Pregnane and Pregnane Glycosides from the Malagasy Plant, *Cynanchum aphyllum*

Tripetch KANCHANAPOOM,[a,b] Ryoji KASAI,[a] Kazuhiro OHTANI,[a] Marta ANDRIANTSIFERANA,[c] and Kazuo YAMASAKI*,[a]

[a] *Division of Medicinal Chemistry, Graduate School of Biochemical Sciences, Hiroshima University; 1–2–3 Kasumi, Minami-ku, Hiroshima 734–8551, Japan:* [b] *Department of Pharmaceutical Botany and Pharmacognosy, Faculty of Pharmaceutical Sciences, Khon Kaen University; Khon Kaen 40002, Thailand: and* [c] *Laboratoire de Chimie Organigue, Produits Naturels, Universite' d'Antananarivo; Madagascar.* Received February 12, 2002; accepted April 15, 2002

A new 8,14-*seco*-pregnane type of steroid called cynaphyllogenin and its eight glycosides, cynaphyllosides A—H, were isolated from the aerial parts of *Cynanchum aphyllum*. The structures of these compounds were elucidated based on chemical and spectroscopic evidence.

Key words cynaphyllosides A—H; 8,14-*seco*-pregnane; *Cynanchum aphyllum*; cynaphyllogenin; pregnane glycosides; Asclepiadaceae

Cynanchum aphyllum L. (Asclepiadaceae, Malagasy name: Vahimasy) is a leafless and succulent shrub which secretes yellow latex. No phytochemical investigation has been carried out on this species. In our continuing study on the chemical constituents of Malagasy plants, we isolated a pregnane called cynaphyllogenin (**1**) and its eight glycosides, cynaphyllosides A—H (**2**—**9**), from the aerial parts of this plant. The present paper deals with the isolation and structural determination of these compounds.

The methanolic extract of the aerial part of *C. aphyllum* was partitioned with *n*-hexane, Et_2O, and H_2O. The Et_2O and H_2O soluble fractions were purified by column chromatography and then by preparative HPLC to afford compounds **3**, **5** and **6** from the former fraction and **1**, **2**, **4**, and **7**—**9** from the latter fraction.

The molecular formula of cynaphyllogenin (**1**) was determined as $C_{30}H_{36}O_7$ by negative high resolution (HR)-FAB mass spectrometry and ^{13}C-NMR spectral data. The ^{13}C-NMR spectrum of **1** revealed the presence of 30 signals: three methyls, six methylenes, four methines (two of them bearing an oxygen atom), three quarternary (one of them bearing an oxygen atom), two di-substituted double bonds, one mono-substituted benzene ring and four carbonyl (three ketones and one ester). Of these signals, nine due to the ester carbonyl, benzene ring and one of the di-substituted double bond carbons were easily assigned to cinnamoyl moiety. The double bond of this moiety was determined to be *trans*-configuration from the coupling constants of its two olefinic protons.

The other 21 carbon signals were correlated by heteronuclear multiple-bond connectivity (HMBC) experiments (Table 1). From this result and the chemotaxonomical fact that the presence of pregnanes and their glycosides in this genus are well known,[1,2] we assumed that **1** is an 8,14-*seco*-pregnane. This type of pregnane has already been isolated as a glycoside called sarcovimiside B (**10**) from *Sarcostemma viminale*.[3] The carbon signals due to the pregnane skeleton (A and B-rings, C-11 and C-12) of **1** were very similar to those of the aglycone of **10**, lacking the acetyl and carbinyl carbon signals attributed to the side chain of **10** and instead had a carbonyl signal for ketone. Moreover, chemical shifts of this carbonyl carbon signal at δ 207.5 and a methyl carbon signal at δ 31.1 as well as a singlet methyl proton signal at δ 2.30 were characteristic of a methyl ketone group. These results demonstrated that **1** is a 3β,5β-dihydroxy-8,14-*seco*-pregn-6-ene-8,14,20-trione type of compound. The configuration of the side chain at C-17 was as follows. The proton signal of H-17 (δ 2.93) was observed as double doublet with the coupling constants 10.5 and 6.4 Hz.[4] The nuclear Overhauser enhancement (NOE) spectrum of **1** provided further

Table 1. ^{1}H- and ^{13}C-NMR Spectral Data of Cynaphyllogenin (**1**) in Pyridine-d_5

No.	^{1}H	^{13}C	HMBC (H→C)
1	1.57 m	25.7	5
	2.21 td (J=14.2, 3.2 Hz)		10
2	1.74 m	28.6	
	1.87 m		
3	4.25 m	66.3	
4	1.95 dd (J=14.4, 2.5 Hz)	38.5	
	2.09 br d (J=14.4 Hz)		2, 3, 5, 10
5		74.9	
6	6.70 d (J=10.1 Hz)	154.5	4, 10
7	5.93 d (J=10.1 Hz)	126.9	5, 9
8		201.9	
9	3.29 br d (J=10.6 Hz)	47.9	5, 8, 10, 11, 12, 19
10		46.0	
11	1.77 br dd (J=14.3, 9.7 Hz)	26.4	8, 12
	2.47 br dd (J=14.3, 10.6 Hz)		8, 9
12	5.99 br d (J=9.7 Hz)	71.3	9, 11, 13, 17, 18, 1′
13		57.4	
14		215.7	
15	2.32 m	35.2	14, 16, 17
	3.09 ddd (J=20.2, 9.8, 7.6 Hz)		14,17
16	1.90 m	20.3	13,14
	2.56 m		17,20
17	2.93 dd (J=10.5, 6.4 Hz)	59.2	12, 13, 14, 15, 18, 20
18	1.70 s	17.1	12, 13, 14, 17
19	1.00 s	17.9	1, 5, 9, 10
20		207.5	
21	2.30 s	31.1	17, 20
1′		167.0	
2′	6.83 d (J=16.0 Hz)	118.3	
3′	8.01 d (J=16.0 Hz)	146.0	
4′		134.9	
5′,9′		128.7	
6′,8′		129.3	
7′		130.8	

* To whom correspondence should be addressed. e-mail: kazuoy@hiroshima-u.ac.jp

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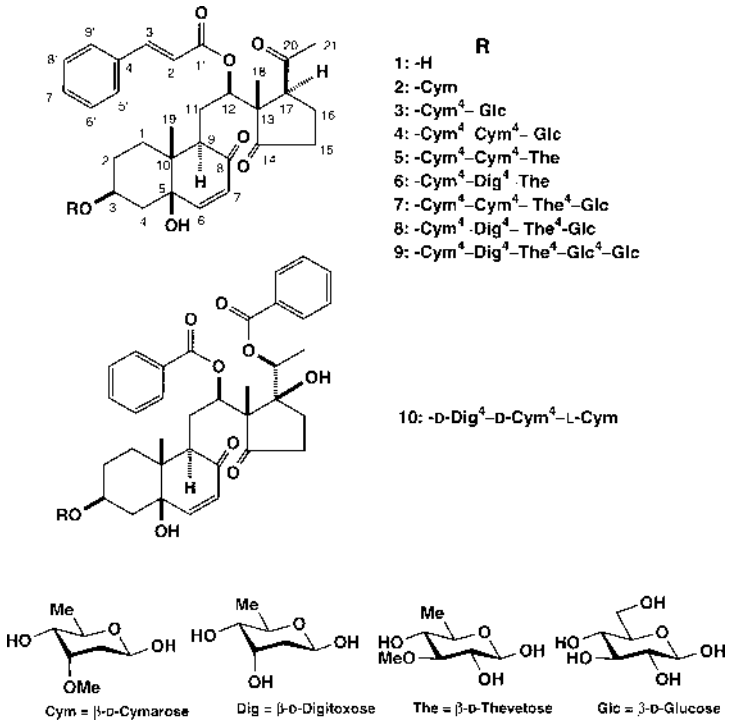

Fig. 1

confirmation of the strong correlation between H-18 (δ 1.70) and H-21 (δ 2.30). The position of the cinnamoyl moiety on C-12 was determined from HMBC experiment (Table 1).

These results led to the formulation of cynaphyllogenin (**1**) as 12(*R*)-*O*-cinnamoyloxy-3β,5β-dihydroxy-8,14-*seco*-17β-pregn-6-ene-8,14,20-trione.

Cynaphyllosides A—H (**2**—**9**) were assigned as the glycosides of cynaphyllogenin with different sugar moiety (Tables 2, 3) from the ^{13}C- and ^{1}H-NMR data. Comparison of the ^{13}C-NMR spectra of **2**—**9** showed glycosylation shifts at C-3, C-2 and C-4 indicating that the sugar moiety of all these compounds is located at C-3 of the aglycone.

The component sugars isolated from acid hydrolysate of the glycosides were all confirmed as D-form by measurement of their optical rotations.[5] The linkages of all sugars were assigned to be in the β-form base on the coupling constant of anomeric protons in ^{1}H-NMR spectra.

The molecular formula of cynaphylloside A (**2**) was determined as $C_{37}H_{48}O_{10}$. The ^{1}H- and ^{13}C-NMR spectra indicated the presence of one monosaccharide unit. Acid hydrolysis of **2** gave cymarose. Accordingly, the structure of **2** was elucidated as shown in Fig. 1.

Cynaphylloside B (**3**) had a molecular formula $C_{43}H_{58}O_{15}$. Acid hydrolysis provided cymarose and glucose. In the ^{1}H-NMR spectrum of **3**, two anomeric protons were observed. The ^{13}C-NMR spectrum showed the presence of a terminal β-D-glucopyranosyl unit. Consequently, the structure of **3** was determined as shown in Fig. 1.

Cynaphylloside C (**4**) and cynaphylloside D (**5**) had the molecular formula $C_{50}H_{70}O_{18}$ and $C_{51}H_{72}O_{17}$, respectively. Cymarose and glucose were detected from the acid hydrolysate of **4**, and cymarose and thevetose from that of **5**. The ^{1}H- and ^{13}C-NMR spectra revealed the presence of two units of cymarose and one terminal glucose in **4** and two units of cymarose and one terminal thevetose in **5**. Moreover, the order of these sugar sequences was confirmed by observation of the peak at *m*/*z* 795 [(M−terminal Glc or The)$^-$] in the negative FAB-MS spectra of both **4** and **5**. Therefore, the structures of **4** and **5** were formulated as shown in Fig. 1.

Cynaphylloside E (**6**) had a molecular formula $C_{50}H_{70}O_{17}$. The component sugars were identified as cymarose, digitoxose and thevetose by acid hydrolysis. The ^{1}H- and ^{13}C-NMR spectra indicated the presence of one unit of each of β-cymarose, β-digitoxose and a terminal β-thevetose. Mild acid hydrolysis of **6** yielded **2** as a partially hydrolyzed product together with **1** indicating that the sugar sequence is –cymarose–thevetose–digitoxose. The linkage of the thevetose to C-4 of the digitoxose was determined from observation of the downfield shift of C-4 and the upfield of C-3 and C-5 of digitoxose in the ^{13}C-NMR spectrum of **6**. Therefore, the structure of **6** was assigned as shown in Fig. 1.

Cynaphylloside F (**7**) had a molecular formula $C_{57}H_{82}O_{22}$. The ^{1}H- and ^{13}C-NMR spectra of **7** showed four anomeric signals. Acid hydrolysis gave cymarose, thevetose and glucose. The electron impact (EI)-MS of its acetyl derivative displayed a fragment ion at *m*/*z* 331 due to terminal β-glucopyranose. This was confirmed by obtaining **5** on enzymatic hydrolysis of **7** with crude hesperidinase. The position of the terminal glucose at C-4 of the thevetose moiety was determined by observation of the glycosylation shifts for the signals due to C-4 (+7.2 ppm), C-3 (−2.0 ppm) and C-5 (−0.9 ppm) in comparison with the ^{13}C-NMR spectra of **5** and **7**. Based on these results, the structure of **7** was formulated as shown in Fig. 1.

The molecular formula of cynaphyllosides G (**8**) and H (**9**) was determined as $C_{56}H_{80}O_{22}$ and $C_{62}H_{90}O_{27}$, respectively. By the same method as used for **7**, the structures of **8** and **9** were established as shown in Fig. 1.

Table 2. ^{1}H-NMR Spectral Data of **2**—**9** in Pyridine-d_5

No.	2	3	4	5	6	7	8	9
Aglycone								
6	6.64 d (10.3)[a)]	6.62 d (10.2)	6.62 d (10.4)	6.62 d (10.4)	6.62 d (10.3)	6.62 d (10.3)	6.61 d (10.5)	6.62 d (10.5)
7	5.92 d (10.3)	5.91 d (10.2)	5.91 d (10.4)	5.91 d (10.4)	5.91 d (10.3)	5.91 d (10.3)	5.90 d (10.5)	5.91 d (10.5)
9	3.27 br d (10.4)	3.27 br d (10.5)	3.24 br d (10.5)	3.24 br d (10.5)	3.24 br d (10.7)	3.24 br d (10.7)	3.22 br d (10.7)	3.23 br d (10.2)
12	5.97 br d (8.8)	5.96 br d (8.8)	5.94 br d (9.0)	5.93 br d (8.8)	5.94 br d (8.8)	5.94 br d (8.8)	5.94 br d (8.8)	5.94 br d (8.6)
17	2.92 dd (10.2, 6.3)	2.92 dd (10.0, 6.6)	2.92 dd (10.0, 6.6)	2.91 dd (10.0, 6.6)	2.91 dd (10.5, 6.6)	2.91 dd (10.3, 6.6)	2.92 dd (10.0, 6.6)	2.92 dd (10.0, 6.8)
18	1.68 s	1.67 s	1.67 s	1.66 s	1.67 s	1.67 s	1.66 s	1.67 s
19	0.92 s	0.92 s	0.90 s	0.90 s	0.89 s	0.89 s	0.89 s	0.90 s
21	2.31 s	2.31 s	2.34 s	2.30 s	2.31 s	2.31 s	2.30 s	2.31 s
Sugar								
Anomeric	4.98 br d (9.0)	5.01 br d (9.0)	5.02 br d (9.3)	5.03 br d (9.5)	5.27 br d (9.3)	5.10 d (7.8)	5.25 br d (9.3)	5.25 br d (9.4)
		4.88 d (7.8)	4.98 br d (9.5)	4.98 br d (9.0)	4.98 br d (9.3)	5.03 br d (9.8)	5.07 d (7.8)	5.14 d (7.8)
			4.90 d (7.8)	4.73 d (7.6)	4.79 d (7.6)	4.98 br d (9.0)	4.97 br d (9.2)	5.04 d (8.0)
						4.66 d (7.8)	4.71 d (7.6)	5.01 br d (9.3)
								4.71 d (7.6)
OMe	3.35 s	3.42 s	3.50 s	3.87 s	3.96 s	3.91 s	3.88 s	3.86 s
			3.49 s	3.52 s	3.51 s	3.53 s	3.50 s	3.50 s
				3.50 s		3.49 s		
6-Me	1.38 d (6.1)	1.46 d (5.8)	1.56 d (5.8)	1.55 d (5.9)	1.56 d (6.1)	1.71 d (6.1)	1.64 d (5.8)	1.64 d (5.8)
			1.17 d (5.8)	1.54 d (5.9)	1.49 d (6.1)	1.50 d (6.1)	1.52 d (6.1)	1.51 d (6.1)
				1.18 d (5.9)	1.17 d (6.1)	1.18 d (6.1)	1.17 d (5.9)	1.17 d (5.9)

a) *J* values in Hz are given in parentheses.

We isolated a 17-epimer having an α-oriented side chain of cynaphylloside G (**8**), that is, 12(*R*)-*O*-cinnamoyloxy-3β,5β-dihydroxy-8,14-*seco*-17α-pregn-6-ene-8,14,20-trione. However, this compound might be converted from **8** by keto–enol interconversion of the side chain during the process of extraction and isolation. There have been only two reports of 8,14-*seco*-pregnane type of compounds from plant sources.[3,6)]

Experimental

General Procedure NMR spectra were recorded in C_5D_5N using a JEOL JNM A-400 spectrometer (400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR) with tetramethylsilane (TMS) as internal standard. MS were recorded on a JEOL JMS-SX 102 spectrometer. Optical rotations were measured with a Union PM-1 digital polarimeter. Preparative HPLC was carried out on columns of ODS (150×20 mm i.d., YMC), Polyamine II (250×20 mm i.d., YMC) and Diol (300×8 mm i.d., YMC) with a Tosoh reflection index (RI-8) detector. Medium pressure liquid chromatography (MPLC) was carried out on a column of Polyamide C-200. For CC, silica gel G 60 (Merck), YMC-gel ODS (50 mm, YMC) and a highly porous copolymer of styrene and divinylbenzene (Mitsubishi Chem. Ind. Co., Ltd.) were used. The solvent systems were: (I) 60% MeOH, (II) EtOAc–MeOH (9 : 1), (III) 70% MeOH, (IV) 65% MeOH, (V) 90% MeCN, (VI) 92% MeCN, (VII) 50% MeCN, (VIII) 55% MeCN, (IX) 50% MeCN and (X) MeCN. The spray reagent used for TLC was 10% H_2S_4O in 50% EtOH. Acid hydrolysis of glycosides followed by identification of the resulting monosaccharides including absolute configuration was carried out as previously described.[5)]

Plant Material The aerial parts of *Cynanchum aphyllum* were collected in November 1998 from Ambalavao, Madagascar and identified by Dr. Armand Rakotozafy, Institut Malgache de Recherches Appliquees, Madagascar. A voucher specimen is kept in the Herbarium of the Institute of Pharmaceutical Sciences, Faculty of Medicine, Hiroshima University, Japan.

Extraction and Isolation The dried aerial parts (800 g) of *C. aphyllum* were extracted with hot methanol. After removal of the solvent by evaporation, the residue (166 g) was extracted with *n*-hexane and Et_2O, successively. The aqueous layer was subjected to a column of highly porous copolymer of styrene and divinylbenzene, and successively eluted with H_2O, 50% MeOH, MeOH and acetone. The fraction eluted with MeOH (10.5 g) was subjected to a column of RP-18 (system I) affording eight fractions. Fraction 5 (2.8 g) was chromatographed on a column of silica gel (system II), followed by HPLC-ODS (systems III and IV) to provide compounds **1** (18 mg), **8** (1.2 g) and **9** (43 mg). Fraction 6 (2.3 g) was subjected to a column of MPLC-Polyamide (system V), followed by HPLC-Polyamine II (system VI) to afford compounds **2** (24 mg), **4** (18 mg) and **7** (185 mg).

The Et_2O extract (59 g) was subjected to a column of silica gel using a gradient system (EtOAc to 80% EtOAc in MeOH) affording six fractions. Fraction 2 (1.6 g) was chromatographed on RP-18 columns (system VII), followed by HPLC-ODS (system VIII) to provide compounds **5** (58 mg) and **6** (380 mg). Fraction 4 (4.0 g) was further purified by RP-18 (system IX), HPLC-ODS (system VII) and HPLC-Diol (system X) to afford compounds **3** (18 mg) and **10** (45 mg).

Cynaphyllogenin (**1**): White amorphous powder, $[\alpha]_D^{21}$ −115.8° (MeOH, *c*=0.61), ^{1}H- and ^{13}C-NMR: Table 1, HR-FAB-MS (negative mode) *m/z*: 507.2379 (Calcd for $C_{30}H_{35}O_7$, $[M-H]^-$ 507.2382).

Cynaphylloside A (**2**): White amorphous powder, $[\alpha]_D^{21}$ −63.9° (MeOH, *c*=0.81), ^{1}H-NMR: Table 2, ^{13}C-NMR: Tables 3 and 4, HR-FAB-MS (negative mode) *m/z*: 651.3163 (Calcd for $C_{37}H_{47}O_{10}$, $[M-H]^-$: 651.3169).

Cynaphylloside B (**3**): White amorphous powder, $[\alpha]_D^{21}$ −63.8° (MeOH, *c*=0.89), ^{1}H-NMR: Table 2, ^{13}C-NMR: Tables 3 and 4, HR-FAB-MS (negative mode) *m/z*: 813.3689 (Calcd for $C_{43}H_{57}O_{15}$, $[M-H]^-$: 813.3697).

Cynaphylloside C (**4**): White amorphous powder, $[\alpha]_D^{21}$ −42.4° (MeOH, *c*=0.96), ^{1}H-NMR: Table 2, ^{13}C-NMR: Tables 3 and 4, HR-FAB-MS (negative mode) *m/z*: 957.4480 (Calcd for $C_{50}H_{69}O_{18}$, $[M-H]^-$: 957.4483).

Cynaphylloside D (**5**): White amorphous powder, $[\alpha]_D^{21}$ −38.2° (MeOH, *c*=1.10), ^{1}H-NMR: Table 2, ^{13}C-NMR: Tables 3 and 4, HR-FAB-MS (negative mode) *m/z*: 955.4687 (Calcd for $C_{51}H_{71}O_{17}$, $[M-H]^-$: 955.4691).

Cynaphylloside E (**6**): White amorphous powder, $[\alpha]_D^{21}$ −61.2° (MeOH, *c*=0.50), ^{1}H-NMR: Table 2, ^{13}C-NMR: Tables 3 and 4, HR-FAB-MS (negative mode) *m/z*: 941.4550 (Calcd for $C_{50}H_{69}O_{17}$, $[M-H]^-$: 941.4534).

Cynaphylloside F (**7**): White amorphous powder, $[\alpha]_D^{21}$ −53.9° (MeOH, *c*=0.59), ^{1}H-NMR: Table 2, ^{13}C-NMR: Tables 3 and 4, HR-FAB-MS (negative mode) *m/z*: 1117.5243 (Calcd for $C_{57}H_{81}O_{22}$, $[M-H]^-$: 1117.5219).

Cynaphylloside G (**8**): White amorphous powder, $[\alpha]_D^{21}$ −52.6° (MeOH, *c*=0.91), ^{1}H-NMR: Table 2, ^{13}C-NMR: Tables 3 and 4, HR-FAB-MS (negative mode) *m/z*: 1103.5058 (Calcd for $C_{56}H_{79}O_{22}$, $[M-H]^-$: 1103.5062).

Cynaphylloside H (**9**): White amorphous powder, $[\alpha]_D^{21}$ −56.1° (MeOH, *c*=0.71); ^{1}H-NMR: Table 2, ^{13}C-NMR: Tables 3 and 4, HR-FAB-MS *m/z*: 1265.5580 (Calcd for $C_{62}H_{89}O_{27}$, $[M-H]^-$: 1265.5591).

Partial Acid Hydrolysis of 6 A solution of **6** (45.0 mg) in 2.0 ml of 1,4-dioxane and 1.0 ml of 0.2 N H_2SO_4 was heated at 50 °C for 1 h. After 3.0 ml of H_2O was added the mixture was extracted with EtOAc. The EtOAc was evaporated, followed by HPLC-ODS (60% MeOH) to provide **1** (14.0 mg) and **2** (4.5 mg). The structures were confirmed by ^{1}H- and ^{13}C-NMR spectral data.

Enzymatic Hydrolysis of 7—9 Cynaphyllosides F (**7**, 30 mg), G (**8**, 30 mg) and H (**9**, 15 mg) were dissolved in 0.5 ml of MeOH. A solution of crude hesperidinase (100 mg in 20 ml of H_2O) was added. After stirring at 37 °C for 1 week, the mixtures were extracted with EtOAc. The EtOAc was

Table 3. ^{13}C-NMR Spectral Data of Aglycone Moieties of **2**—**9** in Pyridine-d_5

No.	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
1	26.0	25.9	25.9	25.9	25.9	25.9	25.9	25.9
2	26.7	26.7	26.7	26.7	26.7	26.7	26.7	26.7
3	74.1	74.1	74.0	74.0	74.0	74.0	74.0	74.0
4	36.5	36.5	36.4	36.4	36.5	36.4	36.4	36.4
5	74.2	74.2	74.2	74.2	74.2	74.1	74.2	74.1
6	154.1	154.1	154.1	154.1	154.1	154.0	154.1	154.1
7	127.0	127.0	127.0	127.0	127.0	127.0	127.0	127.0
8	201.8	201.8	201.8	201.8	201.8	201.8	201.8	201.8
9	48.0	47.9	48.0	47.9	47.9	47.9	47.9	47.9
10	45.8	45.7	45.8	45.7	45.7	45.7	45.7	45.7
11	26.3	26.2	26.2	26.3	26.2	26.2	26.2	26.2
12	71.3	71.3	71.3	71.3	71.2	71.2	71.3	71.2
13	57.5	57.5	57.5	57.4	57.4	57.4	57.4	57.4
14	215.7	215.7	215.7	215.7	215.7	215.7	215.7	215.7
15	35.3	35.2	35.3	35.2	35.3	35.2	35.2	35.2
16	20.3	20.3	20.3	20.3	20.2	20.2	20.2	20.2
17	59.2	59.2	59.2	59.2	59.2	59.2	59.2	59.2
18	17.1	17.1	17.1	17.1	17.1	17.1	17.1	17.1
19	17.8	17.8	17.8	17.8	17.8	17.8	17.8	17.8
20	207.1	207.1	207.1	207.1	207.1	207.1	207.1	207.1
21	31.1	31.1	31.1	31.1	31.1	31.1	31.1	31.1
1′	167.0	167.0	167.0	167.0	167.0	166.9	167.0	167.0
2′	118.2	118.3	118.2	118.2	118.2	118.2	118.2	118.2
3′	146.0	146.0	146.0	146.0	146.0	146.0	146.0	146.0
4′	134.8	134.8	134.8	134.7	134.7	134.7	134.7	134.7
5′,9′	128.7	128.7	128.7	128.7	128.7	128.6	128.7	128.6
6′,8′	129.3	129.3	129.3	129.3	129.3	129.3	129.3	129.3
7′	130.8	130.8	130.8	130.8	130.8	130.8	130.8	130.8

evaporated to provide **5** (23.0 mg) from **7**, **6** (21.0 mg) from **8** and **6** (8.0 mg) from **9**. The structures were confirmed by ^{1}H- and ^{13}C-NMR spectral data.

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Table 4. ^{13}C-NMR Spectral Data of Sugar Moieties of **2**—**9** in Pyridine-d_5

No.	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
	Cym	Cym	Cym	Cym	Cym	Cym	Cym	Cym
1	97.6	97.5	97.5	97.5	97.5	97.4	97.5	97.5
2	35.6	36.4	36.4[a]	36.6[a]	36.6	36.6[a]	36.7	36.6
3	78.6	77.9	77.7[b]	77.7[b]	77.8	77.7[b]	77.8	77.8
4	73.9	82.8	82.8[c]	82.8[c]	82.8	82.8[c]	82.8[a]	82.8
5	71.0	69.4	69.0[d]	69.0[d]	69.1	69.0[d]	69.1[b]	69.1
6	18.8	18.5	18.3[e]	18.3[e]	18.3[a]	18.2[e]	18.3[c]	18.2[a]
OMe	58.0	58.5	58.7[f]	58.8[f]	58.8	58.7[f]	58.8	58.8
		Glc	Cym	Cym	Dig	Cym	Dig	Dig
1		106.5	100.3	100.3	100.4	100.3	100.4	100.4
2		75.4	36.7[a]	36.9[a]	39.1	36.9[a]	39.1	39.1
3		78.4	77.9[b]	78.1[b]	67.8	78.0[b]	67.7	67.7
4		71.8	83.0[c]	83.0[c]	83.4	82.9[c]	83.4[a]	83.4[b]
5		78.4	69.3[d]	69.3[d]	68.8	69.2[d]	68.7[b]	68.7
6		63.0	18.6[e]	18.5[e]	18.5[a]	18.4[e]	18.6[c]	18.4[a]
OMe			58.8[f]	58.8[f]		58.9[f]		
			Glc	The	The	The	The	The
1			106.5	106.2	105.8	105.9	105.6	105.5
2			75.4	75.0	74.8	74.7	74.5	74.5[c]
3			78.4[g]	87.8	87.8	85.8	85.7	86.0
4			71.8	75.8	75.8	83.0	82.9[a]	83.1[b]
5			78.3[g]	72.7	72.7	71.9	71.9	71.5[d]
6			63.0	18.5[e]	18.5[a]	18.6[e]	18.5[c]	18.6[a]
OMe				60.9	60.9	60.6	60.6	60.6
						Glc	Glc	Glc
1						104.7	104.7	104.5
2						75.7	75.8	74.8[c]
3						78.5[g]	78.6[d]	76.4[e]
4						71.9	71.9	81.6
5						78.1[g]	78.2[d]	76.8[e]
6						63.0	63.0	62.4[f]
								Glc
1								104.9
2								75.3
3								78.4[g]
4								71.8[d]
5								78.2[g]
6								62.3[f]

a—*g*) Assignments may be interchanged in each vertical column.

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