Influence of an Ethynyl or a Buta-1,3-diynyl Group on the Chemical Shifts of Hydroxy Groups of Glucopyranoses

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Dedicated to *Hans-Jürgen Hansen* in friendship on the occasion of his 65th birthday

A comparison of the OH chemical shifts for 1-mono-, 4-mono-, and 1,4-diethynylated and 1,4-buta-1,3-diynylated glucopyranoses with those of β-D-glucopyranose (**1**) identified characteristic increments for the OH (downfield) shifts of the alkynylated glucopyranoses in (D_6)DMSO solution. For ethynylated derivatives, the increments vary from 0.05 ppm for HO–C(6) (replacement of HO–C(1) by an axial ethynyl group) to 0.5 ppm for HO–C(2) (replacement of HO–C(1) by an equatorial ethynyl group). The increments for buta-1,3-diynylated derivatives are larger, and vary from 0.1 to 0.7 ppm. The influence on the shift for vicinal OH groups is stronger for such a substitution at C(1) rather than at C(4).

Introduction. – Intra- and intermolecular H-bonds in mono- and oligosaccharides in (D_6)DMSO [1][2] are readily assigned by a combined analysis of chemical shifts δ(OH), coupling constants ^2J(H,OH), and temperature coefficients $\Delta\delta$(OH)/ΔT. The chemical shift for fully solvated OH groups can be calculated from the δ(OH) values of β-D-glucopyranose (**1**; *Fig. 1*) and the increments we have deduced [2]. Thus, the effect of the alkylation of an OH group is expressed by an increment of 0.2–0.25 ppm (downfield shift) for a vicinal OH group and an increment of 0.1 ppm for the other OH groups of the same glycosyl unit. We expected that replacement of an OH group will generally lead to characteristic increments for the chemical shift of the other OH groups of the same unit.

We required such increments characterising the effect of the substitution of an OH by an ethynyl or buta-1,3-diynyl group for the analysis of models of cellulose I [3–5]. Unfortunately, the CP-MAS ^{13}C-NMR spectrum of a templated bis-cellooctaoside (parallel chains) prepared in this context [3] resembles closely that of cellulose II (antiparallel chains in neighbouring sheets), probably due to the inappropriate mimicking of the phase shift and the high flexibility of the linker [4]. An improved model takes these factors into account [5]; rigid ethynyl and buta-1,3-diynyl linkers should fix the parallel orientation of the cellosyl chains and induce the desired phase shift. An assessment of the influence on δ(OH) and J(H,OH) values of the substitution of an OH group by an ethynyl or buta-1,3-diynyl group is essential for the detection and assignment of weakly persistent interchain H-bonds in (D_6)DMSO solution. The knowledge of the corresponding increments will be useful also for the analysis of H-bonding in modified cyclodextrins [6][7] where substitution of one glycosidic O-atom by a buta-1,3-diyne-1,4-diyl group interrupts the intramolecular flip-flop H-bonding network.

Analysis. – We first compared the chemical-shift values for β-D-glucopyranose (**1**) and the alkyne **3**, and of β-cellobiose (**2**) and the 1,4′-diethynylated derivative **4** (*Fig. 1*),

and then that of **4** with the butadiynes **5** and **6** (*Fig. 2*). Following the analysis of the monoalkynylated derivatives, we analysed the dialkynylated derivatives **7**–**11** (*Fig. 3*). The influence of the configuration was evaluated by examining the axial mono- and dialkynylated linear and cyclic derivatives **12**–**17** (*Fig. 4*). Finally, we checked the application of the increments to arylethynyl-substituted glucopyranose derivatives (*Fig. 6*).

The OH groups of β-D-glucopyranose (**1**) in (D_6)DMSO are fully solvated, with HO–C(2), HO–C(3), and HO–C(4) resonating at 4.81, and HO–C(6) at 4.45 ppm [8]. Due to signal overlap, J(2,OH), J(3,OH), and J(4,OH) values could only be determined approximately; values of 4.5–6.0 Hz indicate free rotation about the C–O bonds [1]. Also J(2,OH) = 4.7 Hz for **3** [9][10] (*Fig. 1*) is in agreement with free rotation about the C(2)–O bond. This coupling constant is similar to J(2,OH) = 5.0 Hz of methyl β-D-glucopyranoside [8], while the chemical shift for HO–C(2) is strongly affected by the introduction of the ethynyl group ($\Delta\delta = 0.5$ ppm; downfield shift). The other OH signals of **3** are also shifted downfield; $\Delta\delta$(OH) decreasing with increasing distance to the C≡CH group (0.2 ppm for HO–C(3), *ca.* 0.1 ppm for HO–C(4) and HO–C(6)). The scope of these shift increments was checked by comparing the data for the diacetyleno β-cellobioside **4** [11] with those of β-cellobiose (**2**). The signals of the freely rotating HO–C(2) (J(2,OH) = 5.0 Hz) and HO–C(6) of **4** are shifted downfield by *ca.* 0.5 and 0.04 ppm, respectively, while HO–C(3) engaged in a completely persistent inter-residue H-bond proved nearly insensitive to the

	HO–C(4)	HO–C(6)				
δ:	4.81	4.45				ppm
J(H,OH):						Hz

1

	HO–C(3')	HO–C(2')	HO–C(6)		
δ:	5.00	5.21	4.56		ppm
J(H,OH):	4.9	4.8			Hz

	HO–C(4')	HO–C(6')	HO–C(3)	HO–C(2)	
δ:	4.97	4.58	4.60	4.95	ppm
J(H,OH):			1.6	4.9	Hz

2

	HO–C(3)	HO–C(2)	
δ:	4.81	4.81	
J(H,OH):	4.5–6.0	4.5–6.0	

	HO–C(4)	HO–C(6)	
δ:	4.93	4.52	
$\Delta\delta$ (**3**–**1**):	0.12	0.07	
J(H,OH):			

3

	HO–C(3)	HO–C(2)	
δ:	5.01	5.29	
$\Delta\delta$ (**3**–**1**):	0.20	0.48	
J(H,OH):		4.7	

	HO–C(3')	HO–C(2')	HO–C(6)	
δ:	5.31	5.33	4.60	ppm
$\Delta\delta$ (**4**–**2**):	0.31	0.12	0.04	ppm
J(H,OH):	6.3	4.9		Hz

4

	HO–C(6')	HO–C(3)	HO–C(2)	
δ:	4.77	4.63	5.46	ppm
$\Delta\delta$ (**4**–**2**):	0.19	0.03	0.51	ppm
J(H,OH):		1.7	5.0	Hz

Fig. 1. *^{1}H-NMR Chemical shifts and coupling constants for the OH groups of* β-D-*glucopyranose* (**1**) [8], *β-cellobiose* (**2**) [2], *and their acetyleno analogues* **3** [9][10], *and* **4** [11] *in (D_6)DMSO*

introduction of the C≡CH group ($\Delta\delta = 0.03$ ppm). The diacetylene **4** served also to assess whether substitution of a nonanomeric (HO–C(4)) and of an anomeric OH group leads to similar downfield shifts of the other OH groups. This is the case in that all OH signals of the C(4) alkynylated unit of **4** are shifted downfield, but to a lesser extent ($\Delta\delta$ for HO–C(3′) and HO–C(2′) = 0.3 and 0.1 instead of 0.5 and 0.2 ppm, resp.). The downfield shift for HO–C(6′), however, is larger (0.2 instead of 0.1 ppm), in agreement with a shorter distance to the C≡CH group. Remarkably, J(3′,OH) of **4** (6.3 Hz) is distinctly larger than J(3′,OH) of **2** (4.9 Hz), suggesting that the rotation about the C(3′)–O bond is hindered by substituting HO–C(4) with an ethynyl group; this is rationalised by postulating that steric interactions between OH and the C≡CH groups disfavour a synclinal conformation.

The di- and tetrameric acetyleno cellobiosides **5** and **6** [11] allow us to check the validity of the increments obtained from the analysis of **1**–**4**, and to investigate the influence of a buta-1,3-diynyl group on δ(OH) and J(H,OH) (*Fig. 2*). On the one hand, the ethynylated terminal units **A** and **F** of **5** and **6** should show similar δ(OH) and J(H,OH) values as the units **A** and **F** of **4**. This is the case ($\Delta\delta$(OH) ≤ 0.02 ppm for the fully solvated OH groups; ΔJ(H,OH) ≤ 0.2 Hz, except ΔJ(H,HO–C(2_A) = 1–1.2 Hz). On the other hand, a comparison of the δ(OH) and J(H,OH) values for the buta-1,3-diynylated central units **B**–**E** of **5** and **6** with those for units **A** and **F** of **4** reveals that substitution of the anomeric ethynyl group by a buta-1,3-diynyl group (units **C** and **E**) leads to a further downfield shift of *ca.* 0.2 ppm for HO–C(2), whereas HO–C(6) and the intramolecularly H-bonded HO–C(3) are hardly affected ($\Delta\delta \leq 0.04$ ppm). Similarly, substitution of the ethynyl group at C(4) by a buta-1,3-diynyl group (units **B** and **D**) leads to further downfield shifts of *ca.* 0.2 ppm for HO–C(3) and of *ca.* 0.1 ppm for HO–C(2) and HO–C(6). Thus, replacing an OH with a buta-1,3-diynyl group leads to larger downfield shifts than replacement with an ethynyl group, as shown by the increments in *Table 1*.

The δ(OH) values of the 1,4-diethynylated β-D-glucopyranose **7** [12] allow assessment of the additivity of these increments for ethynyl substituents (*Fig. 3*). Assuming additivity, one expects downfield shifts of 0.6 ppm for HO–C(2) of **7**, 0.5 ppm for HO–C(3), and 0.3 ppm for HO–C(6); this is indeed observed. Similarly, the δ(OH) values of units **A** and **C** of **8**–**11** [12][13], which possess an ethynyl and a buta-1,3-diynyl substituent, allow assessment of the additivity of the increments for an ethynyl and a butadiynyl group. The OH signals show the expected downfield shifts of 0.7 ppm for HO–C(2_A) and HO–C(3_A), 0.4 ppm for HO–C(6_A), 0.8 ppm for HO–C(2_C), and 0.3 ppm for HO–C(6_C). The oligomers **8**–**11** are the first compounds where HO–C(3) of a C(1) buta-1,3-diynylated unit is not involved in an inter-residue H-bond. The chemical shift for HO–C(3_C) of **8**–**11** allows, therefore, determination of the influence of the anomeric buta-1,3-diynyl group on the (fully solvated) HO–C(3) group: since 0.3 of the observed 0.55 ppm are due to the ethynyl substituent (*Table 1*), 0.25 ppm must be due to the buta-1,3-diynyl group. Finally, the bis(buta-1,3-diynylated) central units **B** of **9**–**11** show the strong downfield shifts expected from the increments in *Table 1* (0.9 ppm for HO–C(2_B), 0.75 ppm for HO–C(3_B), and 0.4 ppm for HO–C(6_B)). As we have already observed for **3**–**6**, substitution of HO–C(4) of **7**–**11** by an ethynyl or a buta-1,3-diynyl group leads to a stronger increase of J(H,OH) for

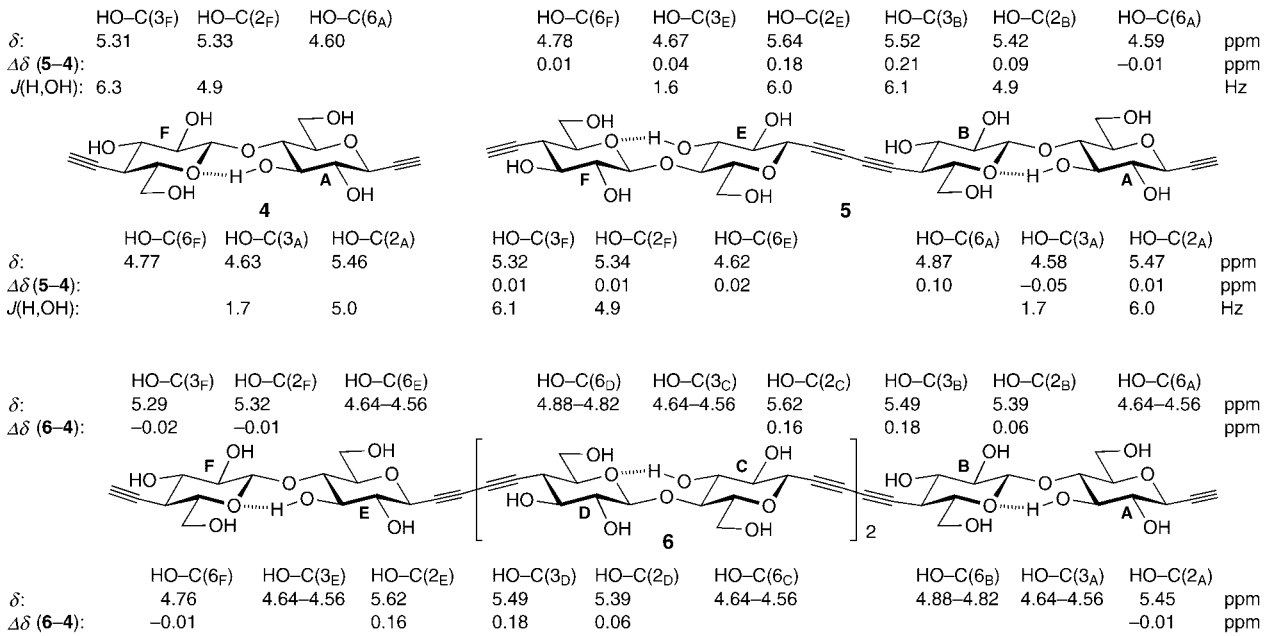

Fig. 2. *^{1}H-NMR Chemical shifts and coupling constants for the OH groups of the acetyleno β-cellobioses* **4**–**6** [11] *in (D_6)DMSO*

Table 1. *Chemical-Shift Increments for the Replacement of an OH of β-D-Glucopyranose* (**1**) *with an Ethynyl or Buta-1,3-diynyl Group*

OH	Δδ(OH) [ppm] for replacement by	
	C≡CH	C≡C−C≡CH
Replacement of HO−C(1) with an equatorial substituent		
HO−C(2)	0.5	0.7
HO−C(3)	0.2	0.25
HO−C(4)	0.1	[a])
HO−C(6)	0.1	0.1
Replacement of HO−C(1) with an axial substituent		
HO−C(2)	0.4	0.6
HO−C(3)	0.1	0.2
HO−C(4)	0.1	[a])
HO−C(6)	0.05	0.1
Replacement of HO−C(4) with an equatorial substituent		
HO−C(2)	0.1	0.2
HO−C(3)	0.3	0.5
HO−C(6)	0.2	0.3

[a]) No data available.

the vicinal OH group than substitution of HO−C(1) ($\Delta J(3,OH) = 1.1$ (**7**) and 1.2–1.7 Hz (**8**–**11**) *vs.* $\Delta J(2,OH) = 0.4$ (**7**) and 0.6–1.5 Hz (**8**–**11**)).

To similarly deduce increments for α-D-glucopyranosylacetylenes, we used β-D-glucopyranose (**1**) as reference compound and not its anomer. This is justified, since the OH groups of α-D-glucopyranosylacetylenes and of **1** in (D_6)DMSO are fully solvated, whereas α-D-glucopyranose possesses a partially persistent intramolecular H-bond of HO−C(2) to HO−C(1) [1]. The axial ethynyl group of **12** [14] (*Fig. 4*) leads to smaller downfield shifts for HO−C(2), HO−C(3), and HO−C(6) than the equatorial ethynyl group of **3** (0.4 *vs.* 0.5, 0.1 *vs.* 0.2, and 0.05 *vs.* 0.1 ppm, resp.; *Table 1*) and to the same downfield shift for HO−C(4) (0.1 ppm). The scope of these increments was assessed by analysing the 1,4-dialkynylated α-D-glucopyranose **13** [14]. The HO−C(2), HO−C(3), and HO−C(6) signals of **13** show the expected downfield shifts of 0.5, 0.4, and 0.3 ppm, respectively. The dimer **14** [15] allows determination of the increments (Δδ(OH) values) due to the anomeric axial buta-1,3-diynyl group. As expected, they are larger than those due to an anomeric axial ethynyl group, but smaller than those due to an anomeric equatorial buta-1,3-diynyl group (*Table 1*). The experimental δ(OH) values of **15** [15], **16** [16], and **17** [15] differ only slightly from the calculated values ($\Delta\delta \leq 0.05$ ppm) with the exception of δ(OH) for HO−C(3_A) of **15** and HO−C(3) of **16**, which show a stronger downfield shift ($\Delta\delta = 0.08$ and 0.14 ppm, resp.) than calculated. The stronger downfield shift for HO−C(3) of **16** appears to be characteristic for the cyclic trimer, as it is not observed for HO−C(3) of the cyclic hexamer **17** and of a series of cyclic tetramers [15]. $J(3,OH)$ of **13**–**17** shows the expected value of 6.1–6.4 Hz, whereas $J(2,OH)$ of **12**–**17** is smaller (4.4–4.8 Hz), and this to a larger extent than for the diequatorial dialkynes **7**–**11** (5.4–6.5 Hz), again evidencing that close contact between the solvated OH group and the vicinal ethynyl substituent is avoided.

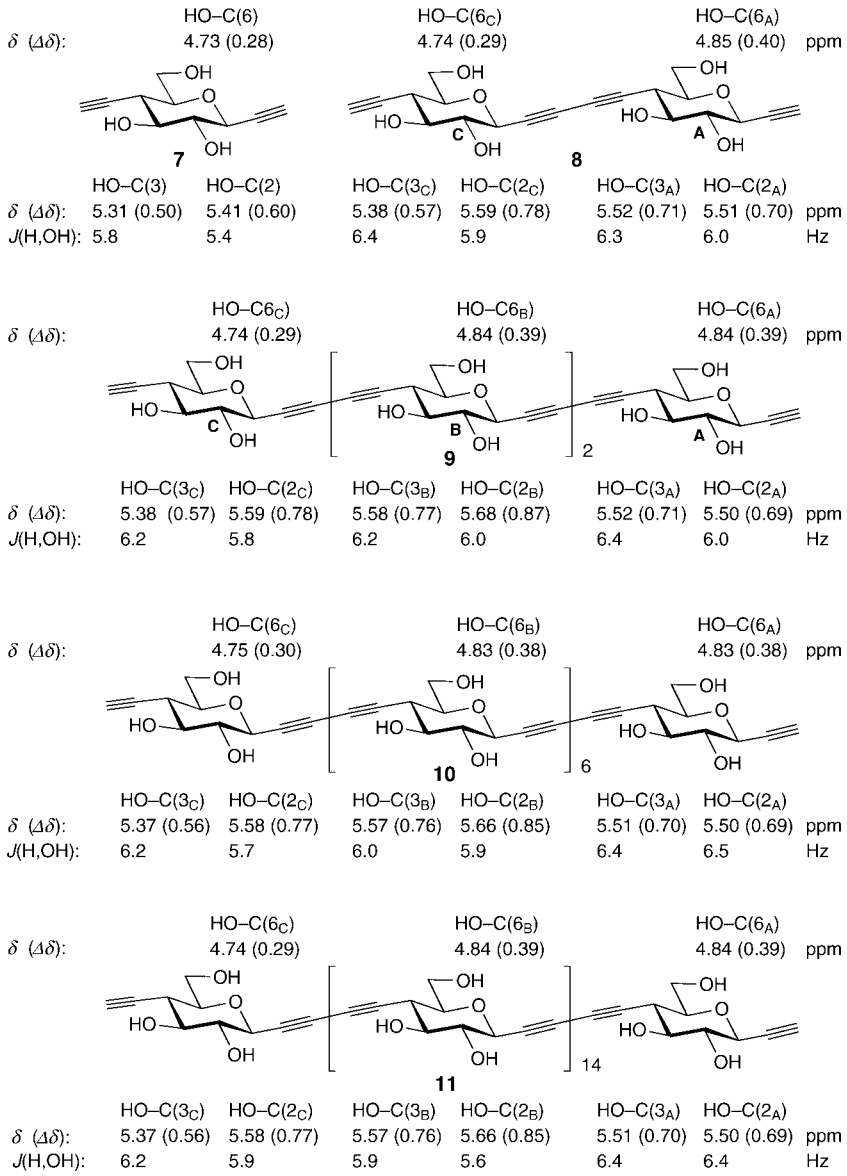

Fig. 3. *^{1}H-NMR Chemical shifts and coupling constants for the OH groups of β-*D*-configured acetyleno glucopyranoses* **7**–**11** [12][13] *in (D$_6$)DMSO* (Δδ(OH) relative to **1**)

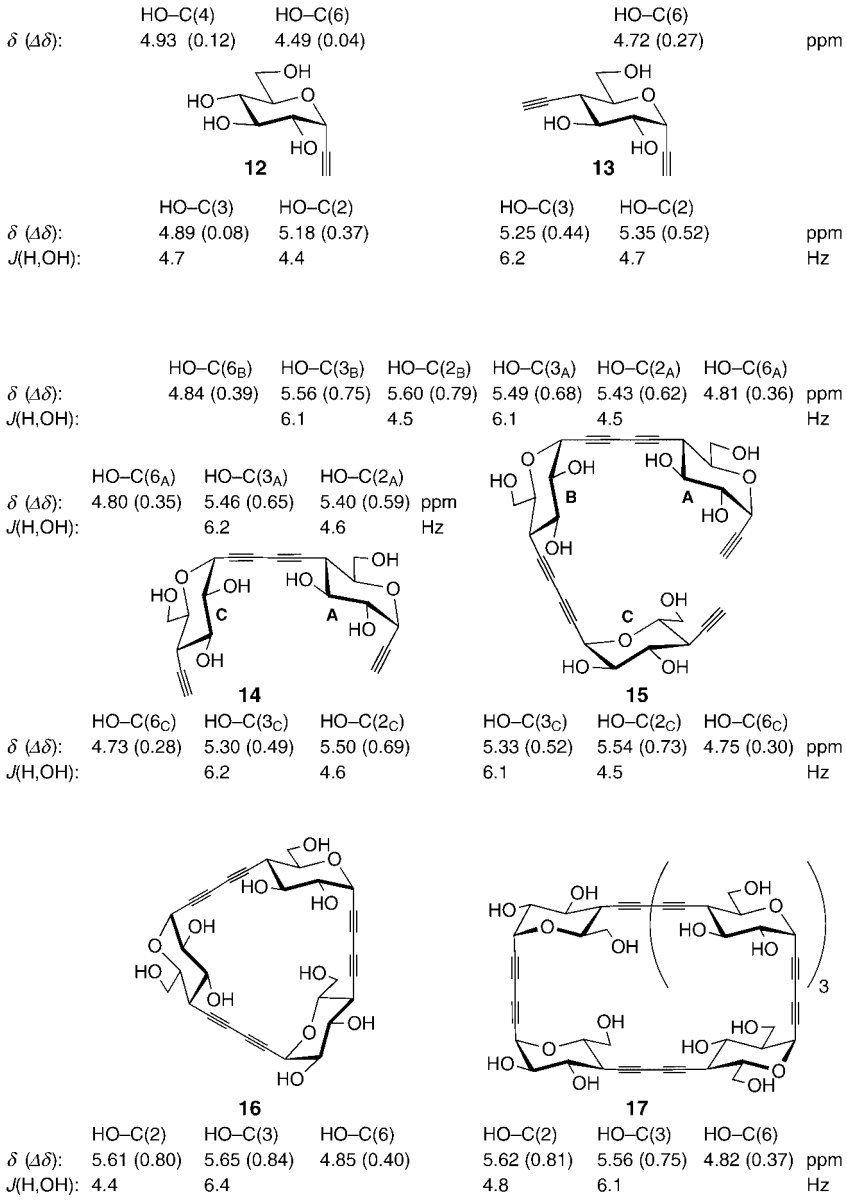

Fig. 4. *^{1}H-NMR Chemical shifts and coupling constants for the OH groups of α-D-configured acetyleno glucopyranoses* **12**–**17** [14–16] *in (D_6)DMSO* (Δδ(OH) relative to **1**)

The crystal structures of the monoalkyne **12** and the dialkyne **13** were established by X-ray-analysis (*Fig. 5,a*)[1]). Both alkynes prefer the $^4C_1$ and *gt* conformations. The chair of **13** is slightly flattened, as evidenced by the larger C(1′)–C(1)–C(2)–C(3) and C(1′)–C(1)–O–C(5) dihedral angles (*Table 2*). All OH groups are involved in intermolecular H-bonds (*Fig. 5,b*). In contradistinction to what is observed in solution in D_6(DMSO), the O–H bonds of HO–C(2) and HO–C(3) of **13** are nearly parallel to the vicinal C≡C bond, whereas the O–H bond of HO–C(2) of **12** deviates more from this orientation. The relatively short distances between the alkynyl and the vicinal OH group (**12**: C(2)OH ··· C(1′) 2.81 Å; **13**: C(2)OH ··· C(1′) 2.82 Å, C(4)OH ··· C(1″) 2.77 Å) suggest a stabilising interaction. It is known that ethynyl groups may act as weak H-bond acceptors[2]). In the solid state, the molecules of **12** and **13** are arranged in such a manner that the ethynyl groups are located in line at a distance of 5.23 and 5.06 Å, respectively (*Fig. 5, c*).

The influence of an ethynyl and a buta-1,3-diynyl group on δ(OH) differs; the difference may correlate with the electronegativity and/or size of these substituents. One expects the influence of an arylated ethynyl group to be similar to that of the buta-1,3-diynyl substituent. Indeed, the downfield shifts for HO–C(2), HO–C(3), and HO–C(6) of the bipyridine **18** [20], and for HO–C(3) and HO–C(6) of the phenylacetylene **19** [21] agree well with the values calculated on the basis of the increments for a buta-1,3-diynyl group ($\Delta\delta \leq 0.05$ ppm), whereas a weaker downfield shift is observed for HO–C(2) of **19** (0.58 instead of 0.7 ppm; *Fig. 6*). Thus, the influence of the Ph–C≡C group on δ(OH) of a vicinal OH group appears to be weaker by *ca.* 0.1 ppm than the influence of the buta-1,3-diynyl group.

We compared the δ(OH) values for **19** in (D_6)DMSO with those for **20** [21] and **21** [22] by assuming a similar increment of the phenylethynyl and the ethynylated phenylethynyl substituent. In agreement with this assumption, HO–C(3), HO–C(4), and HO–C(6) of **20** and – considering the shift increments for the substitution of HO–C(4) by the ethynyl group – also HO–C(3) and HO–C(6) of **21** show very similar δ(OH) values as **19** ($\Delta\delta$(OH) ≤ 0.02 ppm). HO–C(2) of **20** and **21**, however, shows a weaker downfield shift than expected ($\Delta\delta$(OH) = 0.17 and 0.14 ppm, resp.), possibly – and reaching the limits of the interpretation – on account of a weak inter-residue H-bond. A similar observation is made for HO–C(3) of **22** [22]. On the basis of the assumption that a *C*(4)-phenylethynyl and a *C*(4)-buta-1,3-diynyl group lead to a similar downfield shift, one expects a $\Delta\delta$(HO–C(3)) of 0.7 ppm; 0.59 ppm are observed, possibly also due to a weak inter-residue H-bond.

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[1]) The crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-184176 (**12**) and CCDC-184177 (**13**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

[2]) For alkynyl groups acting as H-bond acceptors in the solid state, see [17] and refs. cit. therein, and for calculations of such interactions, see [18][19].

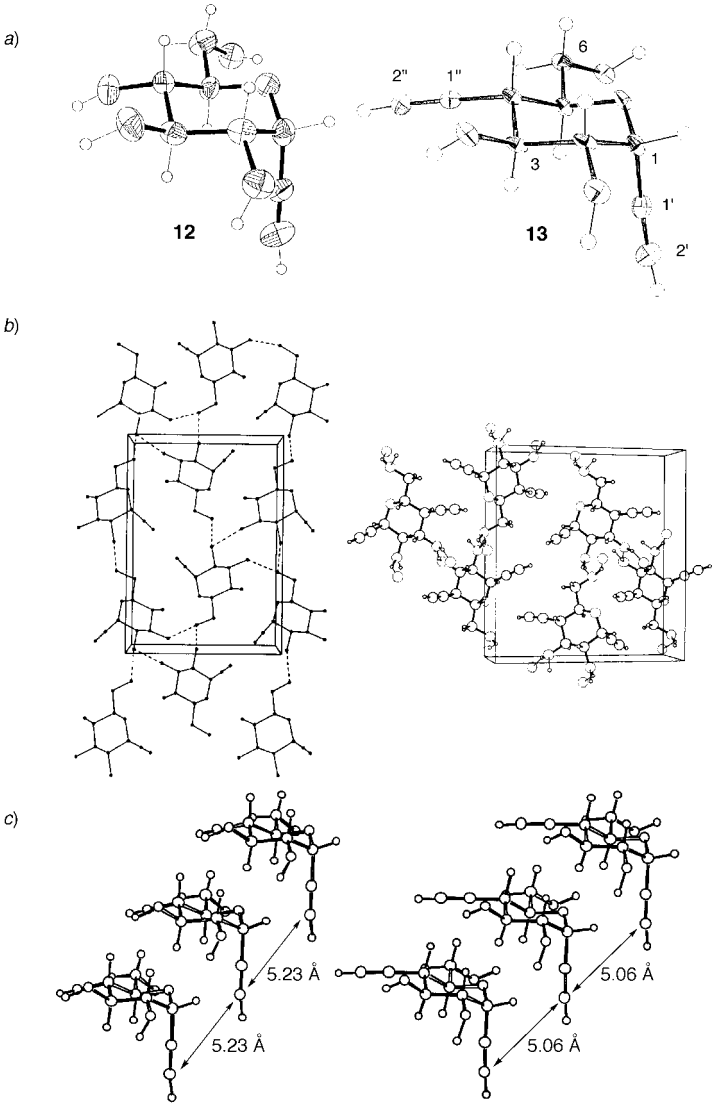

Fig. 5. a) *X-Ray structures of* **12** *and* **13**, b) *their H-bond network, and* c) *the on-line arrangement of their acetylene groups*

Experimental Part

General. See [21].

3,7-Anhydro-1,2-dideoxy-D-glycero-D-gulo-*oct-1-ynitol* (**3**) [9]. ^{1}H-NMR (500 MHz, (D_6)DMSO) [10]: 5.29 (*d*, *J* = 4.7, HO–C(4)); 5.01 (br. *s*, HO–C(5)); 4.93 (*d*, *J* = 4.4, HO–C(6)); 4.52 (*t*, *J* ≈ 5.7, HO–C(8)); 3.78 (*dd*, *J* = 9.2, 2.1, H–C(3)); 3.64 (*ddd*, *J* = 11.2, 5.6, 1.9, H–C(8)); 3.40 (*dt*, *J* = 11.3, 5.7, H′–C(8)); 3.31 (*d*, *J* = 2.1, H–C(1)); 3.09–2.93 (*m*, H–C(4), H–C(5), H–C(6), H–C(7)).

2,6-Anhydro-7,8-dideoxy-D-glycero-L-gulo-*oct-7-ynitol* (**12**). The compound was prepared from laevoglucosan in three steps (bis(trimethylsilyl)diethylsilylation, reductive acetal opening, acetylation, and depro-

Table 2. *Selected Bond Lengths* [Å], *and Bond and Dihedral Angles* [°] *for Crystalline* **12** *and* **13**

Bond	**12**	**13**	Bond or dihedral angle	**12**	**13**
C(2′)≡C(1′)	1.168(6)	1.191(4)	C(2′)≡C(1′)–C(1)	178.7	177.2
C(1′)–C(1)	1.475(5)	1.484(4)	C(2″)≡C(1″)–C(4)	–	176.0
C(1)–C(2)	1.528(5)	1.543(3)	C(1′)–C(1)–C(2)–C(3)	– 69.5	– 73.7
C(1)–O	1.416(4)	1.425(3)	C(1′)–C(1)–O–C(5)	63.5	67.2
C(5)–O	1.435(5)	1.441(3)	C(1″)–C(4)–C(3)–C(2)	–	180.0
C(4)–C(1″)	–	1.470(4)	H–C(2)–O–H	157.8	162.8
C(1″)≡C(2″)	–	1.176(4)	H–C(3)–O–H	– 37.8	– 32.3

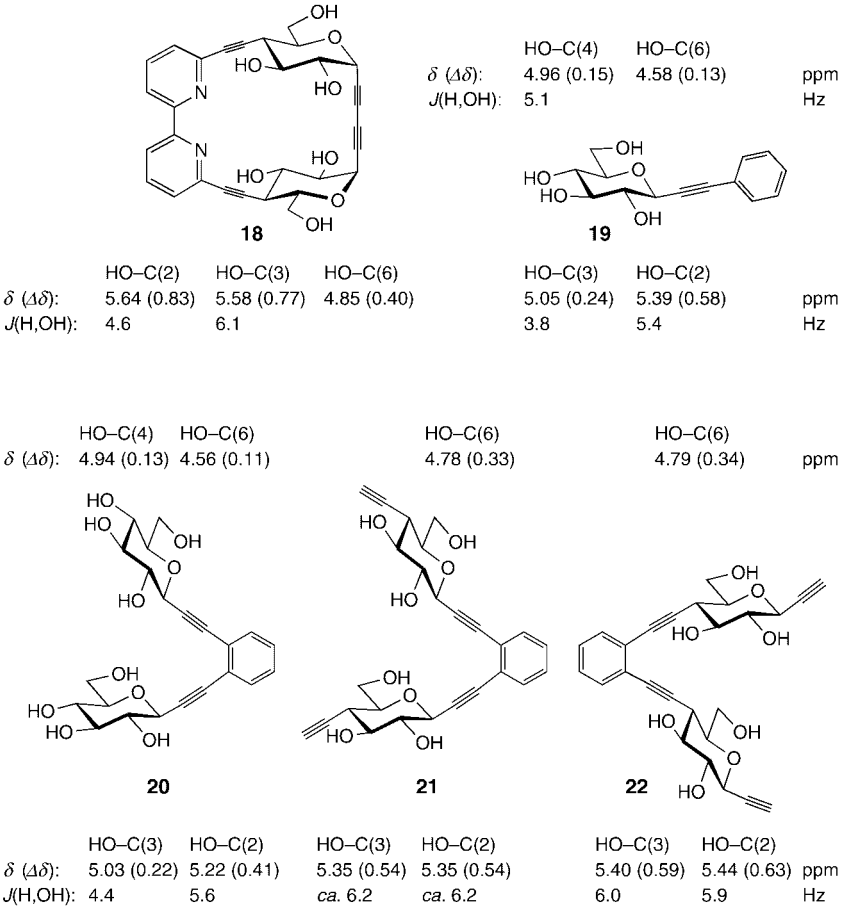

Fig. 6. *^{1}H-NMR Chemical shifts and coupling constants for the OH groups of arylated acetyleno glucopyranoses* **18**–**22** [20–22] *in (D_6)DMSO* (Δδ(OH) relative to **1**)

tection) and 53% yield [14]. R_f (CH_2Cl_2/MeOH 5:1) 0.23. M.p. *ca.* 208°. IR (KBr): 3520*s*, 3250*s* (br.), 2970*m*, 2910*m*, 2890*m*, 2875*m*, 2100*w*. ^{1}H-NMR (200 MHz, CD_3OD): 4.66 (*dd*, *J* = 5.8, 2.1, H–C(6)); 3.58–3.85 (*m*, 2 H–C(1), H–C(2), H–C(4)); 3.47 (*dd*, *J* = 9.6, 5.4, H–C(5)); 3.25 (br. *t*, *J* = 9.2, H–C(3)); 2.97 (*d*, *J* = 2.1, C≡CH). ^{1}H-NMR (300 MHz, (D_6)DMSO): 5.18 (*d*, *J* = 4.4, HO–C(5)); 4.93 (*d*, *J* = 5.3, irrad. at 3.00 → *s*, HO–C(3)); 4.89 (*d*, *J* = 4.7, HO–C(4)); 4.50 (*dd*, *J* = 5.7, 2.2, H–C(6)); 4.49 (*t*, *J* = 5.7, HO–C(1)); 3.60

(*ddd*, J = 11.5, 5.8, 1.7, H–C(1)); 3.52 (*ddd*, J = 9.6, 5.6, 1.7, irrad. at 3.00 → br. *d*, J = 5.5, H–C(2)); 3.41 (*dt*, J = 11.5, 5.9, H′–C(1)); 3.40 (*d*, J = 2.2, H–C(8)); 3.35 (*td*, $J \approx$ 9.5, 4.7, irrad. at 3.00 → change, H–C(4)); 3.25 (*dt*, $J \approx$ 9.6, 4.8, H–C(5)); 3.00 (*td*, J = 9.1, 5.3, H–C(3)).^{13}C-NMR (75 MHz, D_2O): 82.30 (*s*, *C*≡CH); 80.37 (*s*, C≡*C*H); 77.82, 76.93, 72.80, 72.34 (4*d*, C(2), C(3), C(4), C(5)); 70.75 (*d*, C(6)); 63.50 (*t*, C(1)). CI-MS: 206 (100, $[M + NH_4]^+$), 189 (8, $[M + H]^+$).

X-Ray Analysis of **12** (CCDC-184176). Colourless crystals were obtained from MeOH at r.t. $C_8H_{12}O_5$ (188.18); orthorhombic $P2_12_12_1$; a = 5.233(3) Å, b = 10.730(5) Å, c = 15.091(7) Å; V = 847.4(7) Å^3; $D_{calc.}$ = 1.475 Mg/m^3; Z = 4. Intensities were measured in the ω-scan mode on an *Syntex P21* diffractometer (graphite monochromator, CuK_α, λ = 1.54178 Å) at 274 K. Of the 553 total collected reflections, 538 unique reflections were observed. R = 0.0348, R_w = 0.0452. The structure was refined with the *Siemens* SHELTXTL PLUS method.

2,6-Anhydro-3-ethynyl-3,7,8-trideoxy-D-glycero-L-gulo-*oct-7-ynitol* (**13**) [14]. A soln. of 2,6-anhydro-3-ethynyl-3,7,8-trideoxy-8-(trimethylsilyl)-D-glycero-L-gulo-oct-7-initol [23] (1.00 g, 3.72 mmol) in MeOH (10 ml) was treated at 0° with 2% NaOMe in MeOH (0.50 ml), stirred for 1 h, warmed to r.t., stirred for 1 h, and neutralised with *Dowex* (H^+ form). The residue was filtered off and washed with MeOH. Evaporation of the combined filtrate and washings, and FC (toluene/AcOEt 1:4) gave **13** (655 mg, 90%). Colourless solid. R_f (toluene/AcOEt 1:4) 0.15. M.p. 127–128°. $[\alpha]_D^{25} = +100.7$ (c = 0.5, MeOH). CD (c = 11.21 mM, H_2O): 257 (635), 244 (950), 231 (660). IR (KBr): 3422*s* (br.), 3342*s* (br.), 3278*s*, 2955*m*, 2925*m*, 2869*m*, 2109*w*, 1459*m*, 1437*m*, 1391*m*, 1339*m*, 1138*m*, 1083*s*, 1047*s*, 997*m*, 859*m*. ^{1}H-NMR (300 MHz, (D_6)DMSO): 5.35 (*d*, J = 4.7, exchange with D_2O, HO–C(5)); 5.25 (*d*, J = 6.2, exchange with D_2O, HO–C(4)); 4.72 (*t*, J = 5.9, exchange with D_2O, HO–C(1)); 4.58 (*dd*, J = 5.8, 2.3, H–C(6)); 3.71 (*ddd*, J = 10.6, 5.0, 1.9, H–C(2)); 3.63 (*ddd*, J = 11.8, 5.3, 1.9, addn. of D_2O → *dd*, J = 12.0, 1.6, H–C(1)); 3.500 (*dt*, J = 11.8, 5.9, addn. of D_2O → br. *dd*, $J \approx$ 11.9, 5.0, H′–C(1)); 3.498 (*td*, $J \approx$ 9.5, 5.9, addn. of D_2O → *t*, $J \approx$ 9.6, H–C(4)); 3.46 (*d*, J = 2.2, H–C(8)); 3.20 (*dt*, $J \approx$ 9.7, 4.8, addn. of D_2O → *dd*, J = 9.2, 5.6, H–C(5)); 2.93 (*d*, J = 2.2, HC≡C–C(3)); 2.25 (*td*, J = 10.3, 2.2, H–C(3)). ^{13}C-NMR (75 MHz, (D_6)DMSO): 82.73 (*s*, C(7)); 79.65 (*s*, C(8)); 79.09 (*s*, HC≡*C*–C(3)); 73.28 (*s*, HC≡C–C(3)); 74.87 (*d*, C(2)); 71.56, 70.90 (2*d*, C(4), C(5)); 68.09 (*d*, C(6)); 61.99 (*t*, C(1)); 38.52 (*d*, C(3)). CI-MS: 214 (100, $[M + NH_4]^+$). Anal. calc. for $C_{10}H_{12}O_4$ (196.20): C 61.22, H 6.16; found: C 61.26, H 6.04.

X-Ray Analysis of **13** (CCDC-184177). Crystals were obtained from AcOEt by slow evaporation at r.t. $C_{10}H_{12}O_4$ (196.20); orthorhombic $P2_12_12_1$; a = 5.058(2), b = 12.834(5), c = 14.450(4); V = 938.0(5) Å^3; $D_{calc.}$ = 1.389 Mg/m^3; Z = 4. Intensities were measured in the $\omega/2\theta$-scan mode on an *Enraf Nonius CAD-4* diffractometer (graphite monochromator, CuK_α, λ = 1.54184 Å) at 123(2) K. Of the 1038 total collected reflections, 1018 unique reflections were observed. R = 0.0438, R_w = 0.1363. The structure was solved by the direct method with SHELX86. The non-H-atoms were refined anisotropically with SHELXL-92. The H-atoms were obtained from a difference *Fourier* map and refined isotropically.

3,7-Anhydro-1,2-dideoxy-1-phenyl-D-glycero-D-gulo-*oct-1-ynitol* (**19**) [21]. ^{1}H-NMR (300 MHz, (D_6)DMSO) [22]: 7.47–7.36 (*m*, 5 arom. H); 5.39 (*d*, J = 5.4, HO–C(4)); 5.05 (*d*, J = 3.8, HO–C(5)); 4.96 (*d*, J = 5.0, HO–C(6)); 4.58 (*t*, J = 5.7, HO–C(8)); 4.05 (*d*, J = 9.0, H–C(3)); 3.68 (*ddd*, J = 11.5, 5.5, 1.2, H–C(8)); 3.67 (*dt*, J = 11.6, 5.6, H′–C(8)); 3.25–3.03 (*m*, H–C(4), H–C(5), H–C(6), H–C(7)).

1,1′-(1,2-Phenylene)bis(3,7-anhydro-1,2-dideoxy-D-glycero-D-gulo-*oct-1-ynitol*) (**20**) [21]. ^{1}H-NMR (300 MHz, (D_6)DMSO) [22]: 7.49–7.44 (*m*, 2 arom. H); 7.38–7.34 (*m*, 2 arom. H); 5.22 (*d*, J = 5.6, HO–C(4)); 5.03 (*d*, J = 4.4, HO–C(5)); 4.94 (*d*, J = 4.6, HO–C(6)); 4.56 (*t*, J = 5.9, HO–C(8)); 4.08 (*d*, J = 9.3, H–C(3)); 3.66 (br. *dd*, $J \approx$ 11.6, 5.6, H–C(8)); 3.43 (*dt*, J = 11.6, 5.6, H′–C(8)); 3.24–3.06 (*m*, H–C(4), H–C(5), H–C(6), H–C(7)).

1,1′-(1,2-Phenylene)bis(3,7-anhydro-1,2-dideoxy-6-C-*ethynyl*-D-glycero-D-gulo-*oct-1-ynitol*) (**21**). The compound was prepared from 3,7-anhydro-1,2-dideoxy-6-*C*-[(trimethylsilyl)ethynyl]-D-*glycero*-D-*gulo*-oct-1-ynitol [9] in four steps (triethylsilylation, condensation with 1,2-diiodobenzene, and *O*- and *C*-desilylation) and 10% yield [22]. M.p. 113–115°. R_f (CH_2Cl_2/MeOH 10:1) 0.37. $[\alpha]_D^{25} = +8.0$ (c = 0.30, MeOH). UV (MeOH): 273 (11500), 259 (13200), 231 (45500). IR (KBr): 3655*w*, 3388*s* (br.), 3288*s*, 2911*w*, 2844*m* (br.), 2220*w*, 2111*w*, 1638*w*, 1483*w*, 1455*w*, 1350*m*, 1305*m*, 1105*s*, 972*m*, 894*w*. ^{1}H-NMR (300 MHz, CD_3OD): 7.47 (*dd*, J = 5.8, 3.3, H–C(3′)); 7.32 (*dd*, J = 5.8, 3.3, H–C(4′)); 4.24 (*d*, J = 9.4, H–C(3)); 3.94 (*dd*, J = 12.3, 2.0, H–C(8)); 3.76 (*dd*, J = 12.1, 5.3, H′–C(8)); 3.57 (*ddd*, J = 10.4, 5.3, 2.1, H–C(7)); 3.51 (*dd*, J = 10.2, 9.0, H–C(5)); 3.39 (*t*, J = 9.2, H–C(4)); 2.57 (*d*, J = 2.2, HC≡C–C(6)); 2.56 (*td*, J = 10.0, 2.0, H–C(6)). ^{1}H-NMR (300 MHz, (D_6)DMSO): 7.48 (*dd*, J = 6.0, 3.3, H–C(3′)); 7.36 (*dd*, J = 5.9, 3.4, H–C(4′)); 5.35 (br. *d*, $J \approx$ 6.2, HO–C(4), HO–C(5)); 4.78 (*t*, J = 5.9, HO–C(8)); 4.16 (*d*, J = 9.3, H–C(3)); 3.72 (br. *dd*, $J \approx$ 11.0, 5.6, H–C(8)); 3.51 (*dt*, J = 11.5, 5.8, H′–C(8)); 3.43–3.31 (*m*, H–C(5), H–C(7)); 3.16 (*td*, J = 9.4, 5.5, H–C(4)); 2.95 (*d*, J = 2.5, HC≡C–C(6)); 2.35 (*td*, J = 10.3, 2.2, H–C(6)). ^{13}C-NMR (75 MHz, CD_3OD): 133.02 (*d*, C(3′)); 129.61

(*d*, C(4′)); 126.56 (*s*, C(1′)); 91.51 (*s*, C(2)); 84.95 (*s*, C(1)); 82.09 (*s*, HC≡*C*−C(6)); 81.38 (*d*, C(7)); 77.06 (*d*, C(5)); 75.68 (*d*, C(4)); 73.46 (*s*, HC≡C−C(6)); 72.84 (*d*, C(3)); 63.74 (*t*, C(8)); 38.85 (*d*, C(6)). CI-MS: 466 (3, M^+), 31 (100).

6,6′-[1,2-Phenylene(diethynyl)]bis(3,7-anhydro-1,2,6-trideoxy-D-glycero-D-gulo-*oct-1-ynitol*) (**22**). The compound was prepared from 3,7-anhydro-1,2-dideoxy-6-*C*-ethynyl-4-*O*-(triisopropylsilyl)-1-*C*-(trimethylsilyl)-D-glycero-D-gulo-oct-1-ynitol [9] in four steps (triethylsilylation, condensation with 1,2-diiodobenzene, and *O*- and *C*-desilylation) and 17% yield [22]. M.p. 248–249°. R_f (CH_2Cl_2/MeOH 10:1) 0.25. $[\alpha]_D^{25} = -15.3$ ($c = 0.32$, MeOH). UV (MeOH): 273 (12500), 259 (14000), 233 (53800), 222 (32200). IR (KBr): 3655*w*, 3355*s* (br.), 3288*s*, 2900*w*, 2844*w*, 2288*w*, 2111*w*, 1483*w*, 1455*w*, 1350*m*, 1305*w*, 1100*s*, 1072*m*, 1055*m*, 988*w*, 966*m*. ^{1}H-NMR (300 MHz, CD_3OD): 7.43 (*dd*, $J = 5.9$, 3.4, H−C(3′)); 7.26 (*dd*, $J = 5.7$, 3.4, H−C(4′)); 4.02 (*dd*, $J = 9.6$, 2.1, H−C(3)); 4.01 (*dd*, $J = 12.1$, 1.9, H−C(8)); 3.79 (*dd*, $J = 12.0$, 5.5, H′−C(8)); 3.59 (*ddd*, $J = 10.3$, 5.6, 1.9, H−C(7)); 3.57 (*dd*, $J = 10.4$, 8.8, H−C(5)); 3.29 (*dd*, $J = 9.6$, 8.8, H−C(4)); 2.89 (*d*, $J = 2.2$, H−C(1)); 2.75 (*t*, $J = 10.3$, H−C(6)). ^{1}H-NMR (300 MHz, (D_6)DMSO): 7.39 (*dd*, $J = 5.7$, 3.4, H−C(3′)); 7.29 (*dd*, $J = 5.6$, 3.3, H−C(4′)); 5.44 (*d*, $J = 5.9$, irrad. at 3.06 → change, HO−C(4)); 5.40 (*d*, $J = 6.0$, HO−C(5)); 4.79 (*t*, $J = 5.9$, HO−C(8)); 3.90 (*dd*, $J = 9.6$, 1.9, irrad. at 3.06 → change, H−C(3)); 3.75 (br. *dd*, $J = 10.9$, 5.6, H−C(8)); 3.55 (*dt*, $J = 11.8$, 5.9, H′−C(8)); 3.45 (br. *dd*, $J \approx 10.3$, 4.4, H−C(7)); 3.39–3.23 (*m*, H−C(5)); 3.35 (*d*, $J = 2.2$, H−C(1)); 3.06 (*dt*, $J = 9.0$, 6.0, irrad. at 3.90 → *dd*, $J = 9.0$, 6.0, H−C(4)); 2.58 (*t*, $J = 10.3$, H−C(6)). ^{13}C-NMR (75 MHz, CD_3OD): 133.28 (*d*, C(3′)); 129.04 (*d*, C(4′)); 126.89 (*s*, C(1′)); 91.64 (*s*, C≡*C*−C(6)); 83.57 (*s*, *C*≡C−C(6)); 81.92 (*s*, C(2)); 81.42 (*d*, C(7)); 77.02 (*d*, C(5)); 75.79 (*d*, C(4)); 75.36 (*s*, C(1)); 72.19 (*d*, C(3)); 64.13 (*t*, C(8)); 39.80 (*d*, C(6)). CI-MS: 466 (7, M^+), 31 (100).

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