Complete ^{1}H and ^{13}C NMR assignments of a series of pergalloylated tannins

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Introduction

Tannins are secondary metabolites widely distributed in the plant kingdom.[1] A common feature of tannins is their phenolic units, which can be linked together to form highly diverse chemical structures.[2] Since these compounds constitute an important fraction of the food and beverage ingested,[3] they have been thoroughly studied for their biological effects.[4-6] Recently, we have performed a phytochemical study on *Cornus canadensis*, an abundant flowering plant growing wild in North America and giving edible fruits.[7] A preliminary bioactivity screening was performed and revealed that an extract from *C. canadensis* was active toward *Herpes simplex* virus type-1 (HSV-1).[8] Following bioassay-guided fractionations, hydrolysable tannins were identified.[9] One of these compounds, namely 1,2,3,4,6-penta-*O*-galloyl-*β*-D-glucopyranose (PGG), has been the subject of several pharmaceutical studies as recently reviewed by Zhang.[10] The biological and medicinal properties of PGG are diverse and include anticancer, antioxidant, antimutagenic, anti-inflammatory, anti-allergy, hypocholesterolemic, anticoagulation, antinephrolithiasis, anticonvulsion, antiviral, and antibacterial activities. Furthermore, a series of PGG analogs were synthesized and found to be an optimal scaffold to stimulate glucose transport in adipocytes.[11] Some of these compounds were also prepared in our laboratory in order to assess their antiherpetic activities. Since these analogs were only partially characterized by NMR,[11] we would like to report herein the complete ^{1}H and ^{13}C assignments of pergalloylated D-glucose (**1**), D-mannose (**2**), D-galactose (**3**), D-xylose (**4**), L-ribose (**5**), L-arabinose (**6**), L-rhamnose (**7**), and D-fucose (**8**), by using a combination of one- and two-dimensional NMR experiments.

Results and Discussion

The synthesis of the pergalloylated sugars **1**–**8** (Figure 1) was performed in a two-step process via a modified Steglich esterification followed by a catalytic hydrogenolysis. HPLC separations of the anomeric mixtures provided sixteen compounds, eight *α*- as well as eight *β*-configured derivatives, which were fully characterized by NMR spectroscopy (Tables 1–4). It is worth to mention that *α*- and *β*- sugars are named according to the relative position of the oxygen functions at the reference carbon and anomeric position.[12] By convention, in the Fischer projection, the anomer having the same orientation at these two positions is called *α*- and vice versa. The proton signals of the sugar cores were assigned on the basis of ^{1}H-^{1}H COSY and were transferred to carbon through HSQC experiments. The anomeric configurations of derivatives **1**, **3**–**6** and **8** were determined from the $^{3}J_{\mathrm{H1,H2}}$ coupling constants. While it is generally accepted that axial protons are at a lower frequency compared to equatorial protons,[13] some atypical differences were observed after careful examination of ^{1}H chemical shifts. For instance, D-mannose **2*β*** (δ_{H} 6.49, vs 6.33 for *α* anomer) and L-rhamnose **7*β*** (δ_{H} 6.36, vs 6.22 for *α* anomer) showed deshielded axial anomeric protons. Since the anomeric configurations of these two saccharides are not trivial to determine due to the small ^{1}H-^{1}H coupling for both anomers, their irregular chemical shifts could have led to incorrect assignments. The anomeric configurations of compounds **2** and **7** were thus determined with the help of $^{1}J_{\mathrm{C1\text{-}H1}}$ measured in the ^{1}H dimension of a coupled HSQC experiment (Table 5).[14, 15]

In another case, H-5_{ax} of L-ribose **5*α*** was found at a higher frequency compared to H-5_{eq} (δ_{H} 4.29 and 4.07, respectively). Moreover, the coupling constant of H-5_{ax} with H-4 ($J = 8.5$ Hz) was found significantly below the expected value of 10.7 Hz for axial-axial coupled protons.[16] This atypical behaviour of derivative **5*α*** could be explained by a time-averaging spectrum of the $^{4}C_{1}$ conformation with the dominant $^{1}C_{4}$ conformation, the latter being depicted in Figure 1. In addition, the irregular axial/equatorial chemical shift differences could be attributed to the magnetic anisotropy of galloyl units. The arabinose derivative **6*α*** ($^3J_{\mathrm{H1,H2}}$ = 6.2 Hz) also exhibited a conformational equilibrium between $^4C_1$ and $^1C_4$ based on a smaller than average coupling constant (mean $^3J_{\mathrm{H1,H2}}$ = 8.1 Hz).

The four or five galloyl groups were first assigned with the help of HMBC. Indeed, the H-2′,6′ protons of each galloyl unit correlated with C-1′, C-3′,5′, C-4′ and C-7′. To discriminate each group of carbon, semi-selective HSQC, semi-selective HMBC or semi-selective long-range optimized HSQC[17] were acquired with 0.1–1 KHz F1 spectral width (Figure 2). Once all the galloyl carbons were assigned, including the carbonyl function, their positions on the sugar core were determined from the respective oxymethine proton HMBC correlation with a carbonyl of one galloyl unit.

Compound **6*α*** was a complicated case. Indeed, protons H-2 and H-3 of the sugar core were perfectly overlapped at δ_{H} 5.69. On the semi-selective HMBC, it was possible to distinguish the correlation between H-1 and the corresponding galloyl carbonyl at δ_{C} 164.36. However, the correlation of H-4 was not visible and those of H-2 and H-3 were unusable. Thus, another strategy was used consisting in a sequence of 1D selective ROESY experiments (Figure 3). The selective irradiation of G-1 (H-2′,6′ of galloyl unit on O-1) at δ_{H} 6.94, followed by a mixing time of 200 ms, resulted in a spectrum with correlation at δ_{H} 6.87, which was assigned to G-2. Three other ROESY spectra were acquired in order to successively assign G-2 to G-4. Once the H-2′,6′ protons were ascribed, the chemical shifts of the other positions were readily determined.

In the course of the galloylation of galactose and ribose, a third compound was isolated from both reaction mixtures (Figure 4). Careful examination of ^{1}H-^{1}H DQF-COSY suggested that these compounds were the furanose forms of their respective sugars. Indeed, H-4 of 1,2,3,5,6-penta-*O*-galloyl-*β*-D-galactofuranose (**3*f***) showed a shielded signal at δ_{H} 4.60 in comparison with H-4 signals of compounds **3*α*** and **3*β*** at δ_{H} 5.88 and 5.71, respectively, indicating that the galloyl group was at O-5 rather than at O-4 (Table 6). Moreover, H-1 showed an HMBC correlation with C-4 further supporting the furanoside form of **3*f***. The *β*-configuration was determined on the basis of the $^3J_{\mathrm{H1,H2}}$ coupling constant of 4.7 Hz[18]. 1,2,3,5-Tetra-*O*-galloyl-*β*-L-ribofuranoside (**5*f***) was assigned based on the same approach (a low-frequency H-4 signal at δ_{H} 4.65 and an HMBC correlation from H-1 to C-4). A broad singlet was observed on the ^{1}H NMR spectrum, which was consistent with the *β*-configured ribofuranose. In comparison, Houseknecht *et al.* measured the $^3J_{\mathrm{H1,H2}}$ coupling constant for methyl *α*- and methyl *β*-ribofuranoses and obtained values of 4.4 and 1.3 Hz, respectively.[19]

Conclusion

In summary, a series of *α*- and *β*-configured pergalloylated tannins were synthesized and their structures fully characterized by NMR using a combination of 1D and 2D experiments. Semi-selective HMBC, 1D selective ROESY as well as ^{1}H-^{1}H DQF-COSY were useful in order to assign some difficult cases such as compounds **6*α*** and furanoses **3*f*** and **5*f***.

Experimental

General procedure for the synthesis of pergalloylated tannins 1–8

To a solution of the free sugar (1.0 equiv) suspended in CH_2Cl_2 (120 mL·mmol^{-1}) were added 4-dimethylaminopyridine (DMAP, 8.6 equiv.), *N*,*N′*-dicyclohexylcarbodiimide (DCC, 9.1 equiv.), and 3,4,5-tri(benzyloxy)benzoic acid[11] (7.3 equiv).The mixture was stirred for 18 h under reflux. The mixture was cooled to room temperature, filtered and the solvents were concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (hexanes/EtOAc 8:2) to give an inseparable α/β mixture of the pertribenzylgalloylated sugar. The latter compound was dissolved in THF (240 mL·mmol^{-1}) and 10% Pd/C was added (0.1 equiv). The suspension was flushed with H_2 for 1 h and stirred under H_2 for 15 h (15 psi). Then, the mixture was filtered over Celite and the solvents of the filtrate were concentrated under reduced pressure. The residue was purified by preparative HPLC (30 → 50 % MeOH in 15 min) to give the pergalloylated tannins **1**–**8** as pure α- and β-anomers (8–49%, over two steps).

1,2,3,4,6-Penta-*O*-galloyl-α-D-glucopyranose (**1α**): Yield = 24%; amorphous solid; $[\alpha]_D^{25}$: +116.1 (*c* = 1.3 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 1 and 3, respectively.

1,2,3,4,6-Penta-*O*-galloyl-β-D-glucopyranose (**1β**): Yield = 25%; amorphous solid; $[\alpha]_D^{25}$: +13.9 (*c* = 1.4 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 1 and 3, respectively.

1,2,3,4,6-Penta-*O*-galloyl-α-D-mannopyranose (**2α**): Yield = 16%; amorphous solid; $[\alpha]_D^{25}$: −59.0 (*c* = 1.2 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 1 and 3, respectively.

1,2,3,4,6-Penta-*O*-galloyl-β-D-mannopyranose (**2β**): Yield = 31%; amorphous solid; $[\alpha]_D^{25}$: −80.1 (*c* = 1.0 in MeOH)). ^{1}H and ^{13}C NMR: refer to Tables 1 and 3, respectively.

1,2,3,4,6-Penta-*O*-galloyl-α-D-galactopyranose (**3α**): Yield = 11%; amorphous solid; $[\alpha]_D^{25}$: +320.7 (*c* = 0.9 in MeOH)). ^{1}H and ^{13}C NMR: refer to Tables 1 and 3, respectively.

1,2,3,4,6-Penta-*O*-galloyl-β-D-galactopyranose (**3β**): Yield = 7%; amorphous solid; $[\alpha]_D^{25}$: +170.5 (*c* = 0.1 in MeOH)). ^{1}H and ^{13}C NMR: refer to Tables 1 and 3, respectively.

1,2,3,5,6-Penta-*O*-galloyl-β-D-galactofuranose (**3*f***): Yield = 6%; amorphous solid; $[\alpha]_D^{25}$: +45.4 (*c* = 0.1 in MeOH)). ^{1}H and ^{13}C NMR: refer to Table 6.

1,2,3,4-Tetra-*O*-galloyl-α-D-xylopyranose (**4α**): Yield = 14%; amorphous solid; $[\alpha]_D^{25}$: +67.6 (*c* = 1.1 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 1 and 3, respectively.

1,2,3,4-Tetra-*O*-galloyl-β-D-xylopyranose (**4β**): Yield = 25%; amorphous solid; $[\alpha]_D^{25}$: −8.3 (*c* = 2.6 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 1 and 3, respectively.

1,2,3,4-Tetra-*O*-galloyl-α-L-ribopyranose (**5α**): Yield = 10%; amorphous solid; $[\alpha]_D^{25}$: −52.9 (*c* = 0.8 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 2 and 4, respectively.

1,2,3,4-Tetra-*O*-galloyl-β-L-ribopyranose (**5β**): Yield = 30%; amorphous solid; $[\alpha]_D^{25}$: +54.8 (*c* = 2.2 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 2 and 4, respectively.

1,2,3,5-Tetra-*O*-galloyl-β-L-ribofuranose (**5*f***): Yield = 5%; amorphous solid; $[\alpha]_D^{25}$: +5.5 (*c* = 0.5 in MeOH). ^{1}H and ^{13}C NMR: refer to Table 6.

1,2,3,4-Tetra-*O*-galloyl-*α*-L-arabinopyranose (**6*α***): Yield = 29%; amorphous solid; $[\alpha]_D^{25}$: +170.1 (*c* = 2.2 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 2 and 4, respectively.

1,2,3,4-Tetra-*O*-galloyl-*β*-L-arabinopyranose (**6*β***): Yield = 9%; amorphous solid; $[\alpha]_D^{25}$: +78.5 (*c* = 0.8 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 2 and 4, respectively.

1,2,3,4-Tetra-*O*-galloyl-*α*-L-rhamnopyranose (**7*α***): Yield = 26%; amorphous solid; $[\alpha]_D^{25}$: +70.5 (*c* = 1.5 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 2 and 4, respectively.

1,2,3,4-Tetra-*O*-galloyl-*β*-L-rhamnopyranose (**7*β***): Yield = 23%; amorphous solid; $[\alpha]_D^{25}$: +32.0 (*c* = 1.8 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 2 and 4, respectively.

1,2,3,4-Tetra-*O*-galloyl-*α*-D-fucopyranose (**8*α***): Yield = 5%; amorphous solid; $[\alpha]_D^{25}$: +165.7 (*c* = 0.03 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 2 and 4, respectively.

1,2,3,4-Tetra-*O*-galloyl-*β*-D-fucopyranose (**8*β***): Yield = 3%; amorphous solid; $[\alpha]_D^{25}$: +19.0 (*c* = 0.4 in MeOH). ^{1}H and ^{13}C NMR: refer to Tables 2 and 4, respectively.

Spectra

The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 at 19–20 °C with a Bruker Avance spectrometer (Bruker BioSpin Corporation, Milton, Canada) working at 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR, respectively. Chemical shifts are given in the δ-scale and are referenced to the solvent residual peak (DMSO-d_6: δ_c = 39.52 ppm and δ_H = 2.50 ppm). Pulse program of all experiments [^{1}H, ^{13}C, DEPT-135, DQF-COSY, HSQC, HMBC, sel. HSQC, sel. HMBC] were taken from the Bruker software library. In the one-dimensional measurements, 64 K data points were used for the FID, sweep widths: 6400 and 24000 Hz, for ^{1}H and ^{13}C respectively. The ROESY spectra were acquired with a 200 ms mixing time. For two-dimensional measurements, sweep width in F2 was adjusted to the observed resonance, between 1400 to 2800 Hz, and all data points ($t_2 \times t_1$) were acquired with 2 K × 256. In F1, linear prediction was applied to enhance the resolution. The heteronuclear 2D experiments were recorded with a one-bond heteronuclear coupling value set to 140 Hz and a long-range coupling value set to 10 Hz. The selective HSQC and HMBC were recorded using a Gaussian shaped inversion or excitation pulse of 1468 μs and 4244 μs, respectively.

Declaration of interest

The authors report no conflicts of interest.

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Supporting information

Additional supporting information may be found in the online version of this article at the publisher's web site.

Figure Captions

Figure 1. Structures of tannins **1–8**

Figure 2. HMBC (a) and selective HMBC (b) of 1,2,3,4,6-penta-*O*-galloyl-*β*-D-glucopyranoside (**1*β***). (a) is an expansion of the HMBC recorded with a spectral width of 12 KHz in F1. (b) is the full semi-selective HMBC recorded with a spectral width of 0.1 KHz in F1 and centered at 145.9 ppm

Figure 3. 1D selective ROESY (200 ms mixing time) of **6*α*** with irradiation of H-2′,6′ for G-1 (b), G-2 (c), G-3 (d) and G-4 (e). (a) is the 1D ^{1}H spectrum

Figure 4. Structures of furanoses **3*f*** and **5*f***

Table 1. ^{1}H NMR spectral data (400 MHz)[a] of derivatives **1–4** in DMSO-d_6

No.	**1*α***	**1*β***	**2*α***	**2*β***
1	6.63 d (3.6)	6.39 d (8.3)	6.33 d (2.2)	6.49 s
2	5.42 dd (10.0, 3.6)	5.44 dd (10.2, 8.3)	5.62 dd (2.8,2.2)	5.78 d (3.2)
3	5.99 t (10.0)	5.97 dd (10.2, 9.2)	5.72 dd (10.0, 2.8)	5.81 dd (9.8, 3.2)
4	5.60 t (10.0)	5.46 dd (10.5, 9.2)	5.66 dd (10.4, 10.0)	5.50 dd (10.3, 9.8)
5	4.51 br d (10.0)	4.60 br d (10.5)	4.48 dd (10.4, 6.7)	4.47 dd (10.3, 7.8)
6	4.33 br s	4.32 br s	4.43 br d (11.4)	4.41 br d (12.0)
			4.35 dd (11.4, 6.7)	4.30 dd (12.0, 7.8)
G-1[b]	7.11 s	6.93 s	7.15 s	6.83 s
G-2[b]	6.80 s	6.83 s	7.03 s	7.05 s
G-3[b]	6.84 s	6.78 s	6.79 s	6.74 s
G-4[b]	6.90 s	6.86 s	6.98 s	6.93 s
G-6[b]	7.01 s	6.99 s	6.93 s	6.95 s

No.	**3*α***	**3*β***	**4*α***	**4*β***
1	6.66 d (3.6)	6.32 d (8.2)	6.51 d (3.8)	6.17 d (8.1)
2	5.64 dd (10.8, 3.6)	5.68 dd (10.3, 8.2)	5.43 dd (10.3, 3.8)	5.43 dd (9.6, 8.1)
3	5.83 dd (10.8, 3.3)	5.80 dd (10.3, 3.4)	5.90 t (10.3)	5.85 t (9.6)
4	5.88 d (3.3)	5.71 d (3.4)	5.37 td (10.3, 5.9)	5.26 td (9.6, 5.6)
5	4.81 dd (6.7, 6.2)	4.80 t (6.4)	4.14 dd (11.1, 5.9)	4.19 dd (11.6, 5.6)
			3.83 dd (11.1, 10.3)	3.91 dd (11.6, 9.6)
6	4.29 dd (10.4, 6.2)	4.30 dd (11.7, 6.4)	–	–
	4.18 dd (10.4, 6.7)	4.22 dd (11.7, 6.4)		
G-1[b]	7.10 s	6.95 s	7.05 s	6.90 s
G-2[b]	6.78 s	6.84 s	6.78 s	6.82 s
G-3[b]	6.76 s	6.74 s	6.87 s	6.82 s
G-4[b]	7.01 s	7.01 s	6.89 s	6.86 s
G-6[b]	6.88 s	6.93 s	–	–

[a] δ_H mult. (*J* in Hz); [b] G1 to G6 represent H-2,6 of gallic acid positioned on the corresponding sugar hydroxy.

Table 2. ^{1}H NMR spectral data (400 MHz)[a] of derivatives **5–8** in DMSO-d_6

No.	***5α***	***5β***	***6α***	***6β***
1	6.38 d (3.9)	6.24 d (8.1)	6.12 d (6.2)	6.57 d (3.6)
2	5.55 t (3.9)	5.36 dd (8.1, 3.0)	5.69 m	5.64 dd (10.8, 3.6)
3	5.94 t (3.9)	5.98 t (3.0)	5.69 m	5.78 dd (10.8, 3.4)
4	5.36 dt (8.5, 3.9)	5.39 m	5.56 br s	5.70 d (3.4)
5	4.29 dd (11.7, 8.5)	4.22 dd (10.8, 5.1)	4.26 br d (12.7)	4.30 br d (13.3)
	4.03 dd (11.7, 3.9)	4.07 t (10.8)	4.10 br d (12.7)	4.00 br d (13.3)
6				
G-1[b]	7.02 s	6.95 s	6.94 s	7.07 s
G-2[b]	6.88 s	6.78 s	6.87 s	6.81 s
G-3[b]	7.03 s	7.02 s	6.78 s	6.79 s
G-4[b]	6.86 s	6.81 s	7.02 s	7.02 s

No.	***7α***	***7β***	***8α***	***8β***
1	6.22 br s	6.36 s	6.57 d (3.7)	6.18 d (8.0)
2	5.59 d (3.6)	5.77 d (3.2)	5.59 dd (10.9, 3.7)	5.62 dd (10.4, 8.0)
3	5.63 dd (10.0, 3.6)	5.65 dd (9.9, 3.2)	5.78 dd (10.9, 3.4)	5.68 dd (10.4, 3.4)
4	5.47 t (10.0)	5.37 t (9.9)	5.64 d (3.4)	5.48 d (3.4)
5	4.21 dq (10.0, 6.2)	4.13 dq (9.9, 6.0)	4.59 q (6.5)	4.48 q (6.4)
6	1.26 d (6.2)	1.27 d (6.0)	1.12 d (6.5)	1.14 d (6.4)
G-1[b]	7.12 s	6.83 s	7.07 s	6.93 s
G-2[b]	7.02 s	7.05 s	6.79 s	6.83 s
G-3[b]	6.77 s	6.74 s	6.76 s	6.73 s
G-4[b]	6.95 s	6.91 s	7.02 s	7.01 s

[a] δ_H mult. (*J* in Hz); [b] G1 to G4 represent H-2,6 of gallic acid positioned on the corresponding sugar hydroxy.

Table 3. ^{13}C NMR spectral data (100 MHz) of derivatives **1**–**4** in DMSO-d_6

Pos.	***1α***	***1β***	***2α***	***2β***	***3α***	***3β***	***4α***	***4β***
Sugar								
1	89.22	91.96	91.04	91.33	89.35	92.18	89.22	92.53
2	70.09	70.82	68.37	68.51	67.01	68.19	69.85	70.39
3	69.71	72.19	69.42	70.75	67.62	70.91	69.14	71.63
4	67.62	67.98	65.72	66.14	67.62	67.71	68.57	69.17
5	70.52	72.40	71.30	72.97	69.26	71.78	60.74	62.89
6	61.50	61.68	63.20	63.54	61.23	61.60	–	–
G-1								
1	118.12	117.60	117.87	117.72	117.84	117.52	117.99	117.55
2,6	109.35	109.28	109.29	109.02	109.18	109.18	109.06	109.01
3,5	146.07	145.92	145.98	145.65	145.81	145.84	145.89	145.68
4	139.97	139.92	139.82	139.47	139.63	139.81	139.68	139.60
7	164.29	164.21	163.43	163.55	164.06	164.23	164.21	164.16
G-2								
1	117.97	118.18	118.27	118.37	117.72	118.21	117.87	118.04
2,6	109.07	109.05	109.16	109.11	108.70	108.83	108.88	108.79
3,5	145.74	145.71	145.83	145.67	145.54	145.63	145.57	145.50
4	139.57	139.41	139.41	139.13	139.30	139.25	139.30	139.11
7	165.23	164.86	164.71	165.03	165.16	164.86	165.03	164.54
G-3								
1	118.36	118.35	118.22	118.11	118.15	118.41	118.33	118.26
2,6	109.01	108.97	108.86	108.71	108.70	108.83	108.88	108.80
3,5	145.67	145.63	145.59	145.48	145.48	145.54	145.54	145.46
4	139.28	139.18	139.26	139.12	139.09	139.10	139.07	138.94
7	165.26	165.08	165.20	164.92	165.06	165.09	165.12	164.87
G-4								
1	118.22	118.32	118.04	118.02	118.07	118.38	118.12	118.19
2,6	109.19	109.14	109.10	108.95	108.85	108.95	108.97	108.87
3,5	145.79	145.74	145.73	145.62	145.76	145.85	145.66	145.57
4	139.43	139.37	139.41	139.31	139.25	139.33	139.21	139.11
7	164.68	164.72	165.03	165.18	164.69	164.94	164.95	164.96
G-6								
1	119.22	119.15	118.92	118.82	118.58	118.74	–	–
2,6	109.07	109.01	108.92	108.79	108.77	108.90	–	–
3,5	145.82	145.80	145.67	145.62	145.57	145.73	–	–
4	139.02	139.03	138.92	138.83	138.89	139.05	–	–
7	165.71	165.69	165.78	165.73	165.34	165.54	–	–

Table 4. ^{13}C NMR chemical shifts for derivatives **5–8** in DMSO-d_6

Pos.	***5α***	***5β***	***6α***	***6β***	***7α***	***7β***	***8α***	***8β***
Sugar								
1	89.13	90.72	92.75	89.79	90.92	91.24	89.49	92.17
2	67.04	68.61	68.34	67.17	68.54	65.61	66.99	68.06
3	67.33	67.91	70.83	67.28	69.38	70.97	67.96	71.19
4	66.33	66.56	68.36	68.50	70.06	70.59	70.54	70.35
5	59.13	62.26	65.15	62.90	68.98	68.87	67.62	69.91
6	–	–	–	–	17.68	17.67	15.92	15.87
G-1								
1	118.58	117.54	117.66	117.86	117.93	117.98	118.07	117.63
2,6	109.39	108.98	109.10	109.01	109.14	109.09	109.07	109.03
3,5	145.66	145.73	145.77	145.78	145.90	145.69	145.80	145.72
4	139.33	139.68	139.70	139.63	139.68	139.49	139.52	139.61
7	165.03	164.37	164.36	164.23	163.55	163.80	164.25	164.31
G-2								
1	118.58	118.01	118.28	117.72	118.24	118.61	117.85	118.23
2,6	109.12	108.72	108.82	108.68	109.02	109.18	108.70	108.72
3,5	145.50	145.55	145.60	145.51	145.74	145.71	145.53	145.53
4	139.07	139.20	139.18	139.32	139.32	139.16	139.25	139.10
7	165.15	164.52	164.81	165.15	164.60	165.15	165.23	164.79
G-3								
1	118.99	118.36	118.44	118.17	118.24	118.38	118.27	118.39
2,6	109.26	108.92	108.82	108.68	108.76	108.80	108.65	108.72
3,5	145.55	145.69	145.52	145.46	145.49	145.52	145.47	145.45
4	138.90	139.10	139.07	139.10	139.13	139.10	139.05	138.98
7	165.70	164.80	165.09	165.04	165.20	165.05	165.09	165.02
G-4								
1	118.67	118.34	118.86	118.55	118.24	118.49	118.30	118.50
2,6	108.99	108.82	108.91	108.79	108.87	108.91	108.81	108.84
3,5	145.57	145.55	145.74	145.66	145.67	145.68	145.74	145.74
4	138.99	139.07	139.10	139.05	139.19	139.16	139.12	139.11
7	164.98	164.78	165.05	164.85	165.04	165.22	165.19	165.33

Table 5. ${}^{1}J_{\mathrm{C1\text{-}H1}}$ (Hz) for derivatives **1–8** in DMSO-d_6.

Compound	α	β
1	181.0	170.3
2	179.7	167.0
3	177.7	171.5
4	177.7	170.8
5	174.4	170.0
6	170.3	179.8
7	177.7	166.3
8	179.1	169.0

Table 6. ^{1}H and ^{13}C NMR spectroscopic data for derivatives **3*f*** and **5*f*** in DMSO-d_6

Pos.	**3*f***		**5*f***	
	^{13}C	^{1}H	^{13}C	^{1}H
Sugar				
1	93.04	6.57 d (4.7)	98.51	6.37 br s
2	75.91	5.68 dd (7.3, 4.7)	73.95	5.66 br d (5.4)
3	73.29	5.97 t (7.3)	71.35	5.59 t (5.4)
4	77.98	4.59 t (7.3)	79.69	4.65 m
5	71.60	5.57 dd (7.3, 3.2)	65.70	4.65 m
				4.23 dd (12.5, 8.9)
6		4.51 dd (12.3, 3.2)		–
	62.23	4.37 dd (12.3, 7.3)		
G-1				
1	118.45	–	118.09	–
2,6	109.10	7.00 s	109.05	7.03 s
3,5	145.69	–	145.76	–
4	139.30	–	139.46	–
7	164.49	–	164.15	–
G-2				
1	117.90	–	117.99	–
2,6	109.00	6.90 s	108.91	6.95 s
3,5	145.67	–	145.66	–
4	139.30	–	139.20	–
7	165.07	–	164.50	–
G-3				
1	118.09	–	118.04	–
2,6	109.21	7.01 s	108.91	6.90 s
3,5	145.70	–	145.60	–
4	139.33	–	139.15	–
7	165.09	–	165.03	–
G-5				
1	118.85	–	118.75	–
2,6	109.00	6.89 s	108.74	6.97 s
3,5	145.65	–	145.64	–
4	138.97	–	138.80	–
7	164.95	–	165.57	–
G-6				
1	118.72	–	–	–
2,6	108.78	6.83 s	–	–
3,5	145.57	–	–	–
4	138.85	–	–	–
7	165.59	–	–	–