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Bibenzyls and bisbibenzyls from a neotropical *Plagiochila* species ☆

Hermann Anton, Ralph Schoeneborn, Ruediger Mues*

FB 13 Botanik, Universität des Saarlandes, P.O. Box 151150, D-66041, Saarbrücken, Germany

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Abstract

Three bibenzyls and eight bisbibenzyls were isolated from a neotropical *Plagiochila* species, taxonomically related to *P. oresitropha* or *P. permista*. Besides the known 4′-hydroxy-3-methoxybibenzyl, 3,4-dihydroxy-3′-methoxybibenzyl, isoplagiochin C, D, F and riccardin C, the structures of the new compounds 3,3′-dimethoxy-4-hydroxybibenzyl, the benzoyl substituted bisbibenzyl isoplagiochin G, plagilin, isoplagilin and plagiolin, the latter three bisbibenzyls each distinct in just one different linkage of two 3,4-dihydroxy-3′-methoxybibenzyls, were established by spectroscopic techniques.

Keywords: *Plagiochila* sp; Plagiochilaceae; Hepaticae; Bibenzyls; Bisbibenzyls

1. Introduction

The liverwort genus *Plagiochila* is a rich source of terpenoids and aromatic compounds as bibenzyls and bisbibenzyls (Asakawa, 1995). The neotropic taxa are taxonomically difficult to determine, thus the correct name of the investigated species from Costa Rica is still not certain, but it belongs to the section *Permistae* Carl and shows affinities to *Plagiochila oresitropha* Spruce or *P. permista* Spruce (J. Heinrichs, personal communication). In the course of our phytochemical investigations of neotropical *Plagiochila* species, we report here, a new bibenzyl and four new bisbibenzyls from the methanolic extract of this taxon.

2. Results and discussion

Air-dried plant material was sequentially extracted with methylene chloride and 80% aqueous methanol. Different chromatographic procedures for the methanolic extract yielded three bibenzyls (**1**–**3**) and eight bisbibenzyls (**4**–**11**). The structures of all compounds were determined mainly by NMR spectroscopy, especially 2D experiments (^{1}H–^{1}H-COSY, NOESY, HMQC, HMBC).

2.1. Bibenzyls

The NMR spectral data and the EI mass spectrum ($[M]^+$, m/z 244) of **1** led to a bibenzyl with the molecular formula $C_{15}H_{16}O_3$. The mass spectral fragmentation pattern indicated a dihydroxybenzyl (m/z 123, $C_7H_7O_2^+$) and a methoxybenzyl fragment (m/z 121, $C_8H_9O^+$). The ^{1}H-NMR spectral pattern of **1** was that of 3,4-dihydroxy-3′-methoxybibenzyl, a compound recently isolated from *Plagiochila exigua* (Rycroft, Cole & Aslam, 1998) (for HMBC data see Table 1). Compound **2** gave an EI mass spectrum $[M]^+$ at m/z 258, suggesting the molecular formula $C_{16}H_{18}O_3$. The ^{1}H- and ^{13}C-NMR spectra were very similar to those of **1**, except for the resonances of an additional methoxyl group (δH 3.82, δC 55.9). The NOESY spectrum showed not only correlations between H-2 (δ 6.61) and the protons of one methoxyl group (δ 3.82), but also between H-2′ (δ 6.70) respectively, H-4′ (δ 6.73) and the protons of the second methoxyl group (δ 3.77) in-

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* Corresponding author.
E-mail address: r.mues@rz.uni-sb.de (R. Mues).

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Table 1
HMBC correlations for compounds **1**, **2**

H	Correlated carbons[a]	
	1	**2**
2	(1), (3), 4, 6, α	(1), (3), 4, 6, α
5	1, 3, (4)	1, 3, (4)
6	2, 4, α	2, 4, α
α	1, 2, 6, 1′, β	1, 2, 6, 1′, 2′, 6′, α, β
β	1, 1′, 2′, 6′, α	1, 2, 6, 1′, 2′, 6′, α, β
2′	4′, 6′, β	(3′), 4′, 6′, β
4′	2′, 6′	2′, 6′
5′	1′, 3′	1′, 3′
6′	2′, 4′,β	2′, 4′, β
3-OCH$_3$	–	3
3′-OCH$_3$	3′	3′

[a] Values in parenthesis are with lower intensities.

dicative of a new natural product 3,3′-dimethoxy-4-hydroxybibenzyl, which was confirmed by heteronuclear 2D-NMR experiments (see Table 1). Compound **3** was identified as the well known 4′-hydroxy-3-methoxybibenzyl, already isolated from several other liverworts (Asakawa, 1995).

2.2. Bisbibenzyls

The NMR spectra of compound **4** indicated a bibenzyl with the same skeleton as **1**. However, the ^{1}H-NMR spectrum possessed only two singlets for the aromatic ring substituted with two vicinal hydroxyl groups and the ^{13}C-NMR spectrum showed in addition to only six tertiary carbons, the resonance of a quaternary carbon at δ 133.8. As the $[M]^+$ peak of the EI mass spectrum was observed at m/z 486.7 ($C_{30}H_{30}O_6$) compound **4** had to be a symmetric dimer of **1**. The 5-5′-biphenyl bond was evident from long range couplings ($3J$) of H-3 (δ 6.70) to C-5 (δ 133.8) and C-7 (δ 36.7), respectively, and of H-6 (δ 6.56) to C-4 (δ 132.7) and C-5′ (δ 133.8) (see also Table 2). The 5-5′-linkage explained the NOESY correlations between H-3 as well as H-6 to the protons of the ethanobridge. We propose the name plagilin for the new compound **4**. The FAB mass spectrum ($[M+H]^+$, m/z 487) and the NMR spectral data of compound **5** indicated the same molecular formula as compound **4**, but with an asymmetrical linkage of two molecules of **1**. Correlations in the HMQC and HMBC spectra were indicative of a 5-6′-biphenyl (see Table 2). These findings were in accordance with NOESY correlations between H-6 (δ 6.65) and H-5′ (δ 6.34), as well as between H-5′ and the protons of both ethanobridges. As the C–C-linkage is the only difference to **4**, we propose the name isoplagilin for **5**. Compound **6** showed the same molecular formula as **4** and **5** (EI mass spectrum: $[M]^+$ m/z 486.5), and similar NMR spectra. Nevertheless, besides the resonances of one ethanobridge (δH 2.43 and 2.57, δC 35.3 and 39.0), characteristic for bisbibenzyls, a remarkable downfield shift was observed for the signals of the second ethanobridge (δH 3.13 and 4.19, δC 44.4 and 48.4). Detailed analysis of the HMQC and HMBC spectra

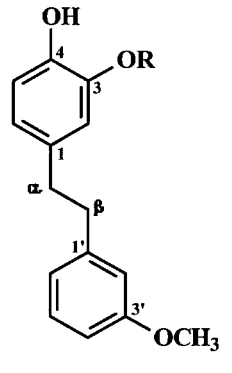
Table 2
HMBC correlations for compounds **4**, **5**, **6**

H	Correlated carbons[a]		
	4	**5**	**6**
3	1, (2), 5, 7	1, (2), 5, 7, (6)′	1 and/or 2, 5, 7
6	(1), 2, 4, 5′	(1), 2, 4, 6′	1 and/or 2, 4, 7′
7	3, 4, 5, 9, 10, 14	4, 7, 10, 14	3, 4, 5, 8, 9
8	3, 4, 5, 9, 10, 14	4, 7, 10, 14	4, 7, 9, 10, 14
10	8, 12, 14	8, (11), 12, 14	8, 12, 14
12	10, 14	10, 14	10, 14
13	9, 11	9, 11	9, 11
14	8, 10, 12	8, 10, 12	8, 10, 12
3′	1′, (2′), 5′, 7′	1′, (2′), 5′, 7′	1′, (2′), 5′, 7′
5′	–	5, 1′, 3′, 7′	1′, 3′, 7′
6′	(1′), 2′, 4′, 5	–	(1′), 2′, 4′
7′	3′, 4′, 5′, 9′, 10′, 14′	3′, 4′, 5′, 7′, 8′, 9′, 10′, 14′	4, 5, 6, 3′, 4′, 5′, 8′, 9′
8′	3′, 4′, 5′, 9′, 10′, 14′	3′, 4′, 5′, 7′, 8′, 9′, 10′, 14′	5, 4′, 7′, 9′, 10′, 14′
10′	8′, 12′, 14′	8′, 12′, 14′	8′, 12′, 14′
12′	10′, 14′	10′, 14′	10′, 14′
13′	9′, 11′	9′, 11′	9′, 11′
14′	8′, 10′, 12′	8′, 10′, 12′	8′, 10′, 12′
11-OCH$_3$	11	11	11
11′-OCH$_3$	11′	11′	11′

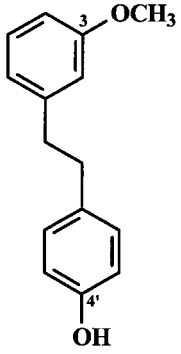
[a] Values in parenthesis are with lower intensities.

(see Table 2) resulted in a 5-7′-linkage of two molecules 3,4-dihydroxy-3′-methoxybibenzyl, which was confirmed by the NOESY correlations (Fig. 1). Although **6** is isomeric with **4** and **5**, we propose the new name plagiolin, as this is the first report of a bisbibenzyl with a C–C-linkage of a phenyl C-atom to a C-atom of the ethanobridge.

Four of eight isolated bisbibenzyls (**7**–**10**) represented known compounds. Riccardin C (**7**) was first isolated from *Reboulia hemisphaerica* (Asakawa & Matsuda, 1982). Subsequently, it has been detected in several further liverworts (Asakawa, 1995), but this is



1 R=H
2 R=CH_3



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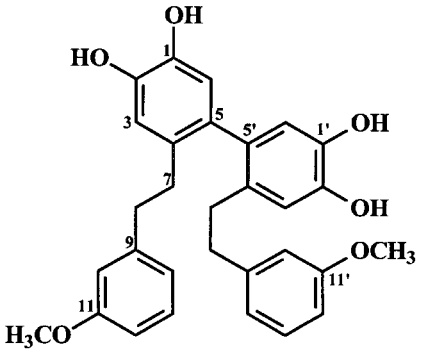

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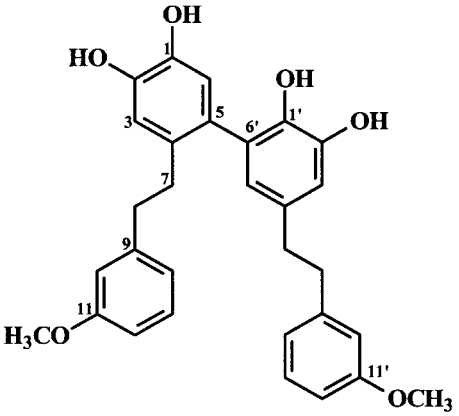

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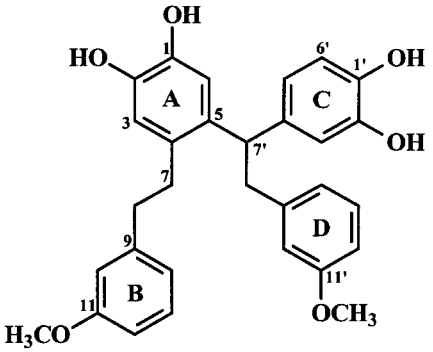

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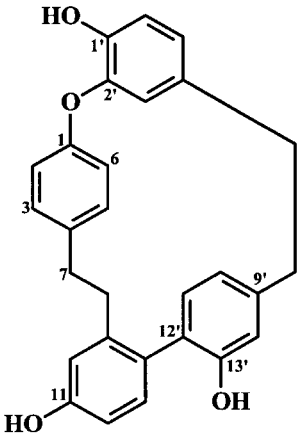

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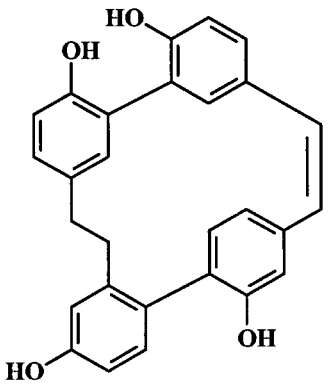

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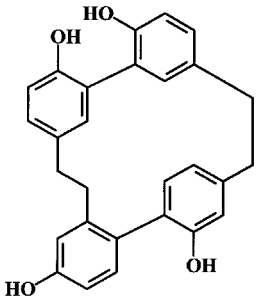

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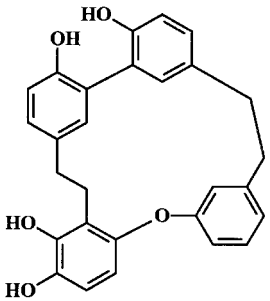

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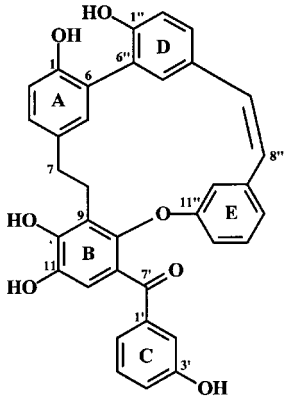

11

the first observation in a *Plagiochila* species. According to our knowledge, the ^{13}C-NMR data of **7** have not been published in detail, so they are included in Section 3. Among the bisbibenzyls presented in this paper, the main components were isoplagiochin C (**8**) and isoplagiochin D (**9**), first described from *Plagiochila fruticosa* (Hashimoto, Kanayama, Kan, Tori & Asakawa, 1996). Isoplagiochin F (**10**) has only been reported previously in another neotropical *Plagiochila* species (Anton, Kraut, Mues & Morales, 1997), which has been identified as *P. permista* Spruce var. *integerrima* Herzog (J. Heinrichs, personal communication).

Table 3
HMBC correlations for compound **11**

H	Correlated carbons[a]
2	(1), 4, 6
3	1, 5
5	1, 3, 6″
7, 8	–
12	10, (11), 14, 7′
2′	4′, 6′, 7′
4′	2′, 6′
5′	1′, 3′
6′	2′, 4′, 7′
2″	4″, 6″
3″	1″, 5″, 7″
5″	6, 1″, 3″
7″, 8″	3″, 4″, 5″, 7″, 8″, 9″, 10″
10″	8″, (11″), 12″, 14″
12″	10″, 14″
13″	9″, 11″
14″	8″, 10″, 12″

[a] Values in parenthesis are with lower intensities.

The structure of compound **11** was elucidated as a benzoyl substituted isoplagiochin type bisbibenzyl. The molecular formula was determined to be $C_{35}H_{26}O_7$ by FAB mass spectrum ([M–H]$^-$, *m*/*z* 557, 100%). The ^{1}H- and ^{13}C-NMR spectra showed the signals of two benzylic methylenes (δ_H 2.74, 4H, m, δ_C 30.1 and 35.4), a disubstituted double bond (δ_H 6.50, 2H, s, δ_C 129.3 and 131.2), 29 benzene ring carbons, including 15 aromatic protons and a keto group (δ_C 197.5). The analysis of the 2D NMR spectra including ^{1}H–^{1}H-COSY, HMQC, HMBC and NOESY (see also Table 3

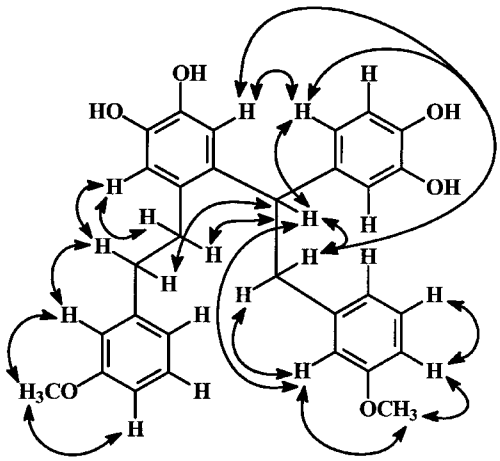

Fig. 1. Significant NOESY correlations of compound **6**.

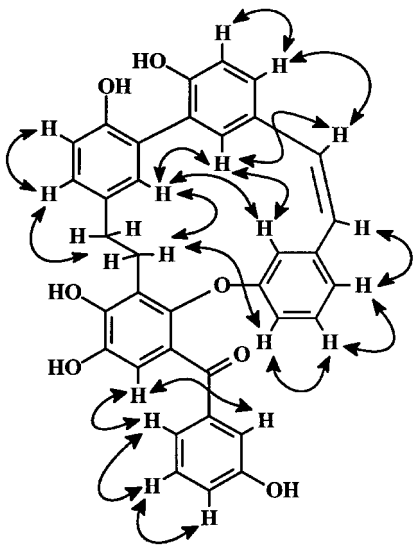

Fig. 2. NOESY correlations of compound **11**.

and Fig. 2) indicated, that one element with the rings A, D and E of **11** had the same skeleton as isoplagiochin A, being in good agreement with the chemical shifts of its published NMR data (Anton et al., 1997). The cis configuration of the olefinic bond between ring D and E was established from another ^{1}H-NMR spectrum with DMSO-d_6 as solvent, in which separate resonances for the H-7″ and H-8″ were observed as doublets (δ 6.41 and δ 6.48) with characteristic coupling constants of $J = 12$ Hz. The second unit in **11** was found to be benzophenone, from the long range couplings (^3J) from H-12 (δ 6.92), H-2′ (δ 7.02) and H-6′ (δ 7.09) to C-7′ (δ 197.5). The chemical shifts indicated that both parts of **11** were connected with an ethanobridge and an ether bond to form a cyclic bisbibenzyl of the isoplagiochin type. The 14–11″-ether bond was deduced from the NOESY correlation between H-12″ (δ 6.30) and the protons of the ethanobridge (Anton et al., 1997). The absence of a NOESY correlation between the proton of ring B (δ 6.92) to the protons of the ethanobridge and the chemical shift of the attached carbon (δ 115.1) suggested, this proton was in a meta or para position to the ethanobridge. The strong long range couplings (^3J) to C-10 (δ 145.2) and C-14 (δ 149.9) besides a weak one (^2J) to C-11 (δ 143.4) favoured the para position. The proposed structure **11** is also the more probable one, as the resulting substitution pattern of ring B is almost that of isoplagiochin F, of which, the corresponding NMR data including the ethanobridge are in good agreement. The new natural product **11** was named isoplagiochin G.

3. Experimental

3.1. General

Solvents used for spectral measurements: $CDCl_3$ with TMS as int. standard, MeOH-d_4, DMSO-d_6. ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz for 1D-spectra, 500 and 125 MHz for 2D-spectra, respectively. MeOH (UV). EI-MS (direct inlet, 70 eV), CI-MS (methane, 120 eV), FAB-MS (xenon, glycerol matrix, 5–7 kV)

3.2. Plant material

The investigated *Plagiochila* species was collected at 16th September 1994 in Costa Rica, Heredia: Parque Nacional Volcán Barva, altitude 2650–2900 m. A voucher specimen (5670) is deposited in the herbarium SAAR.

3.3. Extraction and isolation

Cleaned, air-dried and powdered gametophytic plant material (196 g) was extracted with CH_2Cl_2, followed by 80% aq. MeOH. The 80% aq. MeOH-extract was prefractionated by SPE on RP 18, using a MeOH-H_2O gradient. Fr. 3 (eluted with 70% aq. MeOH) was chromatographed on Sephadex LH-20 (70% aq. MeOH) yielding **1** (137 mg). Fr. 4 (eluted with 75% aq. MeOH) was chromatographed on Sephadex LH-20 using a MeOH-H_2O gradient (60–80% MeOH) to yield 8 frs 4.1–4.8. Further purification of fr. 4.1 by HPLC (Nucleosil 100 RP 18, 7 μm, 65% aq. MeOH) afforded **4** (3 mg), **6** (3 mg), **7** (3 mg) and **5** (5 mg). Fr. 4.2 was chromatographed by HPLC (Nucleosil 100 RP 18, 7 μm, 65% aq. MeOH) yielding 150 mg of **9**. From fr. 4.4, 44 mg of **8** were isolated by HPLC (Nucleosil 100 RP 18, 7 μm, 70% aq. MeOH). Chromatography of fr. 4.5 by HPLC (Nucleosil 100 RP 18, 7 μm, 70% aq. MeOH) separated **10** (3 mg) and **11** (3 mg). Fr. 4.8 was chromatographed by HPLC (Nucleosil 100 Si, 7 μm, *n*-hexane-EtOAc, 4 : 1) yielding **2** (9 mg) and **3** (84 mg).

Table 4
^{1}H-NMR data of compounds **1**, **2** ($CDCl_3$, TMS, 400 MHz)

H	**1**	**2**
2	6.66 *d* (1.4)	6.61 *d* (2.2)
5	6.74 *d* (7.5)	6.82 *d* (8.0)
6	6.58 *dd* (1.5/8.2)	6.67 *dd* (2.0/8.2)
α	2.76 *m*	2.84 *s*
β	2.82 *m*	2.84 *s*
2′	6.70 *br s*	6.70 *t* (2.0)
4′	6.73 *d* (9.3)	6.73 *br d* (8.0)
5′	7.17 *t* (8.0)	7.18 *t* (8.0)
6′	6.75 *d* (8.0)	6.75 *br d* (8.8)
O<u>H</u>	5.58 *br s*	5.45 *s*
3-OMe	–	3.82 *s*
3′-OMe	3.76 *s*	3.77 *s*

Table 5
^{13}C-NMR data of compounds **1**, **2** ($CDCl_3$, TMS, 100 MHz)

C	**1**	**2**
1	135.0	133.7
2	115.7	111.2[a]
3	143.4[a]	146.3
4	141.6	143.9
5	115.4	114.2
6	120.9	121.1[b]
α	36.9	37.5
β	37.9	38.3
1′	143.5[a]	143.5
2′	114.4	114.4
3′	159.5	159.7
4′	111.3	111.3[a]
5′	129.3	129.3
6′	121.1	121.0[b]
3-OMe	–	55.9
3′-OMe	55.3	55.2

[a,b] Values interchangeable within the same column.

Table 6
^{1}H- and ^{13}C-NMR data of compound **4** (MeOH-d_4, 400 and 100 MHz)

	H	C
1, 1′	–	143.9
2, 2′	–	145.2
3, 3′	6.70 *s*	117.1
4, 4′	–	132.7
5, 5′	–	133.8
6, 6′	6.56 *s*	118.6
7, 7′	2.42–2.60 *m*	36.7
8, 8′	2.42–2.60 *m*	39.0
9, 9′	–	145.2
10, 10′	6.35 *t* (1.3)	114.4
11, 11′	–	161.1
12, 12′	6.60 *dd* (2.6/8.4)	112.8
13, 13′	7.02 *t* (7.7)	130.0
14, 14′	6.51 *br d* (7.5)	121.7
11, 11′ OMe	3.64 *s*	55.6

3.4. Compound *1*

UV λ_{max} nm: 223 sh, 273 sh, 280, 290 sh. EIMS *m*/*z* (rel. int.): 244 $[M]^+$ (35), 123 (28), 121 (22), 77 (100). ^{1}H-NMR: Table 4. ^{13}C-NMR: Table 5.

3.5. Compound *2*

UV λ_{max} nm: 225 sh, 273 sh, 279, 287 sh. EIMS *m*/*z* (rel. int.): 258 $[M]^+$ (11), 137 (100), 121 (1), 107 (9). ^{1}H-NMR: Table 4. ^{13}C-NMR: Table 5.

Table 7
^{1}H-NMR data of compounds **5**, **6** (MeOH-d_4, 400 MHz)

H	**5**	**6**
3	6.81 *s*	6.47 *s*
6	6.65 *s*	6.88 *s*
7	2.62 *s*	2.57 *m*
8	2.62 *s*	2.43 *m*
10	6.42 *br s*	6.51 *m*
12	6.66 *dd* (2.2/8.4)	6.68 *dd* (2.7/8.4)
13	7.08 *t* (7.7)	7.10 *t* (8.0)
14	6.49 *d* (7.5)	6.60–6.62 *m*
3′	6.75 *s*	6.60–6.62 *m*
5′	6.34 *d* (1.3)	6.45 *dd* (2.0/8.2)
6′	–	6.60–6.62 *m*
7′	2.83 *m*	4.19 *t* (7.6)
8′	2.83 *m*	3.13 *m*
10′	6.69 *s*	6.51 *m*
12′	6.70 *d*[a]	6.63 *dd*[a]
13′	7.14 *t* 8.0 Hz	7.04 *t* 8.0 Hz
14′	6.74 *d*[a]	6.60–6.62 *m*
11-OMe	3.69 *s*	3.70 *s*
11′-OMe	3.75 *s*	3.61 *s*

[a] Coupling constants not determinable.

Table 8
^{13}C-NMR data of compounds **5**, **6** (MeOH-d_4, 100 MHz)

C	**5**	**6**
1	141.9	144.1[a]
2	143.9	144.2[a]
3	116.7	117.8
4	133.8	132.7
5	127.7	135.0
6	117.4	116.1
7	34.5	35.3
8	37.6	39.0
9	143.1	145.0
10	114.0	114.9
11	159.6	161.1
12	111.5	112.5
13	129.2	130.1
14	120.8	121.8
1′	138.2	144.2[a]
2′	143.9	146.0
3′	114.5	116.6
4′	134.2	138.5
5′	121.9	120.6
6′	127.0	116.1
7′	37.1	48.4
8′	38.0	44.4
9′	143.4	143.8
10′	114.4	115.8
11′	159.6	160.8
12′	111.3	112.6
13′	129.3	129.9
14′	121.0	122.8
11-OMe	55.1	55.6
11′-OMe	55.2	55.5

[a] Values interchangeable.

3.6. Compound *4*

UV λ_{max} nm: 273 sh, 281, 296 sh. EIMS *m*/*z* (rel. int.): 486.7 $[M]^+$ (42), 424.6 (18), 365.5 (16), 255.4 (16), 243.4 (52), 242.4 (69), 123.3 (100). CIMS *m*/*z* (rel. int.): 424.5 (100), 279.4 (39), 254.3 (61), 243.3 (15), 242.3 (69), 149.2 (95), 123.2 (38). ^{1}H-NMR and ^{13}C-NMR: Table 6.

3.7. Compound *5*

UV λ_{max} nm: 274 sh, 280, 292 sh. FABMS *m*/*z*: 487 $[M+H]^+$, 365, 363, 243. CIMS *m*/*z* (rel. int.): 486.6 $[M]^+$ (2), 424.5 (60), 307.5 (25), 279.4 (38), 244.3 (25), 242.3 (37), 149.2 (100). ^{1}H-NMR: Table 7. ^{13}C-NMR: Table 8.

3.8. Compound *6*

UV λ_{max} nm: 274 sh, 281, 293 sh. EIMS *m*/*z* (rel. int.): 486.5 $[M]^+$ (9), 424.5 (31), 376.5 (22), 255.3 (33), 242.3 (51), 123.2 (100). CIMS *m*/*z* (rel. int.): 375.8 (12), 242.9 (16), 241.9 (100), 123.0 (28). ^{1}H-NMR: Table 7. ^{13}C-NMR: Table 8.

Table 9
^{1}H- and ^{13}C-NMR data of compound **11** (MeOH-d_4, 400 and 100 MHz)

	H	C
1	–	152.4
2	6.75 *d* (8.4)	117.0[a]
3	7.02 *dd* (2.4/8.2)	129.1
4	–	137.0
5	6.47 *d* (2.2)	134.2
6	–	128.0
7	2.74 *m*	35.4
8	2.74 *m*	30.1
9	–	125.0[b]
10	–	145.2
11	–	143.4
12	6.92 *s*	115.1
13	–	125.2[b]
14	–	149.9
1′	–	141.3
2′	7.02 *d* (1.8)	117.0[a]
3′	–	158.4
4′	6.94 *dd* (2.2/8.4)	120.7
5′	7.19 *t* (8.0)	130.1
6′	7.09 *d* (8.0)	122.1
7′	–	197.5
1″	–	154.1
2″	6.85 *d* (8.4)	117.7
3″	7.11 *dd* (2.2/8.4)	131.6
4″	–	130.5[c]
5″	7.25 *d* (2.2)	133.5
6″	–	127.4
7″	6.50 *s*	131.2
8″	6.50 *s*	129.3
9″	–	142.3
10″	6.86 *br s*	116.9[a]
11″	–	160.8
12″	6.30 *dd* (2.2/8.4)	112.3
13″	7.08 *t* (8.0)	130.6[c]
14″	6.63 *br d* (7.5)	123.4

[a–c] Values interchangeable.

3.9. Compound 7

UV λ_{max} nm: 250 sh, 284. CIMS *m*/*z* (rel. int.): 424.9 $[M+H]^+$ (25), 423.9 $[M]^+$ (100), 213.0 (25), 212.1 (21), 211.0 (69), 199.1 (7), 177.0 (11), 175.0 (15). ^{13}C-NMR (assignment confirmed by HMQC and HMBC): 35.0 (C-8), 37.0 (C-7′), 37.7 (C-8′), 38.1 (C-7), 114.3 (C-12), 114.9 (C-6′), 116.1 (C-3′, C-14′), 117.5 (C-10), 121.7 (C-10′), 122.2 (C-5′), 122.4 (C-2, C-6), 124.4 (C-12′), 128.3 (C-14), 129.3 (C-3, C-5), 131.4 (C-11′), 132.9 (C-13), 133.1 (C-4′), 139.8 (C-4), 142.0 (C-9′), 143.4 (C-1′), 143.8 (C-9), 146.3 (C-2′), 151.9 (C-13′), 152.7 (C-1), 155.9 (C-11).

3.10. Compound 11

UV λ_{max} nm: 255 sh, 294. FABMS *m*/*z* 557 $[M-H]^-$. CIMS *m*/*z* (rel. int.): 500.7 (11), 334.8 (30), 284.8 (19), 171.1 (56), 149.0 (36). ^{1}H-NMR and ^{13}C-NMR: Table 9.

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