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GLYCOSYLATIONS WITH TETRA-O-ACETYL-N-ALLYLOXYCARBONYLAMINO-2-DEOXY-β-D-GLUCOSE IN POLAR SOLVENTS

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Abstract- Glycosylations with the title compound were performed in dimethylformamide, acetonitrile, and nitromethane. The latter solvent was found to give good results whereas DMF caused 1-O-deacetylation.

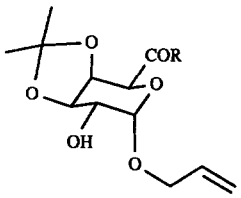
Within the context of synthesizing structural analogues of moenomycin A, we were faced with the problem to couple a suitable derivative of 2-amino-2-deoxy-D-glucosamine with acceptors such as **1**.[1]

One of the standard methods uses the oxazoline **2** as glycosyl donor. A handicap of **2** is its low reactivity. Furthermore, we found that some compounds of type **1**[2] have insufficient solubilities in the solvents usually employed for glycosylations with **2**. Recent publications of *Boullanger et al.*[3-6] suggested to test tetra-O-acetyl-2-allyloxycarbonylamino-β-D-glucose (**3**) as glycosyl donor, since it was reported to be superior to **2** as far as reactivity is concerned.

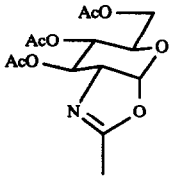
According to Boullanger's results, **3** can be glycosylated with one equivalent of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as promotor in dichloromethane at -35°C either in the presence or absence of molecular sieves 4Å. A neighbouring group assistence of the allyloxycarbonylamino group ensures selective formation of β-glycosides.[5,6]

In model glycosylations, besides dichloromethane we tried dimethylformamide, acetonitrile, and nitromethane as polar solvents. Methanol and isopropanol were selected as alcoholic acceptors. The reaction temperature was set to 20°C, furthermore, the influence of added molecular sieves on the outcome of the reaction was investigated.

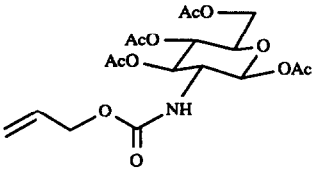
In dichloromethane, the reaction of **3** with methanol in the presence of 1 equivalent of TMSOTf both with and without molecular sieves led to the exclusive formation of the β-methyl glycoside **4c** after 1 h in nearly quantitative yield (Table 1, entries 1-2).



1	R
a	OMe
b	NH_2

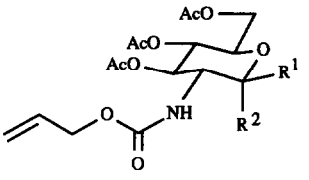


2



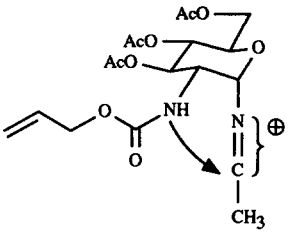
3

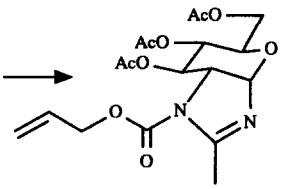
ROH , TMSOTf
DMF or CH_3NO_2



4	R^1	R^2
a	H	OH
b	H	OMe
c	OMe	H
d	H	O^iPr
e	O^iPr	H

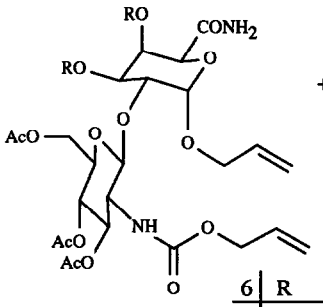
3 TMSOTf
CH_3CN





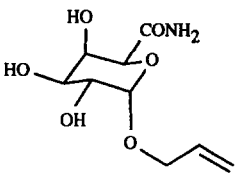
5

1b , TMSOTf



6	R
a	$C(CH_3)_2$
b	H

+



7

On the other hand, in DMF as solvent and under otherwise identical conditions, α-hydroxy compound **4a** was the sole product after 24 h. **4a** was also formed when no alcohol was added. Presumably DMF acts as nucleophile to give an intermediate from which **4a** is formed on work up. This reaction may be useful as a method for a selective removal of 1-O-acetyl groups.

For glycosylations in acetonitrile with various glycosyl donors high β-selectivities have been reported.[7,8] The stereoselectivity is presumably due to intermediate α-acetonitrilium ions.[7,9] Nucleophilic substitution at C-1 of the sugar moiety with acetonitrile as nucleofuge ensures the formation of β-glycosides whereas reaction of the nucleophil at the nitrilium carbon explains the by-products, isolated in some cases.[10-13]

When **3** in acetonitrile solution was treated with methanol in the presence of molecular sieves and 1 eq. TMSOTf, the β-glycoside **4c** was formed as main product alongside with some imidazoline **5**. On the other hand, **5** was the main product (79%) when the reaction was run without molecular sieves. The α- (**4b**) and β- (**4c**) methyl glycosides were isolated in only 13 and 8% yield, respectively. In the absense of methanol, **5** was isolated in almost quantitative yield (see Table 1).

Next, nitromethane was investigated. It proved to be a suitable solvent for glycosylations, but the stereochemical outcome of the reaction was influenced by the amount of added TMSOTf and the presence or absence of molecular sieves.

As in the glycosylation in dichloromethane, the reaction of **3** whith methanol and 1 eq. TMSOTf in the presence of molecular sieves furnished exclusively the β-methyl glycoside **4c** (Table 1, entry 6). Without molecular sieves, only the α-glycoside **4b** was isolated (entry 7). The reduction of the amount of the promotor to 0.7 eq. led to the formation of both the α- and the β-glycoside (entry 8).

The secondary alcohol isopropanol did not react under the conditions of entry 6; 3 equivalents of TMSOTf were necessary for complete reaction (entry 9). On the other hand, in the absence of molecular sieves reactions occurred with 1 and even 0.1 eq. TMSOTf (entries 10-13).

An explanation for this puzzling behaviour may be that for the less reactive isopropanol the reaction is critically dependend on the concentration of the promotor (probably trifluoromethanesulfonic acid, formed from TMSOTf with isopropanol and nitromethane, respectively[14]) and that its concentration is diminished by the molecular sieves.

The stereochemistry of the glycosylations with isopropanol is similar to that with methanol: in the presence of molecular sieves β-glycoside **4e** was the main product (entry 9), in absence of molecular sieves the α-glycoside **4d** (entry 10). Reducing the amount of TMSOTf shifted the product ratio to **4e**. With 0.1 eq. TMSOTf no α-product could be observed (entries 11-13).

Under the reaction conditions leading to β-glycosides (entry 13) **3** was glycosylated with the galacturonamide derivative **1b**[15] and furnished the disaccharide **6a** after 22 h in 52 % yield (67% after correction for recovered **1b**, not optimized). This compares favourably

with the result using the dichloromethane-molecular sieves variant originally reported by *Boullanger et al.*[3,4] (see Table 2). In contrast to observations of *Boullanger et al.* [5] extensive cleavage of the isopropylidene acetals of both **1b** and **6a** was observed, leading to **7** and **6b**, respectively.

Table 1. Glycosylations of **3** in Dichloromethane, Acetonitrile, and Nitromethane at 20°C.

entry	solvent	ROH	MS 4Å	eq. TMSOTf	t (h)	ß-glyco-sides **4b,4d** (%)	α-glyco-sides **4c,4e** (%)	**5** (%)	**4a** (%)
1	CH_2Cl_2	MeOH	+	1	1	95			
2	"	"	-	1	1	97			
3	CH_3CN	MeOH	+	1	1	74	26		
4	"	"	-	1	1	13	8	79	
5	"	-	-	1	1			99	
6	CH_3NO_2	MeOH	+	1	1		96		
7	"	"	-	1	1	94			
8	"	"	-	0.7	1	41	52		
9	"	^{i}PrOH	+	3	3	4	63		19
10	"	"	-	1	1	80	3		
11	"	"	-	0.7	1	58	7		16
12	"	"	-	0.4	1	32	36		14
13	"	"	-	0.1	2		72		19

Table 2. Glycosylations of **3** with **1b**.

entry	solvent	T (°C)	MS 4Å	eq. TMSOTf	eq. **1b**	t	**6a** (%)[a]	**6b** (%)[a]	**1b** (%)[a]	**7**[b]
1	CH_2Cl_2	-21	+	1.0	0.9	3d	<10	26	≈20	+
2	"	20	+	0.8	0.7	3.5h	11	33		+
3	"	20	+	0.1	0.8	8d	6	8	29	+
4	CH_3NO_2	20	-	0.1	0.5	22h	52		21	-

[a] The yields are based on **1b**.

[b] Identified by TLC comparison with an authentic sample.[15]

Assignment of the anomeric configuration in **4e** and **6a** rests on the ^{13}C NMR spectra. In the ^1H NMR spectra the signals of the protons in the neighbourhood of the carbamate group (1-H, 2-H, 3-H, and N-H) were broad and unresolved, probably because of a hindered rotation around the amide bond.[16] In the case of **4e** this question was studied by dynamic NMR.

At 243 K, besides the fully resolved spectrum of one conformer, an additional doublet at δ = 4.42 with J = 8.4 Hz is observed, that is attributed to 1-H of a minor conformer (ratio 83:17; from integration). Stepwise increasing of the temperature showed a

coalescence temperature Tc between 283 K and 293 K. From the Eyring equation for Tc = 288 K a free enthalpy of activation of about 56 kJ/mol was calculated. This is in accord with typical data of carbamates.[16] For amides the Z-conformation is preferred[15], thus the minor conformer has probably E-conformation.

Experimental

General

All reactions were performed in oven-dried glassware under a positive pressure of argon. Liquids and solutions were transferred by syringe and were introduced into reaction flasks through rubber septa. Solvents were distilled from CaH_2. Molecular sieves were activated at 320°C and 13 Pa for 14 h. The instrumentation used was: Melting point (corrected): Kofler hot-stage apparatus (Reichelt); ^1H NMR, ^{13}C NMR: AM 400 (Bruker); IR: Perkin Elmer 1310; EI MS: MAT CH7 (Varian); FAB MS: MAT 731 (Varian); preparative gravitational LC: silica gel (ICN Biomedicals Silica 63-100); analytical TLC: Merck precoated silica gel 60 F_{254} plates (0.2 mm), spots were identified by spraying with a 2.22M H_2SO_4-solution which contained $Ce(SO_4)_2 \cdot 4H_2O$ (10 g/l) and $H_3[PO_4(Mo_3O_9)_4] \cdot xH_2O$ (25 g/l) and heating at 140°C.

1,3,4,6-Tetra-O-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranose (3)

3 was prepared from glucosamine in four steps according to the literature.[4,17]

General procedure for reactions of 3 with nucleophiles

To a solution of **3** (15-20 mg) in 0.5 ml solvent (dimethylformamide, dichloromethane, acetonitrile or nitromethane) 1.1 equivalents of the alcohol (methanol or 2-propanol) and the amounts of trimethylsilyl trifluoromethanesulfonate indicated in Tables 1 and 2 were added. For reaction temperatures and times see Tables. For work up triethylamine (about 0.1 ml) was added and the solvent was evaporated using an argon stream. Reaction mixtures containing DMF were subsequently freeze-dried. The residue was chromatographed on silica gel using ethyl acetate/hexanes eluents; for mixtures containing **5**, a trace of triethylamine was added.

Glycosylations with **1b** (about 20 mg) followed the above procedure. Isolation of **6a** was performed by column chromatography (hexanes/ethyl acetate/ethanol 4:4:1 -> 2:2:1 -> ethyl acetate/ethanol 1:1), followed by preparative HPLC (trichloromethane/ethanol 25:1) of **1b**/**6a** containing fractions.

3,4,6-Tri-O-acetyl-2-allyloxycarbonylamino-2-deoxy-α-D-glucopyranose (4a)

The ^1H NMR spectrum was identical with the reported spectrum.[4]

^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 20.87, 20.98, 21.01 ($COCH_3$); 54.18 (C-2); 62.35 (C-6); 66.08 (allyl C-1); 67.84 (C-4); 68.64 (C-3); 71.17 (C-5); 92.12 (C-1); 118.08 (allyl C-3); 132.73 (allyl C-2); 156.03 (NCOO); 169.71, 171.15, 171.40 ($COCH_3$).- IR ($CHCl_3$): 3435 (NH), 3480-3180 (OH), 1740 (CO), 1510 cm^{-1} (amide II).- $C_{16}H_{23}O_{10}N$ (389.4).

Methyl-3,4,6-tri-O-acetyl-2-allyloxycarbonylamino-2-deoxy-α-D-glucopyranoside (**4b**)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01, 2.02, 2.10 (s, 3H, OAc); 3.41 (s, 3H, OCH_3); 3.92 (ddd, 1H, 5-H, $J_{5,6}$ = 4.8 Hz, $J_{5,6'}$ = 2.4 Hz), 4.02 (dt, 1H, 2-H, $J_{2,3}$ = 10.0 Hz); 4.08 (dd, 1h, 6'-H, $|J_{6,6'}|$ = 12.6 Hz); 4.23 (dd, 1H, 6-H); 4.47-4.59 (mk, 2H, allyl 1-H, 1'-H); 4.74 (d, 1H, 1-H, $J_{1,2}$ = 3.7 Hz); 4.97 (d, 1H, NH, $J_{2,NH}$ = 10.0 Hz); 5.08 (t, 1H, 4-H, $J_{4,5}$ = 10.0 Hz); 5.20 (t, 1H, 3-H, $J_{3,4}$ = 10.0 Hz); 5.21 (m, 1H, allyl 3-H^{trans}); 5.27 (m, 1H, allyl 3-H^{cis}); 5.82-5.92 (m, 1H, allyl 2-H).- ^{13}C NMR (100.6 MHz, $CDCl_3$, DEPT): δ = 20.85-20.96 ($COCH_3$); 53.91 (C-2); 55.72 (OCH_3); 62.27 (C-6); 66.04 (allyl C-1); 67.85 (C-4); 68.54 (C-3); 71.55 (C-5); 98.76 (C-1); 118.03 (allyl C-3); 132.77 (allyl C-2); 155.85 (NCOO); 169.63, 170.91, 171.24 ($COCH_3$).- IR ($CHCl_3$): 3435 (NH), 1755-1725 (CO), 1505 cm^{-1} (amide II).- (Found C, 50.70; H, 6.26. $C_{17}H_{25}O_{10}N$ (403.4) requires C, 50.62; H, 6.25).

Methyl-3,4,6-tri-O-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (**4c**)
The ^{1}H NMR spectrum was identical with the reported spectrum.[3]

(2-Propyl)-3,4,6-tri-O-acetyl-2-allyloxycarbonylamino-2-deoxy-α-D-glucopyranoside (**4d**)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15, 1.22 (d, 3H, $CH(CH_3)_2$); 2.00, 2.01, 2.08 (s, 3H, OAc); 3.88 (sept, 1H, $CH(CH_3)_2$, $J_{CH,Me}$ = 6.2 Hz); 4.00 (m, 1H, 2-H); 4.02 (m, 1H, 5-H); 4.06 (m, 1H, 6'-H); 4.22 (dd, 1H, 6-H, $J_{5,6}$ = 5.5 Hz, $|J_{6,6'}|$ = 12.0 Hz); 4.47-4.60 (mk, 2H, allyl 1-H, 1'-H); 4.90 (d, 1H, NH, $J_{2,NH}$ = 9.8 Hz); 4.94 (d, 1H, 1-H, $J_{1,2}$ = 3.8 Hz); 5.06 (t, 1H, 4-H, $J_{4,5}$ = 9.9 Hz), 5.18 (t, 1H, 3-H, $J_{2,3}$ = $J_{3,4}$ = 9.9 Hz); 5.19 (m, 1H, allyl 3-H^{trans}); 5.26 (m, 1H, allyl 3-H^{cis}); 5.82-5.89 (m, 1H, allyl 2-H).- IR ($CHCl_3$): 3445 (NH), 1760-1720 (CO), 1510 cm^{-1} (amide II).- MS: m/z (%) = 388 (0.2, $[M-^iPr]^{+\cdot}$), 372 (1.2) 371 (1.4), 358 (0.2), 330 (2), 283 (7), 270 (3), 241 (6), 198 (17), 185 (24), 156 (36), 143 (62), 43 (100).- (Found C, 52.99; H, 6.82. $C_{19}H_{29}O_{10}N$ (431.4) requires C, 52.90; H, 6.78).

(2-Propyl)-3,4,6-tri-O-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside (**4e**)
The melting point and the ^{13}C NMR spectrum were identical with the reported data.[4]
^{1}H NMR (400 MHz, $CDCl_3$, 243K, main conformer): δ = 1.10, 1.20 (d, $CH(CH_3)_2$); 2.00, 2.03, 2.07 (s, OAc); 3.35 (dt, 2-H, $J_{2,3}$ = 10.6 Hz); 3.70 (ddd, 5-H, $J_{5,6}$ = 1.8 Hz, $J_{5,6'}$ = 4.7 Hz); 3.92 (sept, $CH(CH_3)_2$, $J_{CH,Me}$ = 6.1 Hz); 4.04 (dd, 6-H, $|J_{6,6'}|$ = 12.1 Hz); 4.23 (dd, 6'-H); 4.45-4.56 (mk, allyl 1-H, 1'-H); 4.81 (d, 1-H, $J_{1,2}$ = 8.4 Hz); 5.03 (t, 4-H, $J_{4,5}$ = 10.0 Hz); 5.10 (d, NH, $J_{2,NH}$ = 8.4 Hz); 5.18 (m, allyl 3-H^{trans}); 5.23 (m, allyl 3-H^{cis}); 5.41 (dd, 3-H, $J_{3,4}$ = 9.5 Hz); 5.79-5.90 (m, allyl 2-H).- $C_{19}H_{29}O_{10}N$ (431.4).

2-Methyl-3-allyloxycarbonyl-(3,4,6-tri-O-acetyl-1,2-dideoxy-α-D-glucopyrano)[2,1-d]-1-imidazoline (**5**)
^{1}H NMR (400 MHz, CD_3CN): δ = 1.94, 1.99, 2.01 (s, 3H, OAc); 2.31 (d, 1H, CH_3, $J_{1,CH3}$ = 1.4 Hz); 3.67 (dddd[a], 1H, 5-H, $J_{5,6}$ = 3.1 Hz, $J_{5,6'}$ = 5.7 Hz); 4.10 (dd, 1H, 6-H, $|J_{6,6'}|$ = 12.0 Hz); 4.17 (dd, 1H, 6'-H); 4.19 (ddd, 1H, 2-H, $J_{2,3}$ = 4.2 Hz, $|J_{2,4}|$ = 1.0 Hz); 4.57-4.69 (mk, 2H, allyl 1-H, 1'-H); 4.82 (ddd, 1H, 4-H, $J_{4,5}$ = 7.7 Hz); 5.25 (m, 1H, allyl 3-H^{trans}); 5.34 (1H, m, allyl 3-H^{cis}); 5.34 (t, broad, 1H, 3-H, $J_{3,4}$ = 4.8 Hz); 5.67 (dq, 1H, 1-H, $J_{1,2}$ = 7.1 Hz); 5.90-6.00 (mk, 1H, allyl 2-H).- ^{13}C NMR (100.6 MHz, CD_3CN, DEPT): δ = 18.33 (CH_3); 20.93-21.16 ($COCH_3$); 57.66 (C-2); 64.60 (C-6); 67.63 (allyl C-1); 68.01 (C-4); 69.25 (C-3); 70.23 (C-5); 92.14 (C-1); 118.86 (allyl C-3);

133.12 (allyl C-2); 151.77 (C=N); 161.728 NCOO); 170.44-171.34 (*C*OCH$_3$).- IR (CH$_3$CN): 3370 (NH), 1705-1760 (CO), 1640 cm^{-1} (C=N).- FAB MS (matrix DMSO/glycerol): m/z (%) = 413 (100, [M+H]$^+$), 353 (4), 329 (18), 311 (4), 293 (11), 269 (5), 251 (29), 227 (15), 209 (31), 167 (72), 125 (57).- (Found C, 52.32; H, 5.99. $C_{18}H_{24}O_9N_2$ (412.4) requires C, 52.43; H, 5.87).

[a] Besides the couplings with 4-H, 6-H, and 6'-H, the signal of 5-H shows a coupling with |J = 0.5 Hz|. The coupling partner could not be found in the remaining spectrum. By comparision with literature data, it may be assumed as a $J_{1,5}$ coupling.[10,18]

Allyl-2-O-(3,4,6-tri-O-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranosyl)-3,4-O-isopropyliden-α-D-galactopyranosiduronamide (**6a**)

M.p. 170-171°C (from trichloromethane-hexanes).- ^{1}H NMR (400 MHz, CDCl$_3$), glucosamine moiety: δ = 1.98, 1.99, 2.03 (s, 3H, OAc); 3.57 (m, 1H, 2-H); 3.64 (ddd, 1H, 5-H); 4.09-4.16 (m, 1H, 6'-H); 4.18 (dd, 1H, 6-H, $J_{5,6}$ = 4.8 Hz, $|J_{6,6'}|$ = 12.0 Hz); 4.95-5.08 (m, 1H, 1-H); 5.02 (t, 1H, 4-H, $J_{3,4} = J_{4,5}$ = 9.8 Hz), 5.22-5.32 (m, 1H, 3-H); glucuronamide moiety: δ = 1.32, 1.47 (s, 3H, CH$_3$), 3.82 (dd, 1H, 2-H, $J_{2,3}$ = 8.0 Hz); 3.99-4.05 4.31 (dd, 1H, 3-H, $J_{3,4}$ = 5.2 Hz); 4.48 (d, 1H, 5-H); 4.52 (dd, 1H, 4-H, $J_{4,5}$ = 2.8 Hz); 4.99 (d, 1H, 1-H, $J_{1,2}$ = 3.4 Hz); allyl groups: δ = 3.99-4.05 (m, 1H, allyl 1-H); 4.09-4.16 (m, 1H, allyl 1'-H); 4.50-4.55 (mk, 2H, allyl 1-H, 1'-H); 5.12-5.18 (mk, 2H, 3-H^{trans}); 5.22-5.32 (mk, 2H, 3-H^{cis}); 5.79-5.95 (mk, 2H, 2-H).- ^{13}C NMR (100.6 MHz, CDCl$_3$, DEPT), glucosamine moiety: δ = 20.89, 20.95, 21.01 (COCH$_3$); 56.42 (C-2); 62.40 (C-6); 68.52[a] (C-4); 72.10[b] (C-5); 73.84[b] (C-3); 101.14 (C-1); 155.87 (NCOO); 169.75, 170.61, 170.79[c] (*C*OCH$_3$); glucuronamide moiety: δ = 26.68, 28.45 (C(*C*H$_3$)$_2$); 68.96[a] (C-5); 72.32[b] (C-4); 75.42[b] (C-3); 77.50 (C-2); 97.70 (C-1); 109.77 (*C*(CH$_3$)$_2$); 170.83[c] (C-6); allyl groups: δ = 65.94, 69.54 (C-1); 116.05, 117.68 (C-3); 132.93, 133.41 (C-2).- IR (CHCl$_3$): 3530, 3410, 3500-3250 (NH$_2$, NH), 1750 (OCONH, amide I), 1700 (CONH$_2$, amide I), 1575 (CONH$_2$, amide II), 1515 cm^{-1} (OCONH, amide II).- $C_{28}H_{40}O_{15}N_2$ (634.6), FAB-MS (matrix DMSO/glycerol): m/z (%) = 645 (0.8, [M+H]$^+$), 603 (0.3), 587 (0.5, [M-OAll]$^+$), 511 (0.7), 451 (1.4), 372 (8, [E]$^+$),[19] 252 (17, [E-2HOAc]$^+$), 210 (20).

[a,b] Assignments are based on comparision with literature data [5,6,15] and may have to be reversed.

[c] Assignments may have to be reversed.

Allyl-2-O-(3,4,6-tri-O-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranosyl)-α-D-galactopyranosiduronamide (**6b**)

^{1}H NMR (400 MHz, [D$_6$]DMSO, H,H-COSY), glucosamine moiety: δ = 1.91, 1.97, 2.02 (s, 3H, OAc); 3.40-3.52 (m, 1H, 2-H); 3.84 (m, 1H, 5-H); 4.07-4.12 (mk, 2H, 6-H, 6'-H); 4.75 (d, 1H, 1-H, $J_{1,2}$ = 8.5 Hz); 4.82 (t, 1H, 4-H, $J_{4,5}$ = 9.8 Hz); 5.08 (t, 1H, 3-H, $J_{2,3} = J_{3,4}$ = 9.8 Hz); 7.25 (m, 1H, NH); glucuronamide moiety: δ = 3.72 (m, 1H, 3-H), 3.78 (dd, 1H, 2-H, $J_{2,3} \approx$ 9.6 Hz); 3.95-4.01 (m, 1H, 4-OH); 4.01 (m, 1H, 4-H); 4.38-4.43 (m, 1H, 3-OH); 4.48 (m, 1H, 5-H); 4.98 (d, 1H, 1-H, $J_{1,2}$ = 2.9 Hz); 6.99 (m, 1H, NH); 7.29 (m, 1H, NH); allyl groups: δ = 3.95-4.01 (m, 1H, 1-H); 4.05-4.12 (m, 1H, 1'-H); 4.37-4.53 (mk, 2H, 1-H, 1'-H); 5.09-5.17 (mk, 2H, 3-H^{trans}); 5.20-5.32 (mk, 2H, 3-H^{cis}); 5.83-5.93 (mk, 2H, 2-H).- ^{13}C NMR (100.6 MHz, [D$_6$]DMSO), glucosamine moiety: δ = 20.44, 20.47, 20.62 (COCH$_3$); 55.47 (C-2); 61.88 (C-6); 68.56[a] (C-4); 72.27 (C-5); 73.15 (C-3); 101.91 (C-1); 156.97 (NCOO); 169.36, 169.63, 170.12[c] (*C*OCH$_3$); glucuronamide moiety: δ = 67.95[a] (C-3); 70.56[b] (C-5); 71.24[b] (C-4); 77.83 (C-2); 97.72 (C-1); 170.77[c] (C-6); allyl groups: δ = 64.31,

69.65 (C-1); 116.42, 119.08 (C-3); 133.68, 134.56 (C-2).- $C_{28}H_{40}O_{15}N_2$ (604.6), FAB-MS (matrix DMSO/glycerol): m/z (%) = 627 (4.5, $[M+Na]^+$), 569 (0.4, $[M+Na-AllOH]^+$), 543 (0.5), 372 (1.2, $[E]^+$),[19] 353 (4.0), 252 (3.6, $[E-2HOAc]^+$), 210 (6), 180 (3).

[a,b] Assignments are based on comparision with literature data [5,6,15] and may have to be reversed.

[c] Assignments may have to be reversed.

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