the preparation of some O-, S- and N-glycosidic derivatives from **1** and **2**.

Treatment of **1** with MeOH or EtOH as the solvent in the presence of Ag_2CO_3[19] gave methyl and ethyl glycosides **3** and **4**, respectively (Table 1, entries 1 and 2). Decreasing the amount of EtOH in CH_2Cl_2 as co-solvent was investigated (entries 3–6) to show that as few as 2 equiv of the alcohol gave satisfactory results. Changing the promoter to the more efficient AgOTf significantly reduced the reaction time and increased the yield (entry 6). A large excess of *n*-BuOH gave the corresponding glycoside **7** in satisfactory yield (entry 7). On the other hand, reactions of **1** with *t*-BuOH or BnOH (entries 8 and 9), and similarly, those of **2** with EtOH or *n*-BuOH (entries 12 and 13) gave significant amounts of the corresponding O-peracylated α-D-*glyco*-hept-2-ulopyranosonamides **15**[2] and **16**[4,5] besides the expected glycosides **7** and **8** as well as **12** and **14**, respectively. The reaction of 2-nitrophenol with **1** in the presence of AgOTf and Et_3N or DBU gave **9** in 32% and 24% yields, respectively. Under phase transfer conditions (2-nitrophenol in CH_2Cl_2, ~1 M NaOH in water, Bu_4NBr) **9** could not be observed in the reaction mixture. Therefore, we turned to the sodium salt of 2-nitrophenol (entry 10), however, this reaction again gave **9** in a low yield accompanied by **15**. On the contrary, sodium 4-nitrophenolate (entry 11) gave the expected **10** in good yield. The steric accessibility of the nucleophilic part of the reagents may be responsible for the large differences in the outcomes of these reactions. Deprotection of glycosides **4** and **12** was effected by the Zemplén protocol, while **10** was deacetylated by KCN/MeOH to give **5**, **13** and **11**, respectively.

For the formation of *N*-phenyl-glycosylamines,[20,21] **1** and **2** were reacted with aniline to give **17** and **18**, respectively (Scheme 1). The latter was deprotected by the Zemplén method to yield **19**.

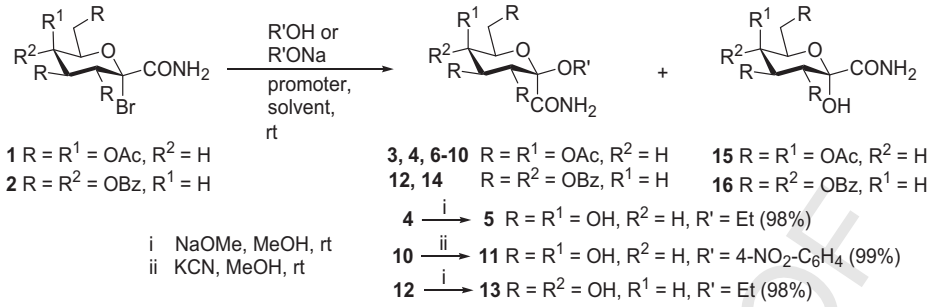
To obtain S-glycosides,[22] **2** was reacted with thiols in acetone in the presence of K_2CO_3 to give the expected products **20**, **22** and **24** in good yields (Scheme 1). For deprotection of these compounds the Zemplén method was applied to give **21**, **23** and **25**, respectively, without difficulties.

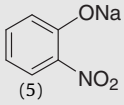
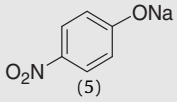
Structure elucidation of the new compounds was straightforward by NMR methods. The $^4C_1$ conformation of the pyranose rings followed from the vicinal proton–proton coupling constants. For most representative compounds, the configuration of the anomeric carbon was established on the basis of three-bond heteronuclear couplings between H-2 (parent sugar numbering) and the

* Corresponding author. Tel.: +36 52 512 900/22348; fax: +36 52 453 836.
E-mail address: somsak@tigris.unideb.hu (L. Somsák).

0008-6215/$ - see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.carres.2009.02.011

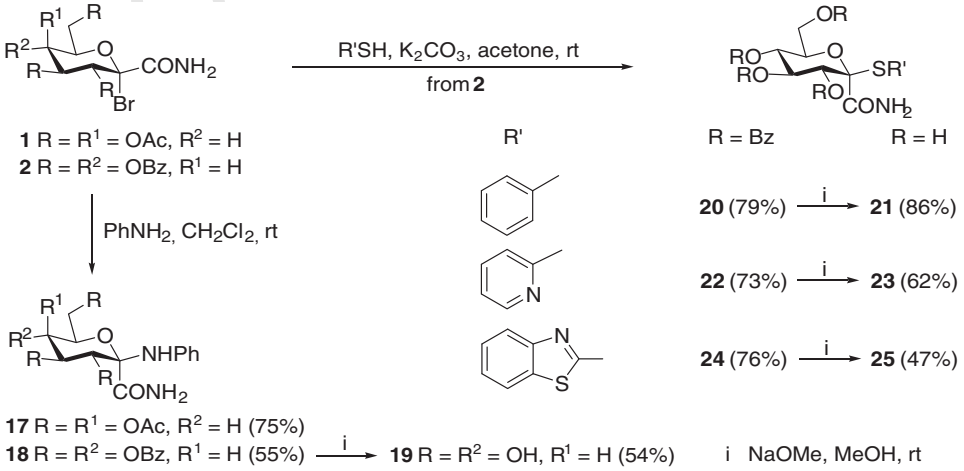
Table 1
Preparation of (alkyl or aryl β-D-*glyco*-hept-2-ulopyranoside)onamides



Entry	Starting compound	R′OH or R′ONa (equiv)	Promoter	Solvent	Reaction time	Product(s) (Yield [%])	
1	**1**	MeOH (as solvent)	Ag_2CO_3	MeOH	2 h	**3** (89)	–
2	**1**	EtOH (as solvent)	Ag_2CO_3	EtOH	2 h	**4** (85)	–
3	**1**	EtOH (70)	Ag_2CO_3	CH_2Cl_2	2 h	**4** (84)	–
4	**1**	EtOH (10)	Ag_2CO_3	CH_2Cl_2	1 d	**4** (93)	–
5	**1**	EtOH (2)	Ag_2CO_3	CH_2Cl_2	2 d	**4** (50)	–
6	**1**	EtOH (2)	AgOTf	CH_2Cl_2	5 min	**4** (80)	–
7	**1**	*n*-BuOH (70)	Ag_2CO_3	CH_2Cl_2	2 d	**6** (90)	–
8	**1**	*t*-BuOH (10)	Ag_2CO_3	CH_2Cl_2	7 d	**7** (21)	**15** (29)
9	**1**	$C_6H_5CH_2OH$ (10)	Ag_2CO_3	CH_2Cl_2	7 d	**8** (31)	**15** (9)
10	**1**	 (5)	–	CH_2Cl_2	36 d	**9** (24)	**15** (25)
11	**1**	 (5)	–	CH_3CN	1 d	**10** (82)	–
12	**2**	EtOH (50)	Ag_2CO_3	CH_2Cl_2	2 d	**12** (87)	**16** (10)
13	**2**	*n*-BuOH (43)	Ag_2CO_3	CH_2Cl_2	6 d	**14** (56)	**16** (31)

exocyclic carbonyl of the amide group measured as earlier.[8] The values larger than 4 Hz suggested *trans* arrangement of the relevant atoms in the $^4C_1$ conformation.[8] In case of **4**, a single crystal X-ray structure determination unequivocally confirmed the anomeric configuration (Fig. 1).

The investigated substitution reactions were clean, that is, disregarding by-products **15** and **16** no other compounds than the isolated products were observed by TLC. This reveals exclusive stereoselectivity for each transformation. An explanation for this can be an S_N2 type replacement of bromine in the cases of phenolates, aniline and thiolates. In the reactions with alcohols promoted by silver salts neighbouring group participation of the 2-acyloxy substituent in the possible intermediate glycosylium ion may account for the inversion. However, given the electron-withdrawing character of the carboxamido group, formation of the glycosylium ion may be unfavourable. Therefore, an electrophilically assisted



Scheme 1.

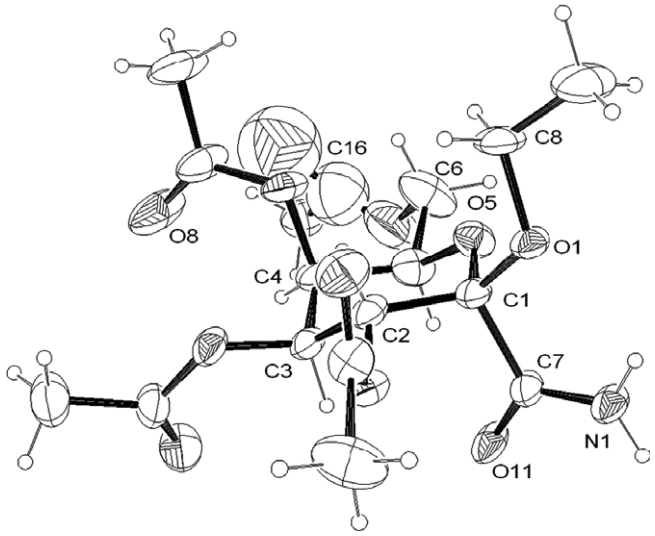


Figure 1. Ortep view at 40% probability level and partial crystallographic numbering scheme of compound **4**. Selected torsion angles (°) for the two molecules in the asymmetric unit: O5–C1–O1–C8: 58 and 46; O1–C1–C7–N1: −3 and −12.

substitution of bimolecular character can also be taken into consideration.

The deprotected compounds were assayed against rabbit muscle glycogen phosphorylase b as described earlier,[3,6] and showed no significant inhibition (**13** 21% at 625 μM; **19** IC_{50} > 60 mM; **21**, **23**, **25** no inhibition at 625 μM).

1. Experimental

1.1. General methods

Melting points were measured in open capillary tubes or on a Kofler hot-stage and are uncorrected. Optical rotations were determined with a Perkin–Elmer 241 polarimeter at rt. NMR spectra were recorded with Bruker 200 (200/50 MHz for $^1H/^{13}C$), Bruker 360 (360/90 MHz for $^1H/^{13}C$) or Avance DRX 500 (500/125 MHz for $^1H/^{13}C$) spectrometers. Chemical shifts are referenced to Me_4Si (^1H) or to the residual solvent signals (^{13}C). TLC was performed on DC-Alurolle Kieselgel 60 F_{254} (Merck), and the plates were visualised under UV light and by gentle heating. For column chromatography, Kieselgel 60 (Merck, particle size 0.063–0.200 mm) was used. Dichloromethane was distilled from P_4O_{10} and acetone from $CaSO_4$) and stored over 4 Å molecular sieves. Organic solutions were dried over anhydrous $MgSO_4$ and were concentrated under diminished pressure at 40–50 °C (water bath).

1.2. General procedure I for the preparation of *C*-(2,3,4,6-tetra-*O*-acetyl-1-alkoxy-α-D-glycopyranosyl)formamides ((alkyl 3,4,5,7-tetra-*O*-acetyl-β-D-*galacto*-hept-2-ulopyranoside)onamides)

To a solution of a *C*-(2,3,4,6-tetra-*O*-acyl-1-bromo-1-deoxy-β-D-glycopyranosyl)formamide, ((3,4,5,7-tetra-*O*-acyl-α-D-*glyco*-hept-2-ulopyranosylbromide)onamide) (**1**[1,2] or **2**,[5] 0.3 mmol) in dry CH_2Cl_2 (2 mL) containing molecular sieves (0.1 g, 3 Å) an alcohol (Table 1) and Ag_2CO_3 (1 equiv, 0.30 mmol, 0.08 g) or silver triflate (1 equiv, 0.30 mmol, 0.07 g) and Et_3N (1 equiv, 0.30 mmol, 39 μL) were added. The reaction mixture was stirred in the dark at rt until TLC (1:1 EtOAc–hexane) showed the complete transformation of the starting material. The mixture was then filtered on a Celite pad, and the solvent was removed under diminished pressure. The crude product was crystallised from EtOAc–hexane or purified by column chromatography.

1.3. General procedure II for the preparation of *C*-(2,3,4,6-tetra-*O*-acyl-1-deoxy-1-phenylamino-α-D-glycopyranosyl)formamides ((*N*-Phenyl 3,4,5,7-tetra-*O*-acyl-β-D-*glyco*-hept-2-ulopyranosylamine)onamides)

To a solution of *C*-(2,3,4,6-tetra-*O*-acyl-1-bromo-1-deoxy-β-D-glycopyranosyl)formamide, ((3,4,5,7-tetra-*O*-acyl-α-D-*glyco*-hept-2-ulopyranosylbromide)onamide) (**1**[1,2] or **2**,[5] 0.3 mmol) in dry CH_2Cl_2 (2 mL) containing molecular sieves (0.1 g, 3 Å), aniline (50 equiv to **1** and 5 equiv to **2**) was added. The reaction mixture was stirred at rt until TLC (1:1 EtOAc–hexane) showed the complete transformation of the starting sugar (1–2 d). The mixture was then filtered on a Celite pad and the solvent was evaporated. The residue was dissolved in EtOAc, the solution was washed with water, diluted hydrochloric acid, and satd aq $NaHCO_3$ solution. After drying and solvent removal the crude product was crystallised from EtOAc–hexane or purified by column chromatography.

1.4. General procedure III for the preparation of *C*-(2,3,4,6-tetra-*O*-benzoyl-1-deoxy-1-aryl or heteroarylsulfanyl-α-D-glucopyranosyl)formamides ((aryl- or heteroaryl- 3,4,5,7-tetra-*O*-benzoyl-2-thio-β-D-*gluco*-hept-2-ulopyranoside)onamides)

To a solution of *C*-(1-bromo-1-deoxy-2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-formamide,[5] ((3,4,5,7-tetra-*O*-benzoyl-α-D-*gluco*-hept-2-ulopyranosylbromide)onamide) (**2**, 0.20 g, 0.28 mmol) in dry acetone (3 mL) containing molecular sieves (0.1 g, 3 Å), a thiol (1.40 mmol) and K_2CO_3 (0.20 g, 1.40 mmol) were added. The reaction was stirred at rt until TLC (1:2 EtOAc–hexane) showed complete transformation of the starting material. The mixture was then filtered, diluted with CH_2Cl_2 (5 mL), washed with satd aq $NaHCO_3$ solution (2 × 5 mL), and water (1 × 5 mL). After drying and solvent removal, the crude product was purified by column chromatography.

1.5. General procedure IV for the Zemplén-deacylation

To a solution of an *O*-acyl protected compound in dry MeOH 1–2 drops of a ~1 M methanolic NaOMe solution were added, and the reaction mixture was maintained at rt until completion of the transformation TLC (1:1 $CHCl_3$–MeOH). Amberlyst 15 (H^+ form) was then added to remove sodium ions, the resin was filtered off, and the solvent was removed under diminished pressure. If the residue was chromatographically not uniform it was purified by column chromatography or crystallisation.

1.6. *C*-(2,3,4,6-Tetra-*O*-acetyl-1-methoxy-α-D-galactopyranosyl) formamide ((Methyl 3,4,5,7-tetra-*O*-acetyl-β-D-*galacto*-hept-2-ulopyranoside)onamide) (3)

This compound was prepared from **1** (0.30 g 0.66 mmol) according to General procedure **I**. The crude product was crystallised to give **3** (0.22 g, 85%) as a yellowish crystalline product. Mp: 120–122 °C; $[\alpha]_D$ +69 (*c* 1.03, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 6.65 (s,1H, NH), 5.93 (s, 1H, NH), 5.86 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.1 Hz, H-3), 5.53 (d, 1H, $J_{2,3}$ 10.5 Hz, H-2), 5.50 (dd, 1H, $J_{3,4}$ 3.1 Hz, $J_{4,5}$ 1.5 Hz, H-4), 4.85 (ddd, 1H, $J_{5,6}$ 6.3 Hz, $J_{5,6'}$ 5.3 Hz, H-5), 4.12 (dd, 1H, $J_{6,6'}$ 11.0 Hz, H-6), 4.05 (dd, 1H, $J_{6,6'}$ 11.0 Hz, H-6′), 3.48 (s, 3H, CH_3), 2.14, 2.04, 2.01, 1.95 (4 × s, 12H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm): 170.4 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~4.7 Hz), 169.7 (2), 169.6 (2) (*C*O), 97.5 (C-1), 71.1, 70.0, 67.4, 64.7 (C-2 to C-5), 61.5 (C-6), 49.8 (OCH_3), 20.7,

20.6, 20.5 ($COCH_3$). Anal. Calcd for $C_{16}H_{23}NO_{11}$ (405.36): C, 47.41; H, 5.72; N, 3.46. Found: C, 47.00; H, 5.52; N, 3.23.

1.7. *C*-(2,3,4,6-Tetra-*O*-acetyl-1-ethoxy-α-D-galactopyranosyl) formamide ((ethyl 3,4,5,7-tetra-*O*-acetyl-β-D-*galacto*-hept-2-ulopyranoside)onamide) (4)

This compound was prepared from **1** (0.20 g 0.44 mmol) according to General procedure **I**. The crude product was crystallised from hexane to give **4** (0.16 g, 85%) as a white crystalline product. Mp 135–137 °C; $[\alpha]_D$ +57 (*c* 1.04, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 6.69 (s, 1H, NH), 6.26 (s, 1H, NH), 5.85 (dd, 1H, $J_{2,3}$ 10.3 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.51 (d, 1H, $J_{2,3}$ 10.3 Hz, H-2), 5.46 (dd, 1H, $J_{3,4}$ 3.6 Hz, $J_{4,5}$ 1.2 Hz, H-4), 4.81 (pseudo t, 1H, $J_{5,6}$ 6.8 Hz, $J_{5,6'}$ 6.7 Hz, H-5), 4.10–3.99 (m, 2H, H-6, H-6′), 3.88–3.70 (m, 2H, CH_2), 2.12, 2.05, 1.99, 1.91 (4 × s, 12H, $OCOCH_3$), 1.19 (m, 3H, CH_3), ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.3 ($CONH_2$ $^3J_{H\text{-}2,CO}$ = ~6.1 Hz), 169.9 (2), 169.7 (2) (*C*O), 97.4 (C-1), 70.9, 70.0, 67.4, 65.4 (C-2 to C-5), 61.4 (C-6). 58.3 (CH_2), 20.7, 20.6, 20.5 (2) ($COCH_3$), 15.3 (CH_3). Anal. Calcd for $C_{17}H_{25}NO_{11}$ (419.10): C, 48.69; H, 6.01; N, 3.34. Found: C, 48.54; H, 6.04; N, 3.49.

1.8. *C*-(1-Ethoxy-α-D-galactopyranosyl)formamide ((ethyl β-D-*galacto*-hept-2-ulopyranoside)onamide) (5)

This compound was prepared from **4** (0.20 g 0.47 mmol) according to General procedure **IV** to give **5** (0.12 g, 98%) as a yellowish oil. R_f = 0.32 (7:3 $CHCl_3$–MeOH); $[\alpha]_D$ +61 (*c* 1.26, H_2O); ^1H NMR (D_2O, 360 MHz): δ (ppm) 4.28–3.55 (m, 8H, H-2, H-3, H-4, H-5, H-6, H-6′, CH_2), 1.18 (t, 3H, *J* 7.3 Hz, CH_3), ^{13}C NMR (D_2O, 90 MHz): δ (ppm) 173.7 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~4.8 Hz), 100.6 (C-1), 76.4, 72.8, 71.0, 70.1 (C-2 to C-5), 62.7 (C-6), 59.4 (CH_2), 15.9 (CH_3). Anal. Calcd for $C_9H_{17}NO_7$ (251.24): C, 43.03; H, 6.82; N, 5.58. Found: C, 43.54; H, 6.63; N, 5.12.

1.9. *C*-(2,3,4,6-Tetra-*O*-acetyl-1-*n*-buthoxy-α-D-galactopyranosyl)formamide ((*n*-buthyl 3,4,5,7-tetra-*O*-acetyl-β-D-*galacto*-hept-2-ulopyranoside)onamide) (6)

This compound was prepared from **1** (0.20 g 0.44 mmol) according to General procedure **I**. The crude product was crystallised from hexane to give **6** (0.18 g, 90%) as a white crystalline product. Mp: 97–99 °C; $[\alpha]_D$ +48 (*c* 1.24, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 6.65 (s, 1H, NH), 6.42 (s, 1H, NH), 5.84 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.1 Hz, H-3), 5.50 (d, 1H, $J_{2,3}$ 10.5 Hz, H-2), 5.47 (dd, 1H, $J_{3,4}$ 3.1 Hz, $J_{4,5}$ 1.2 Hz, H-4), 4.81 (pseudo t, 1H, $J_{5,6}$ 5.8 Hz, $J_{5,6'}$.8 Hz, H-5), 4.15–3.99 (m, 2H, H-6, H-6′), 3.80–3.64 (m, 2H, CH_2), 2.11, 2.01, 1.98, 1.91 (4 × s, 12H, $OCOCH_3$), 1.60–1.55 (m, 2H, CH_2), 1.38–1.32 (m, 2H, CH_2), 0.91 (t, 3H, *J* 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.3, 169.9, 169.7, 169.6 (*C*O), 170.0 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~6.1 Hz), 97.3 (C-1), 70.9, 70.0, 67.3, 65.4 (C-2 to C-5), 62.1 (C-6), 61.3, 31.5 (CH_2), 20.6, 20.5, 20.5 ($COCH_3$) 19.0 (CH_2), 13.6 (CH_3). Anal. Calcd for $C_{19}H_{29}NO_{11}$ (447.44): C, 51.00; H, 6.53; N, 3.13. Found: C, 51.15; H, 6.57; N, 3.29.

1.10. *C*-(2,3,4,6-Tetra-*O*-acetyl-1-*t*-buthoxy-α-D-galactopyranosyl)formamide ((*t*-buthyl 3,4,5,7-tetra-*O*-acetyl-β-D-*galacto*-hept-2-ulopyranoside)onamide) (7)

Q3 This compound was prepared from **1** (0.20 g 0.44 mmol) according to General procedure **I**, and was purified by column chromatography (1:1 EtOAc–hexane) to give **7** (0.04 g, 21%) as a colourless oil, and in the second fraction it gave compound **15** (29%). R_f = 0.42 (3:1 EtOAc–hexane); $[\alpha]_D$ +19 (*c* 1.02, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 6.81 (s, 1H, NH), 6.19 (s, 1H, NH), 5.84 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.1 Hz, H-3), 5.60 (d, 1H, $J_{2,3}$ 10.5 Hz, H-2), 5.50 (dd, 1H, $J_{3,4}$ 3.1 Hz, $J_{4,5}$ 1.5 Hz, H-4), 4.91 (pseudo t, 1H, $J_{5,6}$ 6.3 Hz, $J_{5,6'}$ 6.3 Hz, H-5), 4.13–4.10 (m, 2H, H-6, H-6′), 2.10, 2.02, 2.00, 1.93 (4 × s, 12H, $OCOCH_3$), 1.42 (s, 9H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 171.4 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~5.8 Hz), 170.3, 169.8, 169.7 (2) (*C*O), 98.7 ($C(CH_3)_3$), 80.1 (C-1), 71.3, 70.0, 96.9, 67.5 (C-2 to C-5), 61.4 (C-6), 30.1 ($C(CH_3)_3$), 20.8, 20.6 (3) ($COCH_3$). Anal. Calcd for $C_{19}H_{29}NO_{11}$ (447.44): C, 51.00; H, 6.53; N, 3.13. Found: C, 51.17; H, 6.52; N, 3.30.

1.11. *C*-(2,3,4,6-Tetra-*O*-acetyl-1-benzyloxy-α-D-galactopyranosyl)formamide ((benzyl 3,4,5,7-tetra-*O*-acetyl-β-D-*galacto*-hept-2-ulopyranoside)onamide) (8)

This compound was prepared from **1** (0.20 g 0.44 mmol) according to General procedure **I**, and was purified by column chromatography (1:1 EtOAc–hexane) to give **8** (0.07 g, 31%) as a white crystalline product, and in the second fraction it gave compound **15** (9%). Mp 163–164 °C; $[\alpha]_D$ +16 (*c* 1.03, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.42–7.33 (m, 5H, ArH), 6.63 (s, 1H, NH), 5.93 (dd, 1H, $J_{2,3}$ 10.3 Hz, $J_{3,4}$ 3.1 Hz, H-3), 5.68 (d, 1H, $J_{2,3}$ 10.3 Hz, H-2), 5.58–5.54 (m, 2H, H-4, NH), 4.93 (pseudo t, 1H, $J_{5,6}$ 6.8 Hz, $J_{5,6'}$ 6.6 Hz, H-5) 4.90, 4.74 (2 × d, 2H, *J* 10.5 Hz, CH_2), 4.18–4.12 (m, 2H, H-6, H-6′), 2.17, 2.08, 2.03, 1.98 (4 × s, 12H, $OCOCH_3$), ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.3 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~6.1 Hz), 169.9, 169.8 (2), 169.7 (*C*O), 136.7, 128.5, 128.4, 128.0 (Ar*C*), 97.5 (C-1), 71.2, 69.9, 67.3, 65.7 (C-2 to C-5), 64.7 (CH_2),61.3 (C-6), 20.7, 20.5, 20.5 (3) ($COCH_3$). Anal. Calcd for $C_{22}H_{27}NO_{11}$ (481.46): C, 54.88; H, 5.65; N, 2.91. Found: C, 54.09; H, 5.62; N, 2.92.

1.12. *C*-[2,3,4,6-Tetra-*O*-acetyl-1-(2-nitrophenoxy)-α-D-galactopyranosyl]formamide ((2-nitrophenyl 3,4,5,7-tetra-*O*-acetyl-β-D-*galacto*-hept-2-ulopyranoside)onamide) (9)

To a solution of **1** (0.20 g, 0.44 mmol) in dry CH_2Cl_2 (2 mL) containing molecular sieves (3 Å), sodium 2-nitrophenolate (0.35 g, 2.20 mmol) was added. The reaction mixture was stirred at rt until TLC (1:1 EtOAc–hexane) showed complete transformation of the starting sugar (36 d). Then the mixture was filtered on a Celite pad, and the solvent was removed. The oily residue was purified by column chromatography (1:1 EtOAc–hexane) to give **9** (0.04 g, 24%) as a yellow oil, and in the second fraction it gave compound **15** (0.04 g, 25%). Characterisation of **9**: R_f = 0.72 (1:3 EtOAc–hexane); $[\alpha]_D$ +52 (*c* 0.49, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.97–7.85 (m, 2H, ArH), 7.56 (m, 1H, ArH) 7.28 (s, 1H, NH), 7.26–7.23 (m, 1H, ArH), 6.23 (s, 1H, NH), 5.79 (dd, 1H, $J_{2,3}$ 10.2 Hz, $J_{3,4}$ 3.1 Hz, H-3), 5.62 (d, 1H, $J_{2,3}$ 10.2 Hz, H-2), 5.54 (dd, 1H, $J_{3,4}$ 3.1 Hz, $J_{4,5}$ 1.1 Hz, H-4), 5.19 (pseudo t, 1H, $J_{5,6}$ 6.1 Hz, $J_{5,6'}$ 6.1 Hz, H-5), 4.11–4.06 (m, 2H, H-6, H-6′), 2.09, 2.03, 2.01, 1.89 (4 × s, 12H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm): 170.3, 169.5, 169.3, 168.6 (2) (*C*O), 146.1, 134.0, 126.1, 124.3, 121.5 (Ar*C*), 100.7 (C-1), 72.6, 69.9, 67.3, 65.3 (C-2 to C-5), 61.4 (C-6), 20.5, 20.4, 20.3 (2) ($COCH_3$). Anal. Calcd for $C_{21}H_{24}N_2O_{13}$ (512.43): C, 49.22; H, 4.72; N, 5.47. Found: C, 50.05; H, 4.53; N, 5.29.

1.13. *C*-[2,3,4,6-Tetra-*O*-acetyl-1-(4-nitrophenoxy)-α-D-galactopyranosyl]formamide ((4-nitrophenyl 3,4,5,7-tetra-*O*-acetyl-β-D-*galacto*-hept-2-ulopyranoside)onamide) (10)

To a solution of **1** (1.0 g, 2.20 mmol) in dry CH_3CN (10 mL) containing molecular sieves (3 Å), sodium 4-nitrophenolate (1.77 g, 11 mmol) was added. The reaction mixture was stirred at rt until TLC (1:1 EtOAc–hexane) showed the complete transformation of

the starting sugar (1 d). Then the mixture was filtered on a Celite pad and the solvent was removed. The oily residue was purified by column chromatography (1:1 EtOAc–hexane) to give **10** (0.93 g, 82%) as white crystals from EtOH. Mp: 233–235 °C; $[\alpha]_D$ +27 (*c* 1.10, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.13 (d, 2H, *J* 9.2 Hz, ArH), 7.37 (d, 2H, *J* 9.2 Hz, ArH), 6.87 (s, 1H, NH), 6.67 (s, 1H, NH), 5.77 (dd, 1H, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 2.6 Hz, H-3), 5.54 (d, 1H, $J_{2,3}$ 9.8 Hz, H-2), 5.50 (dd, 1H, $J_{3,4}$ 2.6 Hz, $J_{4,5}$ 1.3 Hz, H-4), 5.00 (pseudo t, 1H, $J_{5,6}$ 6.5 Hz, $J_{5,6'}$ 6.5 Hz, H-5), 4.13 (m, 2H, H-6, H-6′), 2.11, 1.99 (2), 1.96 (3 × s, 12H, $OCOCH_3$), ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.1 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~5.8 Hz), 169.5, 169.4, 168.8 168.3 (*C*O), 157.2, 143.9, 124.8, 120.9, (Ar*C*), 99.8 (C-1), 72.4, 69.8, 67.0, 66.1 (C-2 to C-5), 61.2 (C-6), 20.4, 20.3 (3) ($COCH_3$). Anal. Calcd for $C_{21}H_{24}N_2O_{13}$ (512.43): C, 49.22; H, 4.72; N, 5.47. Found: C, 49.05; H, 4.66; N, 5.32.

1.14. *C*-[1-(4-nitrophenoxy)-α-D-galactopyranosyl]formamide ((4-nitrophenyl β-D-*galacto*-hept-2-ulopyranoside)onamide) (11)

To a solution of **10** (0.20 g, 0.39 mmol) in dry MeOH (5 mL) some crystals of KCN (~5 mg) were added. The reaction mixture was stirred at rt until TLC (7:3 $CHCl_3$–MeOH) showed the complete transformation of the starting material (1 d). The reaction mixture was neutralised with a cation exchange resin Amberlyst 15 (H^+ form). After filtration, the solvent was removed to give **11** (0.15 g, 99%) as a yellowish oil. R_f = 0.65 (7: 3 $CHCl_3$–MeOH); $[\alpha]_D$ +3 (*c* 0.17, H_2O); ^1H NMR (D_2O, 360 MHz): δ (ppm) 8.21 (d, 2H, *J* 8.6 Hz, ArH), 7.45 (d, 2H, *J* 8.6 Hz, ArH), 4.51 (pseudo t, 1H, $J_{5,6}$ 6.8 Hz, $J_{5,6'}$ 5.1 Hz, H-5), 4.15–4.10 (m, 3H, H-2, H-3, H-4), 3.86–3.78 (m, 2H, H-6, H-6′); ^{13}C NMR (D_2O, 90 MHz): δ (ppm) 170.9 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~4.6 Hz), 158.5, 143.5, 125.6 (2), 120.8 (2) (Ar), 101.8 (C-1), 76.9, 70.5, 69.5, 68.2 (C-2 to C-5), 61.4 (C-6). Anal. Calcd for $C_{13}H_{16}N_2O_9$ (344.28): C, 45.35; H, 4.68; N, 8.14. Found: C, 45.33; H, 4.67; N, 8.10.

1.15. *C*-(2,3,4,6-Tetra-*O*-benzoyl-1-ethoxy-α-D-glucopyranosyl)-formamide ((ethyl 3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranoside)onamide) (12)

This compound was prepared from **2** (0.20 g, 0.28 mmol) according to General procedure **I**, and was purified by column chromatography (1:1 EtOAc–hexane) to give **12** (0.16 g, 87%) as a white crystalline product, and in the second fraction it gave compound **16** (0.02 g, 10%). Characterisation of **12**: mp 88–91 °C; $[\alpha]_D$ +65 (*c* 1.08, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.01–7.24 (m, 20H, ArH), 6.82 (s, 1H, NH), 6.62 (t, 1H, *J* 8.8 Hz, *J* 8.8 Hz, H-3 or H-4), 6.18 (s, 1H, NH), 5.88–5.80 (m, 2H, H-2, H-3 or H-4), 5.09 (ddd, 1H, $J_{4,5}$ 8.8 Hz, $J_{5,6}$ 6.7 Hz, $J_{5,6'}$ 3.2 Hz, H-5), 4.73 (dd, 1H, $J_{6,6'}$ 12.1 Hz, $J_{5,6}$ 6.7 Hz, H-6), 4.41 (dd, 1H, $J_{6,6'}$ 12.1 Hz, $J_{5,6'}$ 3.2 Hz, H-6′), 3.89 (q, 2H, *J* 6.8 Hz, CH_2), 1.18 (t, 3H, *J* 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm): 169.8 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~4.1 Hz), 166.0, 165.3, 164.9 (2) (*C*O), 133.4–127.5 (Ar*C*), 97.5 (C-1), 72.1, 72.0, 69.2, 68.8 (C-2 to C-5), 62.5 (C-6), 58.7 (CH_2), 15.2 (CH_3). Anal. Calcd for $C_{37}H_{33}NO_{11}$ (667.68): C, 66.56; H, 4.98; N, 2.10. Found: C, 65.75; H, 4.87; N, 2.22.

1.16. *C*-(1-Ethoxy-α-D-glucopyranosyl)formamide ((ethyl β-D-*gluco*-hept-2-ulopyranoside)onamide) (13)

This compound was prepared from **12** (0.06 g, 0.13 mmol) according to General procedure **IV**, and was purified by column chromatography (7:2:1 $CHCl_3$–MeOH–EtOAc) to give **13** (0.02 g, 98%) as a colourless oil. R_f = 0.25 (7:2:1 $CHCl_3$–MeOH–EtOAc); $[\alpha]_D$ +18 (*c* 0.37, H_2O); ^1H NMR (D_2O, 200 MHz): δ (ppm) 3.90–3.54 (m, 8H, H-2, H-3, H-4, H-5, H-6, H-6′, CH_2), 1.22 (pseudo t, 3H, *J* 7.0 Hz, *J* 6.8 Hz, CH_3); ^{13}C NMR (D_2O, 50 MHz): δ (ppm) 172.6 ($CONH_2$), 99.7 (C-1), 76.4, 75.0, 73.1, 69.5 (C-2 to C-5), 61.4 (C-6), 59.7 (CH_2), 15.0 (CH_3). Anal. Calcd for $C_9H_{17}NO_7$ (251.24): C, 43.03; H, 6.82; N, 5.58. Found: C, 43.12; H, 6.75; N, 5.47.

1.17. *C*-(2,3,4,6-Tetra-*O*-benzoyl-1-*n*-buthoxy-α-D-glucopyranosyl)formamide ((*n*-buthyl 3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranoside)onamide) (14)

This compound was prepared from **2** (0.50 g, 0.71 mmol) according to General procedure **I**, and was purified by column chromatography (1:2 EtOAc–hexane) to give **14** (0.27 g, 56%) as a white crystalline product, and in the second fraction it gave compound **16** (0.14 g, 31%). Characterisation of **14**: mp 171–173 °C; $[\alpha]_D$ +64 (*c* 1.10, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.10–7.24 (m, 20H, ArH), 6.79 (s, 1H, NH), 6.63 (t, 1H, *J* 9.2 Hz, *J* 9.2 Hz, H-3 or H-4), 6.39 (s, 1H, NH), 5.88–5.82 (m, 2H, H-2, H-3 or H-4), 5.09 (ddd, 1H, $J_{4,5}$ 9.2 Hz, $J_{5,6}$ 3.5, $J_{5,6'}$ 3.0 Hz, H-5), 4.75 (dd, 1H, $J_{6,6'}$ 12.1 Hz, $J_{5,6}$ 3.5 Hz, H-6), 4.40 (dd, 1H, $J_{6,6'}$ 12.1 Hz, $J_{5,6'}$ 3.0 Hz, H-6′), 3.85–3.80 (m, 2H, CH_2), 1.57–1.50 (m, 2H, CH_2), 1.32–1.22 (m, 2H, CH_2), 0.83 (t, 3H, *J* 7.1 Hz, *J* 6.8 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 169.9 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~4.7 Hz), 165.3 (2), 164.9 (2) (*C*O), 133.4–128.1 (Ar*C*), 97.5 (C-1), 72.2, 72.1, 69.3, 68.9 (C-2 to C-5), 62.6 (C-6), 62.5, 31.6, 19.0 (CH_2), 13.6 (CH_3); Anal. Calcd for $C_{39}H_{37}NO_{11}$ (695.74): C, 67.33; H, 5.36; N, 2.01. Found: C, 66.95; H, 5.47; N, 2.32.

1.18. *C*-(2,3,4,6-Tetra-*O*-acetyl-1-deoxy-1-phenylamino-α-D-galactopyranosyl)formamide ((*N*-phenyl 3,4,5,7-tetra-*O*-acetyl-β-D-*galacto*-hept-2-ulopyranosylamine)onamide) (17)

This compound was prepared from **1** (0.20 g, 0.44 mmol) according to General procedure **II**. The oily residue was crystallised from Et_2O to give **17** (0.16 g, 75%) as a white crystalline product. Mp: 200–201 °C, $[\alpha]_D$ −30 (*c* 1.02, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.25–7.10 (m, 2H, ArH), 6.88–6.75 (m, H, ArH), 6.47 (s, 1H, NH), 6.02 (s, 1H, NH), 5.56 (dd, 1H, $J_{3,4}$ 2.9 Hz, H-3), 5.52 (dd, 1H, $J_{4,5}$ 0.9 Hz, H-4), 5.42 (pseudo t, 1H, $J_{5,6}$ 7.2 Hz, H-5), 5.38 (d,1H, $J_{2,3}$ 9.8 Hz, H-2), 5.05 (s, 1H, NH), 4.08 (dd, 1H, $J_{6,6'}$ 11.1 Hz, Hz, H-6), 4.02 (dd, 1H, $J_{5,6'}$ 6.8 Hz, H-6′), 2.11 (2), 1.99, 1.96 (3 × s, 12H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$, 90 MHz) δ (ppm) 171.3, 170.9, 170.3, 170.1, 169.5 (*C*O), 141.8, 128.9 (2), 120.7, 117.2 (2) (Ar*C*), 86.82 (C-1), 71.4, 70.2, 68.7, 67.8 (C-2 to C-5), 61.9 (C-6), 20.8, 20.5 (3) ($COCH_3$). Anal. Calcd for $C_{21}H_{26}N_2O_{10}$ (466.45): C, 54.08; H, 5.62; N, 6.01. Found: C, 54.88; H, 5.50; N, 5.84.

1.19. *C*-(2,3,4,6-Tetra-*O*-benzoyl-1-deoxy-1-phenylamino-α-D-glucopyranosyl)formamide ((*N*-phenyl 3,4,5,7-tetra-*O*-benzoyl-β-D-*gluco*-hept-2-ulopyranosylamine)onamide) (18)

This compound was prepared from **2** (0.50 g, 0.71 mmol) according to General procedure **II** and was purified by column chromatography (1:2 EtOAc–hexane) to give **18** (0.26 g, 55%) from EtOH as yellowish crystals. Mp 96–97 °C $[\alpha]_D$ +108 (*c* 1.33, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.11–6.80 (m, 25H, ArH), 6.56 (s, 1H, NH), 6.36 (t, 1H, *J* 9.1 Hz, *J* 9.1 Hz, H-3 or H-4), 5.90–5.68 (m, 3H, H-2, H-3 or H-4, NH), 5.27 (s, 1H, NH), 5.11–4.55 (m, 2H, H-5, H-6), 4.45 (dd,1H, $J_{6,6'}$ 12,1 Hz, $J_{5,6'}$ 3.2, Hz, H-6′); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 171.2 ($CONH_2$, $^3J_{H\text{-}2\text{-}CO}$ = ~4.7 Hz), 166.2 (2), 165.5, 165.4 (*C*O), 142.0, 128.6 (2), 121.0, 117.5 (2) (Ar*C*), 134.1–128.3 (benzoyl Ar*C*), 87.0 (C-1), 73.7, 72.8, 70.9, 69.7 (C-2 to C-5), 64.0 (C-6). Anal. Calcd for $C_{41}H_{34}N_2O_{10}$ (714.74): C, 68.90; H, 4.72; N, 3.92. Found: C, 68.65; H, 4.80; N, 3.26.

1.20. *C*-(1-Deoxy-1-phenylamino-α-D-glucopyranosyl)formamide ((*N*-Phenyl β-D-*gluco*-hept-2-ulopyranosylamine)onamide) (19)

This compound was prepared from **18** (0.15 g, 0.21 mmol) according to General procedure **IV**, and was purified by column

chromatography (7:2:1 $CHCl_3$–MeOH–EtOAc) to give **19** (0.039 g, 54%) as a yellowish crystalline product. Mp 140–143 °C; $[\alpha]_D$ +115 (*c* 0.212, H_2O); ^1H NMR (D_2O, 360 MHz): δ (ppm) 7.24–6.82 (m, 5H, ArH), 3.84–3.77 (m, 3H, H-5, H-6, H-6′), 3.61 (d, 1H, $J_{2,3}$ 9.2 Hz, H-2), 3.60–3.51 (m, 2H, H-3, H-4); ^{13}C NMR (D_2O, 90 MHz): δ (ppm) 175.4 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~4.0 Hz), 144.5, 129.9 (2), 120.1, 115.6 (2) (ArC), 88.7 (C-1), 74.5, 74.4, 73.1, 69.7 (C-2 to C-5), 60.9 (C-6). Anal. Calcd for $C_{13}H_{18}N_2O_6$ (298.30): C, 52.35; H, 6.08; N, 9.39. Found: C, 52.44; H, 6.23; N, 9.16.

1.21. *C*-(2,3,4,6-Tetra-*O*-benzoyl-1-deoxy-1-phenylsulfanyl-α-D-glucopyranosyl)formamide ((phenyl 3,4,5,7-tetra-*O*-benzoyl-2-thio-β-D-*gluco*-hept-2-ulopyranoside)onamide) (20)

This compound was prepared from **2** (0.50 g, 0.70 mmol) according to General procedure **III**, and was purified by column chromatography (1:2 EtOAc–hexane) to give **20** (0.41 g, 79%) as a white crystalline product. Mp: 89–92 °C; $[\alpha]_D$ +33 (*c* 0.25, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.06–7.14 (m, 25H, ArH), 6.59 (s, 1H, NH_2), 6.51 (s, 1H, NH_2), 6.11, 5.78, (2 × pseudo t, 2H, *J* ~9.2 Hz in each, H-3, H-4), 5.72 (d, 1H, $J_{2,3}$ 9.2 Hz, H-2), 4.81–4.76 (m, 2H, H-5, H-6), 4.46 (dd, 1H, *J* = 11.9, 4.0 Hz, H-6′); ^{13}C NMR ($CDCl_3$, 90 MHz) δ (ppm): 168.1 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~4.6 Hz), 166.0, 165.4, 164.9, 164.4 (*C*O), 136.6, 133.2 (2), 129.7 (3) (thiophenyl), 133.1–127.2 (Ar*C* benzoyl), 88.8 (C-1), 73.4, 71.9, 71.2, 68.8 (C-2 to C-5), 62.6 (C-6); Anal. Calcd for $C_{41}H_{33}NO_{10}S$ (731.28): C, 67.30; H, 4.55; N, 1.91. Found: C, 67.35; H, 4.59; N, 1.96.

1.22. *C*-(1-Deoxy-1-phenylsulfanyl-α-D-glucopyranosyl)formamide ((phenyl 2-thio-β-D-*gluco*-hept-2-ulopyranoside)onamide) (21)

This compound was prepared from **20** (0.20 g, 0.27 mmol) according to General procedure **IV**, and was purified by column chromatography (7:3 $CHCl_3$–MeOH) to give **21** (0.07 g, 86%) as a colourless oil. R_f = 0.74 (1:1 $CHCl_3$–MeOH); $[\alpha]_D$ +64 (*c* 0.19, H_2O); ^1H NMR (D_2O 360 MHz): δ (ppm) 7.72–7.46 (m, 5H, ArH), 3.92 (dd, 1H, $J_{6,6'}$ 13.2 Hz, $J_{5,6'}$ 1.0 Hz, H-6), 3.80 (dd, 1H, $J_{6,6'}$ 13.2 Hz, $J_{5,6'}$ 4.0 Hz, H-6′), 3.64 (t, 1H, *J* 9.2 Hz, *J* 9.2 Hz, H-3 or H-4), 3.60–3.51 (m, 3H, H-2, H-3 or H-4, H-5); ^{13}C NMR (D_2O 90 MHz): δ (ppm) 172.2 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~5.8 Hz), 137.3 (2), 130.9, 129.7 (2), 128.0 (tiophenyl), 89.1 (C-1), 78.2, 74.8, 74.6, 69.4 (C-2 to C-5), 61.0 (C-6), Anal. Calcd for $C_{13}H_{17}NO_6S$ (315.35): C, 49.52; H, 5.43; N, 4.44. Found: C, 49.57; H, 5.38; N, 4.48.

1.23. *C*-[2,3,4,6-Tetra-*O*-benzoyl-1-deoxy-1-(2-pyridylsulfanyl)-α-D-glucopyranosyl]formamide ((2-pyridyl 3,4,5,7-tetra-*O*-benzoyl-2-thio-β-D-*gluco*-hept-2-ulopyranoside)onamide) (22)

This compound was prepared from **2** (0.70 g, 0.98 mmol) according to General procedure **III**, and was purified by column chromatography (1:1 EtOAc–hexane) to give **22** (0.56 g, 73%) as a yellow crystalline product. Mp: 78–80 °C; $[\alpha]_D$ +62 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.33 (d, 1H, *J* 2.6 Hz, pyridine), 8.06–7.23 (m, 23H, ArH, pyridine), 7.04 (s, 1H, NH_2), 6.60 (s, 1H, NH_2), 6.21 (pseudo t, 1H, *J* 9.2 Hz, *J* 9.2 Hz, H-3 or H-4), 6.05 (d, 1H, $J_{2,3}$ 9.2 Hz, H-2), 5.89 (pseudo t, 1H, *J* 10.6 Hz, *J* 9.2 Hz, H-3 or H-4), 4.99 (ddd, 1H, *J* 10.6 Hz, *J* 4.0 Hz, *J* 2.6 Hz, H-5), 4.73 (dd, H, *J* 11.9 Hz, *J* 2.6 Hz, H-6), 4.49 (dd, 1H, $J_{6,6'}$ 11.9 Hz, $J_{5,6}$ 4.0 Hz, H-6′); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 168.6 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~5.9 Hz), 165.8, 165.3, 164.9, 164.4 (*C*O), 152.5, 149.4, 136.8, 133.1, 122.7 (pyridine), 133.4–128.1 (Ar*C* benzoyl), 88.1 (C-1), 73.7, 71.9, 71.6, 68.9 (C-2 to C-5), 62.8 (C-6); Anal. Calcd for $C_{40}H_{32}N_2O_{10}S$ (732.77): C, 65.57; H, 4.40; N, 3.82. Found: C, 65.58; H, 4.36; N, 3.86.

1.24. *C*-[1-Deoxy-1-(2-pyridylsulfanyl)-α-D-glucopyranosyl]-formamide ((2-pyridyl 2-thio-β-D-*gluco*-hept-2-ulopyranoside)-onamide) (23)

This compound was prepared from **22** (0.20 g, 0.27 mmol) according to General procedure **IV**, and was purified by column chromatography (7:3 $CHCl_3$–MeOH) to give **23** (0.05 g, 62%) as a colourless oil. R_f = 0.64 (7:3 $CHCl_3$–MeOH); $[\alpha]_D$ +53 (*c* 0.28, H_2O); ^1H NMR (D_2O, 360 MHz): δ (ppm) 8.59–7.55 (m, 4H, pyridine), 3.93 (dd, 1H, $J_{6,6'}$ 11.9 Hz, $J_{5,6}$ 1.0 Hz, H-6), 3.84 (dd, 1H, $J_{6,6'}$ 11.9 Hz, $J_{5,6'}$ 2.6 Hz, H-6′), 3.72 (t, 1H, *J* 9.2 Hz, *J* 9.2 Hz, H-3 or H-4), 3.66–3.58 (m, 3H, H-2, H-3 or H-4, H-5); ^{13}C NMR (D_2O, 90 MHz): δ (ppm) 171.8 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~5.8 Hz), 150.6, 150.4, 139.2, 133.1, 125.5 (pyridine), 89.3 (C-1), 78.2, 74.8 (2), 69.2 (C-2 to C-5), 60.8 (C-6); Anal. Calcd for $C_{12}H_{16}NO_6S$ (316.24): C, 45.56; H, 5.10; N, 8.86. Found: C, 45.59; H, 5.13; N, 8.89.

1.25. *C*-[2,3,4,6-Tetra-*O*-benzoyl-1-deoxy-1-(2-benzothiazolyl-sulfanyl)-α-D-glucopyranosyl]formamide ((2-Benzothiazolyl 3,4,5,7-tetra-*O*-benzoyl-2-thio-β-D-*gluco*-hept-2-ulopyrano-side)onamide) (24)

This compound was prepared from **2** (0.60 g, 0.84 mmol) according to General procedure **III**, and was purified by column chromatography (1:1 EtOAc–hexane) to give **24** (0.51 g, 76%) as a yellow crystalline product. Mp: 105–108 °C; $[\alpha]_D$ −9 (*c* 0.17, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.08–7.10 (m, 24H, ArH, benzothiazole), 7.24 (s, 1H, NH_2), 6.37 (s, 1H, NH_2), 6.18 (t, 1H, *J* 9.2 Hz, *J* 9.2 Hz, H-3 or H-4), 6.07 (d, 1H, $J_{2,3}$ 9.2 Hz, H-2), 5.98 (t, 1H, *J* 9.2 Hz, *J* 9.2 Hz, H-3 or H-4), 5.06 (ddd, 1H, $J_{4,5}$ 9.2 Hz, $J_{5,6}$ 4.0 Hz, $J_{5,6'}$ 1.0 Hz, H-5), 4.84 (dd, 1H, $J_{6,6'}$ 13.2 Hz, $J_{5,6}$ 4.0 Hz, H-6), 4.57 (dd, 1H, $J_{6,6'}$ 13.2 Hz, $J_{5,6'}$ 1.0 Hz, H-6′); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 167.4 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~4.9 Hz), 165.9, 165.3, 164.9, 164.3 (*C*O), 157.1, 152.2, 137.3, 126.2, 125.2, 123.0, 120.9 (benzothiazole), 133.7–128.2 (Ar*C* benzoyl), 88.7 (C-1), 74.3, 71.5 (2), 68.6 (C-2 to C-5), 62.8 (C-6); Anal. Calcd for $C_{42}H_{32}N_2O_{10}S_2$ (788.86): C, 63.95; H, 4.09; N, 3.55. Found: C, 63.99; H, 4.11; N, 3.50.

1.26. *C*-[1-Deoxy-1-(2-benzothiazolylsulfanyl)-α-D-glucopyranosyl]formamide ((2-benzothiazolyl 2-thio-β-D-*gluco*-hept-2-ulopyranoside)onamide) (25)

This compound was prepared from **24** (0.20 g, 0.25 mmol) according to General procedure **IV**, and was purified by column chromatography (7:3 $CHCl_3$–MeOH) to give **25** (0.04 g, 47%) as a yellow crystalline product. Mp: 183–185 °C; $[\alpha]_D$ +95 (*c* 0.27, DMSO); ^1H NMR (DMSO-d_6, 360 MHz): δ (ppm) 8.07–7.41 (m, 4H, benzothiazole), 7.78 (s, 1H, NH_2), 7.54 (s, 1H, NH_2), 6.26 (d, 1H, *J* 5.3 Hz, OH), 5.32 (d, 1H, *J* 4.0 Hz, OH), 5.11 (d, 1H, *J* 5.3 Hz, OH), 4.56 (pseudo t, 1H, *J* 5.3 Hz, *J* 4.0 Hz, OH), 3.78 (dd, 1H, $J_{6,6'}$ 11.9 Hz, $J_{5,6}$ 6.6 Hz, H-6), 3.68–3.56 (m, 5H, H-2, H-3, H-4, H-5, H-6′); ^{13}C NMR (DMSO-d_6, 90 MHz): δ (ppm) 169.6 ($CONH_2$, $^3J_{H\text{-}2,CO}$ = ~5.9 Hz), 159.9, 151.7, 136.9, 126.1, 125.2, 122.1, 121.4 (benzothiazole), 87.8 (C-1), 79.1, 74.7, 74.5, 69.1 (C-2 to C-5), 60.9 (C-6), Anal. Calcd for $C_{14}H_{16}NO_6S_2$ (372.42): C, 45.15; H, 4.33; N, 7.52. Found: C, 45.05; H, 4.35; N, 7.54.

1.27. X-ray data collection and reduction

Crystals of **4** were grown from EtOAc by slow evaporation of the solution. A colourless block crystal (0.67 × 0.56 × 0.4 mm) was

fixed on a glass capillary using epoxy glue. Data were collected at 293(1) K, Bruker-Nonius MACH3 diffractometer, Mo Kα radiation $\lambda = 0.71073$ Å, ω motion, $\theta_{max} = 25.4°$. The structure was solved using the SIR-92 software[23] and was refined on F^2 using SHELX-97 program,[24] publication material was prepared with the WINGX-suite.[25] Crystal data: formula $C_{17}H_{25}NO_{11}$, $M = 419.38$, monoclinic, space group $P2_1$, $a = 8.569(2)$ Å, $b = 18.397(6)$ Å, $c = 13.688(8)$, $\beta = 94.32(2)°$, $V = 2174(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.281$, 4540 measured, 2899 reflections were unique with $I > 2\sigma(I)$, decay: 3%, $R_1 = 0.088$ and $wR_2 = 0.241$ for 4074 reflections and 503 parameters, GOF = 1.11. Residual electron density: 0.7/−0.31 e/Å^3.

Hydrogen atoms were fixed into geometric position except N–H hydrogens which could be found at the difference electron density map, but were also fixed into calculated positions in the final stage of the refinement. There is a remaining electron density (0.7 e$^-$/Å^3) close to the acetyl carbon atom of C16 which may indicate some disorder of this acetyl group. However, this has no effect on our main findings concerning the configuration of the anomeric carbon. Anisotropic refinement of non-hydrogen atoms was performed except atoms of the C16 acetyl group. Orientation of methyl groups was refined using a riding model. There are two molecules found in the asymmetric unit with slightly different bond length and angle data as indicated in Figure 1, too. The structure is stabilised with intermolecular hydrogen bonds between the amide hydrogen atoms and the O8 acetylene or O11 amide carbonyl oxygen atoms of a symmetry related molecule. Intramolecular hydrogen bond between O1 and the amide proton causes nearly planar orientation of O1–C1–C7–O11–N1. The uniqueness of compound **4** is shown by the fact that no similar structure could be found in the Cambridge Structural Database[26] (Ver. 5.29, November 2007 with upgrades in 2008) containing an amide group as well as oxygen connected to the anomeric carbon atom. Additional crystallographic information is provided in the deposited CIF: CCDC 714419.

Acknowledgements

This work was supported by the Hungarian Scientific Research Fund (Grants: OTKA 46081 and 61336). The authors thank P. Gergely and T. Docsa for the glycogen phosphorylase assays.

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