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BIFLAVONOIDS FROM *DAPHNE ODORA**

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Key Word Index— *Daphne odora*; Thymelaeaceae; roots; biflavonoids; daphnodorins E and F.

Abstract—Two new biflavonoids, daphnodorins E and F, were isolated from the roots of *Daphne odora* and their structures established from spectral and chemical evidence.

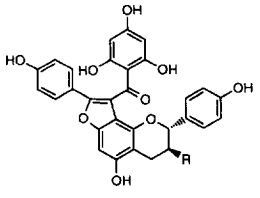
INTRODUCTION

In previous papers [2–5], we reported the isolation of two new furanobiflavonoids, daphnodorins A and B, a new spirobiflavonoide, daphnodorin C, and two C-8/C-3″ biflavonoid, atropisomers, daphnodorin D_1 and D_2, together with four known coumarins, daphnetin, daphnoretin, umbelliferone and daphneticin, from the roots of *Daphne odora*. In the present work, we have isolated two new biflavonoids, daphnodorins E and F (**1** and **2**). This paper deals with their isolation and structural elucidation.

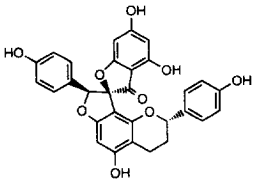
RESULTS AND DISCUSSION

Crushed dried roots of *D. odora* were extracted with ethyl acetate, the combined extracts concentrated and the residue was subjected to repeated chromatographic purification to give the two new biflavonoids, daphnodorins E and F (**1** and **2**).

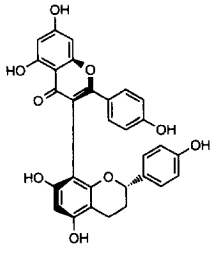
Compound **1** was isolated as a pale yellow amorphous powder and assigned the molecular formula $C_{30}H_{22}O_{10}$ by FD-mass spectrometry (*m/z* 542 $[M]^+$). The UV spectrum showed absorption maxima at 221, 254, 291 and 311 nm. The IR spectrum showed absorption bands at 3433, 2930, 1640 and 1517 cm^{-1}, suggesting the presence of hydroxyl and carbonyl groups and an aromatic ring. The ^1H NMR spectrum (Table 1) showed signals assignable to two pairs of 4-oxyphenyl groups [δ7.34 (2H, *d*, *J* = 8.8 Hz), 6.80 (2H, *d*, *J* = 8.8 Hz) and 7.13 (2H, *d*, *J* = 8.8 Hz), 6.78 (2H, *d*, *J* = 8.8 Hz)], a 2,4,6-trioxyphenyl group [δ6.03 (1H, *d*, *J* = 2.1 Hz), 5.93 (1H, *d*, *J* = 2.1 Hz)], an alcoholic hydroxyl group [δ5.29 (1H, *s*)] and five phenolic hydroxyl groups [δ11.61, 9.85, 8.87, 8.61 and 8.29 (each 1H, *s*)]. Furthermore, the signals owing to the protons at the C-6 (or C-8), C-2, C-3 and C-4 positions of a 2,8 (or 2,6)-disubstituted 5,7-dioxy-3,4-dihydrobenzopyrane ring were observed at δ6.24 (1H, *s*),



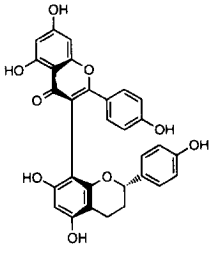
daphnodorin A: R=H
daphnodorin B: R=OH



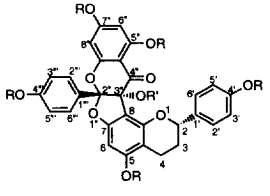
daphnodorin C



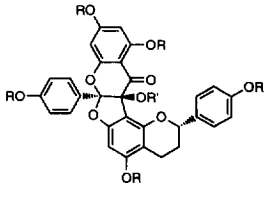
daphnodorin D_1



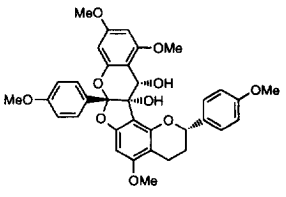
daphnodorin D_2



daphnodorin E (**1**): R=R'=H
3: R=R'=Ac
4: R=Me, R'=H
5: R=R'=Me



daphnodorin F (**2**): R=R'=H
8: R=R'=Ac
9: R=Me, R'=H
10: R=R'=Me



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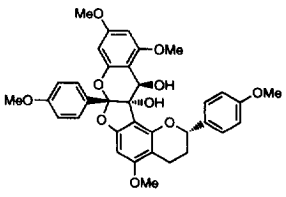

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*Part 12 in the series 'Chemical Studies on the Constituent of Thymelaeaceous Plants'. For part 11 see ref. [1].

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Table 1. ^{1}H NMR spectral data for **1** and **3**–**5** in $CDCl_3$, TMS. (Values in parentheses are coupling constants in Hz)

H	**1** (acetone-d_6)	**3**	**4**	**5**
2	4.95 *dd*(10.1, 1.9)	5.18 *br d*(9.6)	5.08 *dd*(8.5, 2.2)	5.13 *dd*(7.7, 2.2)
3	2.13 *m*	1.83 *m*	2.13 *m*	2.19 *m*
	1.73 *m*		1.84 *m*	1.89 *m*
4	2.61 *m*	2.64 *m*	2.54 *m*	2.59 *m*
				2.44 *m*
6	6.24 *s*	6.30 *s*	6.29 *s*	6.34 *s*
2′, 6′	7.13 *d*(8.8)	7.57 *d*(8.8)	7.18 *d*(8.8)	7.14 *d*(8.8)
3′, 5′	6.78 *d*(8.8)	7.06 *d*(8.8)	6.83 *d*(8.8)	6.81 *d*(8.8)
6″	6.03 *d*(2.1)[a]	6.99 *d*(2.2)[a]	6.12 *d*(2.2)[a]	6.01 *d*(2.2)
8″	5.93 *d*(2.1)[a]	6.69 *d*(2.2)[a]	6.07 *d*(2.2)[a]	6.03 *d*(2.2)
2‴, 6‴	7.34 *d*(8.8)	7.67 *d*(8.8)	7.46 *d*(8.8)	7.51 *d*(8.8)
3‴, 5‴	6.80 *d*(8.8)	7.13 *d*(8.8)	6.88 *d*(8.8)	6.88 *d*(8.8)
	11.61 *s*	2.31 *s*	–OH 4.90 *br s*	3.82 *s*
	9.85 *s*	2.30 *s*	3.80 *s* × 2	3.80 *s* × 2
–OH	8.87 *s*	–OCOMe 2.28 *s* × 2	–OMe 3.79 *s*	–OMe 3.75 *s*
	8.61 *s*	2.09 *s*	3.77 *s*	3.65 *s*
	8.29 *s*	1.55 *s*		3.26 *s*
	5.29 *s*			

Assignments are based on ^{13}C–^{1}H COSY, spin decoupling, long range ^{13}C–^{1}H COSY and HMBC measurements.
[a]Assignments may be reversed in each column.

4.95 (1H, *dd*, J = 10.1, 1.9 Hz), 2.13 (1H, *m*), 1.73 (1H, *m*) and 2.61 (2H, *m*). In the ^{13}C NMR spectrum (Table 2), a carbonyl carbon signal (δ194.6) and a quaternary carbon signal attached to an oxygen atom (δ82.4) were observed, in addition to the signals described above. Upon acetylation with acetic anhydride and pyridine, **1** formed a hexaacetate (**3**), $C_{42}H_{34}O_{16}$. In the ^{1}H NMR spectrum of **3** (Table 1), one of the six acetyl signals was shifted to a higher field at δ1.55. Methylation of **1** with diazomethane afforded a pentamethyl ether (**4**), $C_{35}H_{32}O_{10}$, and subsequent reaction with methyl iodide gave a hexamethyl ether (**5**), $C_{36}H_{34}O_{10}$. Reduction of **4** with sodium borohydride in ethanol and tetrahydrofuran gave two alcohols, **6** and **7** ($C_{35}H_{34}O_{10}$). In the ^{1}H NMR spectrum of **6** (Table 3), a newly formed benzylmethine proton signal at δ5.10 was coupled only with a signal assignable to a hydroxyl group, resulting from the reduction of carbonyl group, by 11 Hz. Furthermore, the ^{13}C NMR of **6** (Table 3) showed the presence of a sp^3 carbon attached to an oxygen atom and the lack of a carbonyl carbon. The NMR profile of the other alcohol **7** (Table 3) coincided with that of **6**. There was also a signal assignable to a benzyl methine proton (δ5.22) coupled by 9.4 Hz with a hydroxy group. From the above results, the structure of **1** was established as shown. This structure was further supported by the HMBC spectra of **3** and **7** and the HR-mass spectrum of **4**

Compound **2** was isolated as a pale yellow amorphous powder and assigned the molecular formula $C_{30}H_{22}O_{10}$, the same as **1**, by FD-mass spectrometry (*m/z* 542 $[M]^+$). The UV spectrum of **2** showed absorption maxima at 219.5, 230.0, 253.5, 290.5 and 313.0 nm. The IR spectrum showed absorption bands at 3427, 2930, 1655, 1620 and 1517 cm^{-1}, indicating the presence of hydroxyl and, carbonyl groups and an aromatic ring. The ^{1}H NMR spectrum of **2** (Table 4) showed signals owing to two pairs of 4-oxyphenyl groups [δ7.30 (2H, *d*, J = 8.8 Hz), 6.84 (2H, *d*, J = 8.8 Hz) and 7.35 (2H, *d*, J = 8.8 Hz), 6.80 (2H, *d*, J = 8.8 Hz)], a 2,4,6-trioxyphenyl group [δ5.95 (1H, *d*, J = 2.2 Hz), 5.92 (1H, *d*, J = 2.2 Hz)], a 2,8 (or 2,6)-disubstituted-5,7-dioxy-3,4-dihydrobenzopyrane ring [δ6.27 (1H, *s*), 4.84 (1H, *br d*, J = 8.4 Hz), 2.26 (1H, *m*), 1.89 (1H, *m*) and 2.65 (2H, *m*)] as well as an alcoholic hydroxyl group [δ5.35 (1H, *s*)] and five phenolic hydroxyl groups [δ11.51 (1H, *s*), 10.07 (1H, *s*), 9.06 (1H, *s*), 8.76 (1H, *s*) and 8.47 (1H, *s*)]. These signals were closely related to those of **1**. On the other hand, the ^{13}C NMR spectrum of **2** (Table 5) was very similar to that of **1**. Furthermore, the NMR profile of the hexaacetate (**8**), pentamethyl ether (**9**) and hexamethyl ether (**10**) (Tables 4 and 5) were also similar to those of **3**–**5**. Thus, **2** was assumed to be a stereoisomer of **1**. The CD spectroscopic studies of the flavans including *d*-catechin and *l*-epicatechin have indicated that the Cotton effect ascribed to the A-chromophore in the range of 250–300 nm is available for the determination of the absolute configuration at C-2 [6]. However, it may not be appropriate to compare the CD spectra of **5** and **10** with those of simple flavans, because **5** and **10** contain two 4-hydroxyphenyl groups which are non-coplanar to each other, and these CD spectra showed strong Davydou splitting of the Cotton effect, [**5**: negative first Cotton (295 nm), positive second Cotton (280 nm), **10**: positive first Cotton (294 nm), negative second Cotton (278 nm), in the neighbourhood of the absorption band of the A-chromophore. It seems reasonable to assume that the absolute configurations at C-2 of **1** and **2** are *S*, similar to those of flavans isolated previously. The relative configurations between C-2″ and C-3″ of both **1** and **2** were concluded to be *trans* by the NOESY spectra of **5** and **10** (data not shown).

Table 2. ^{13}C NMR spectral data for **1** and **3**–**5** (δ in $CDCl_3$, TMS)

C	**1** (acetone-d_6)	**3**	**4**	**5**
2	78.0	77.2	76.8	76.6
3	30.4	29.6	29.4	28.9
4	20.1	20.4	18.8	18.3
4a	105.2	110.3	105.7	105.1
5	154.3[a]	152.7	160.9	160.9[a]
6	92.1	96.9	87.7	88.0
7	158.1[a]	160.0	160.5	161.1[a]
8	108.3	104.7	108.5	104.8
8a	159.7[a]	155.4	152.7	154.0
1′	133.8	139.3	134.2	133.9
2′, 6′	127.9	126.8	126.9	126.9
3′, 5′	116.2	122.0	114.0	113.8[b]
4′	159.9[a]	150.4	159.2	159.1
2″	118.7	116.9	117.6	117.8
3″	82.4	88.7	82.8	87.5
4″	194.6	179.2	188.8	188.2
4″a	100.1	113.8	102.8	104.5
5″	161.2[a]	151.9[a]	162.1	161.9
6″	95.8[b]	110.9[b]	93.7[b]	93.3[c]
7″	163.4[a]	156.3	166.9[a]	165.8
8″	97.5[b]	112.9[b]	93.9[b]	93.8[c]
8″a	165.5[a]	158.7[a]	164.0	163.0
1‴	126.4	133.5	127.3	127.8
2‴, 6‴	129.8	128.9	128.6	128.6
3‴, 5‴	115.8	121.3	113.9	114.0[b]
4‴	168.4[a]	152.2	161.0	161.1[a]
		170.4	56.4	56.2
		170.2	56.1	56.0
		–OCOMe 169.70	–OMe 56.0	–OMe 55.8
		169.0	55.6 × 2	55.5 × 2
		168.7	54.5	
		168.4		
		21.4		
		21.3		
		–OCOMe 21.3		
		21.0 × 2		
		19.9		

Assignments are based on ^{13}C–^{1}H COSY, long range ^{13}C–^{1}H COSY and HMBC measurements.
[a–c]Assignments with the same superscript may be reversed in each column.

The absolute configurations of C-2″ and C-3″ of **1** and **2** have been determined to be 2″*R*, 3″*R* and 2″*S*, 3″*S*, respectively, by application of the dibenzoate rule to the splitting of the Cotton effects described above. Furthermore, comparison of the ^{1}H NMR data of the two alcohols, **6** and **7** (Table 3), reveals shielding of a benzyl methine proton by the 4-oxyphenyl group in **6** relative to the chemical shift of that in **7**, indicating that the relative configuration between C-3″ and C-4″ of **6** is *cis* and that of **7** *trans*.

EXPERIMENTAL

General. EI-MS: 70 eV. FD-MS: 19 mA. ^{1}H and ^{13}C NMR: 300 and 75 MHz with TMS as int. standard. CC: Merck silica gel 60 (70–230 mesh) and Sephadex LH-20. TLC: Merck silica gel 60 F_{254} (0.25 mm) and Whatman silica gel 150A PLK5F (1 mm). Spots and bands were detected by UV irradiation (254 and 365 nm).

Plant material. Plants of *D. odora* Thumb. were cultivated and collected in the botanical garden of the Osaka University of Pharmaceutical Sciences in January 1992. A voucher specimen is deposited in this university.

Extraction and isolation. Air-dried roots (4.5 kg) were chopped into small pieces and extracted with EtOAc (20 l × 5) under reflux. The combined MeOH extracts were concd to dryness *in vacuo*. The residue (825 g) was subjected to CC on silica gel eluting successively with hexane–EtOAc solvent system of increasing polarity. The 30% MeOH eluates were rechromatographed on Sephadex LH-20 with MeOH to give daphnodorin E (**1**) (4.6 g) and daphnodorin F (**2**) (5.0 g).

Daphnodorin E (**1**). Pale yellow amorphous powder, $C_{30}H_{22}H_{10}$. FD-MS *m/z* 542 $[M]^+$. UV $\lambda_{max}^{dioxane}$ nm

Table 3. NMR spectral data for **6** and **7**. (Values in parentheses are coupling constants in Hz, δ in $CDCl_3$, TMS)

	6		**7**	
	H	C	H	C
2	4.99 *dd*(10.0, 2.0)	78.7	5.13 *dd*(8.8, 2.3)	77.1
3	2.15 *m*	29.0	2.15 *m*	28.2
	1.96 *m*		1.93 *m*	
4	2.63 *m*	19.7	2.59 *m*	18.6
4a		104.7		106.7
5		158.7[a]		157.8
6	6.15 *s*	87.2	6.27 *s*	94.5
7		160.1		152.4
8		106.6		107.6
8a		151.9		153.4
1′		133.3		134.1
2′, 6′	7.32 *d*(8.7)	127.9	7.19 *d*(8.4)	127.5
3′, 5′	6.94 *d*(8.7)	114.5	6.86 *d*(8.4)	114.2
4′		160.3[a]		159.7
2″		116.1		116.7
3″		87.0		87.6
4″	5.10 *d*(11.0)	71.3	5.22 *d*(9.4)	71.9
4″a		108.7		107.4
5″		160.4[a]		157.2[a]
6″	6.28 *d*(2.6)	95.3	6.00 *d*(2.3)	93.1
7″		160.8		163.5[a]
8″	6.16 *d*(2.6)	96.5	6.14 *d*(2.3)	88.7
8″a		155.1		162.6
1‴		127.4		129.1
2‴, 6‴	7.57 *d*(9.0)	129.0	7.56 *d*(8.4)	128.7
3‴, 5‴	6.93 *d*(9.0)	113.6	6.94 *d*(8.4)	113.7
4‴		160.8[a]		160.7
–OH	3.94 *d*(11.0)	56.2	–OH 3.93 *d*(9.4)	–OMe 55.8 × 2
	3.49 *br s*	55.9	3.34 *br s*	55.6 × 2
	3.84 *s*	–OMe 55.7	3.82 *s*	55.5
	3.83 *s*	55.6	3.81 *s*	
–OMe	3.79 *s*	55.5	–OMe 3.74 *s*	
	3.74 *s*		3.62 *s*	
	3.72 *s*			

Assignments are based on ^{13}C–^{1}H COSY, spin decoupling, long range ^{13}C–^{1}H COSY and HMBC measurements.
[a]Assignments may be reversed in each column.

(log ε): 221.0 (4.73), 254.0 (3.79), 291.0 (4.22), 311.0 (4.01). IR ν_{max}^{KBr} cm^{-1}: 3433, 2930, 1640, 1517. ORD (dioxane; *c*0.76) $[\alpha]^{18}$ (nm): + 36.8° (589), + 55.3° (550), + 76.3° (500), + 126.3°, + 223.7° (410). CD (dioxane; *c*3.69 × 10^{-5}) $\Delta\varepsilon^{18}$ (nm): 0 (365), − 1.31 (344), 0 (335), + 8.54 (312), + 1.64 (294), + 3.61 (285), 0 (275), − 3.94 (263), − 1.97 (245). ^{1}H and ^{13}C NMR in Tables 1 and 2.

Acetate of compound **1** (**3**). Pale yellow viscous oil. HR-MS *m/z* 794.1850 $[M]^+$ (calcd for $C_{42}H_{34}O_{16}$, 794.1844). UV $\lambda_{max}^{dioxane}$ nm (log ε): 220.5 (4.78), 260.0 (4.20), 300.0 (3.79). CD (dioxane; *c*3.78 × 10^{-5}) $\Delta\varepsilon^{18}$ (nm): 0 (390), + 4.01 (328), 0 (310), − 3.53 (292), − 3.21 (288), − 6.42 (271), − 4.01 (258), − 7.06 (241), 0 (230). ^{1}H and ^{13}C NMR in Tables 1 and 2.

Pentamethyl ether of compound **1** (**4**). Pale yellow viscous oil. HR-MS *m/z* 612.1974 $[M]^+$ (calcd for $C_{35}H_{32}O_{10}$, 612.1993). UV $\lambda_{max}^{dioxane}$ nm (log ε): 214.0 (4.88), 229.0 (4.79), 283.0 (4.28). IR ν_{max}^{KBr} cm^{-1}: 3424, 2938, 1686, 1612, 1578, 1516. ORD (dioxane; *c*0.50) $[\alpha]^{18}$ (nm): 0° (408), + 8.0° (400), + 20.0° (375), + 24.0° (370), + 72.0° (350). CD (dioxane; *c*3.72 × 10^{-5}) $\Delta\varepsilon^{18}$ (nm): 0 (354), + 0.74 (323), 0 (313), − 4.09 (296), 0 (285), + 0.84 (277), 0 (263). ^{1}H and ^{13}C NMR in Tables 1 and 2.

Hexamethyl ether of compound **1** (**5**). Pale yellow viscous oil. HR-MS *m/z* 626.2148 $[M]^+$ (calcd for $C_{36}H_{34}O_{10}$, 626.2149), 447.1798 ($C_{27}H_{27}O_6$, 447.1805), 312.0990 ($C_{18}H_{16}O_5$, 312.0996), 180.0425 ($C_9H_8O_4$, 180.0422), 134.0715 ($C_9H_{10}O$, 134.0730). UV $\lambda_{max}^{dioxane}$ nm (log ε): 237.0 (4.37), 282.0 (4.12). CD (dioxane; *c*3.51 × 10^{-5}) $\Delta\varepsilon^{18}$ (nm): 0 (333), + 1.21 (317), 0 (306), − 3.28 (295), 0 (288), + 5.35 (280), 0 (258). ^{1}H and ^{13}C NMR in Tables 1 and 2.

Reduction of compound **4**. A mixt. of **4** (120 mg) in THF (10 ml) and $NaBH_4$ (200 mg) in EtOH (10 ml) was stirred and allowed to stand at room temp. overnight. The reaction mixt. was diluted with H_2O (50 ml), acidified with

2 M HCl and then extracted with Et_2O. The Et_2O soln was dried and concd *in vacuo*. The residue was purified by prep. TLC with hexane–EtOAc (2:1) to give **6** (20 mg) and **7** (55 mg).

Compound **6**. Viscous oil. FD-MS *m/z* 614 $[M]^+$. UV $\lambda_{max}^{dioxane}$ nm (log ε): 202.0 (4.13), 214.0 (4.77), 278.5 (3.98). CD (dioxane; $c3.26 \times 10^{-5}$) $\Delta\varepsilon^{18}$ (nm): 0 (326), + 0.37 (318), 0 (310), − 2.05 (287), 0 (267). ^1H and ^{13}C NMR in Table 3.

Compound **7**. Amorphous powder. FD-MS *m/z* 614 $[M]^+$. UV $\lambda_{max}^{dioxane}$ nm (log ε): 219.0 (4.91), 274.0 (3.95), 283.0 (3.86). CD (dioxane; $c3.26 \times 10^{-5}$) $\Delta\varepsilon^{18}$ (nm): 0 (320), + 0.37 (296), 0 (288), − 2.14 (270), 0 (260). ^1H and ^{13}C NMR in Table 3.

Daphnodorin F (**2**). Pale yellow amorphous powder, $C_{30}H_{22}O_{10}$. FD-MS *m/z* 542 $[M]^+$. UV $\lambda_{max}^{dioxane}$ nm (log ε): 219.5 (4.70), 230.0 (4.64), 253.5 (3.74), 290.5 (4.15), 313.0 (392). IR ν_{max}^{KBr} cm^{-1}: 3427, 2930, 1655, 1620, 1517. ORD (dioxane; *c*0.60) $[\alpha]^{18}$ (nm): − 120.0° (589), − 150.0° (550), − 206.7° (500), − 300.0° (450), − 500.0° (400), − 646.7° (380). CD (dioxane; $c4.06 \times 10^{-5}$) $\Delta\varepsilon^{18}$ (nm): 0 (372), + 0.90 (345), 0 (337), − 9.41 (314), 0 (297),

Table 4. ^1H NMR spectral data for **2** and **8**–**10**. (Values in parentheses are coupling constants in Hz, δ in $CDCl_3$, TMS)

H	**2** (acetone-d_6)	**8**	**9**	**10**
2	4.84 *br d*(8.4)	5.05 *dd* (10.0, 1.3)	4.83 *br d*(9.6)	4.74 *br d*(9.2)
3	2.26 *m*	1.82 *m*	2.23 *m*	2.36 *m*
	1.89 *m*		1.94 *m*	1.85 *m*
4	2.65 *m*	2.64 *m*	2.59 *m*	2.75 *m*
				2.61 *m*
6	6.27 *s*	6.33 *s*	6.29 *s*	6.32 *s*
2′, 6′	7.30 *d*(8.8)	7.59 *d*(8.7)	7.33 *d*(8.5)	7.39 *d*(8.8)
3′, 5′	6.84 *d*(8.8)	7.10 *d*(8.7)	6.92 *d*(8.5)	6.96 *d*(8.8)
6″	5.95 *d*(2.2)[a]	6.96 *d*(2.2)[a]	6.02 *d*(2.2)[a]	5.99 *d*(2.2)
8″	5.92 *d*(2.2)[a]	6.65 *d*(2.2)[a]	6.10 *d*(2.2)[a]	6.95 *d*(2.2)
2‴, 6‴	7.35 *d*(8.8)	7.56 *d*(8.8)	7.45 *d*(8.5)	7.51 *d*(8.8)
3‴, 5‴	6.80 *d*(8.8)	7.07 *d*(8.8)	6.89 *d*(8.5)	6.88 *d*(8.8)
−OH	11.51 *s*	−OCOMe 2.30 *s* × 2	−OH 4.90 *br s*	−OMe 3.83 *s* × 2
	10.07 *s*	2.29 *s* × 2	−OMe 3.80 *s* × 3	3.80 *s*
	9.06 *s*	2.03 *s*	3.76 *s*	3.71 *s*
	8.76 *s*	1.64 *s*	3.63 *s*	3.44 *s*
	8.47 *s*			3.30 *s*
	5.35 *s*			

Assignments are based on ^{13}C–^1H COSY, spin decoupling, long range ^{13}C–^1H COSY and HMBC measurements.
[a] Assignments may be reversed in each column.

Table 5. ^{13}C NMR spectral data for **2** and **8**–**10** (δ in $CDCl_3$, TMS)

C	**2** (acetone-d_6)	**8**	**9**	**10**
2	77.9	76.6	76.8	77.1
3	29.3	28.3	28.3	29.2
4	20.4	20.1	19.5	20.1
4a	105.6	109.9	105.9	105.1
5	154.4[a]	152.9	160.9[a]	161.1
6	92.2	97.1	87.7	88.1
7	158.2[a]	160.1	160.3	170.0
8	108.5	104.6	109.0	105.8
8a	159.7[a]	155.6	152.8	154.3
1′	133.2	138.9	133.5	133.6
2′, 6′	128.4	127.0	127.3	127.2
3′, 5′	116.2	121.9	113.9	114.0
4′	159.9[a]	150.5	159.4	159.3
2″	118.9	116.8	117.7	118.0
3″	82.2	88.9	82.7	87.7
4″	194.4	178.6	188.8	188.4
4″a	100.1	113.6	103.1	105.2

Table 5. *Continued*

C	**2** (acetone-d_6)	**8**	**9**	**10**
5″	161.1[a]	151.7[a]	161.9[b]	161.4
6″	95.8[b]	110.8[b]	93.7	93.7
7″	163.3[a]	156.3	166.7[b]	165.4
8″	97.5[b]	112.7[b]	93.8	93.4
8″a	165.4[a]	158.7[a]	163.7	162.6
1‴	126.4	133.5	127.4	128.0
2‴, 6‴	129.8	129.1	128.6	128.6
3‴, 5‴	115.9	121.3	114.0	113.8
4‴	168.4[a]	152.1	161.0[a]	160.9
		–OCOMe: 170.2, 170.0, 169.8, 169.1, 168.8, 168.5	–OMe: 56.3, 56.1, 55.9, 55.6 × 2	–OMe: 56.1, 56.0, 55.7, 55.6 × 2, 54.6
		–OCOMe: 21.4 × 3, 21.1, 21.0, 20.0		

Assignments are based on ^{13}C–^{1}H COSY, long range ^{13}C–^{1}H COSY and HMBC measurements.

[a, b] Assignments with the same superscript may be reversed in each column.

+ 0.75 (294), 0 (292), − 1.94 (284), 0 (276), + 4.18 (260), 0 (248), − 2.99 (241), 0 (238). ^{1}H and ^{13}C NMR in Tables 4 and 5.

Acetate of compound **2** (**8**). Pale yellow viscous oil. HR-MS *m/z* 794.1828 $[M]^+$ (calcd for $C_{42}H_{34}O_{16}$, 794.1844). UV $\lambda_{max}^{dioxane}$ nm (log ε): 218.0 (4.71), 262.0 (4.14), 298.0 (3.82). CD (dioxane; $c3.78 \times 10^{-5}$) $\Delta\varepsilon^{18}$ (nm): 0 (386), − 3.69 (328), 0 (310), + 2.73 (294), + 2.25 (281), + 4.81 (272), 0 (259), − 1.60 (254), 0 (248), + 2.41 (240), 0 (235). ^{1}H and ^{13}C NMR in Tables 4 and 5.

Pentamethyl ether of compound **2** (**9**). Pale yellow viscous oil. HR-MS *m/z* 616.2014 $[M]^+$ (calcd for $C_{35}H_{32}O_{10}$, 612.1993). UV $\lambda_{max}^{dioxane}$ nm (log ε): 213.5 (3.76), 227.0 (3.69), 282.5 (3.14), 290.0 (3.11). IR ν_{max}^{KBr} cm^{-1}: 3422, 2938, 1687, 1612, 1578, 1516. ORD (dioxane; *c*0.50) $[\alpha]^{18}$ (nm): − 64.0° (589), − 72.0° (550), − 96.0° (500), − 140.0° (450), − 228.0° (400), − 388.0° (370), − 736.0° (350). CD (dioxane; $c = 3.27 \times 10^{-5}$) $\Delta\varepsilon^{18}$ (nm): 0 (400), − 3.52 (325), 0 (310), + 6.68 (295), 0 (285), − 4.08 (275), − 1.48 (257), − 8.35 (240). ^{1}H and ^{13}C NMR in Tables 4 and 5.

Hexamethyl ether of compound **2** (**10**). Pale yellow viscous oil. HR-MS *m/z* 626.2143 $[M]^+$ (calcd for $C_{36}H_{34}O_{10}$, 626.2149), 447.1799 ($C_{27}H_{27}O_6$, 447.1805), 312.0998 ($C_{18}H_{16}O_5$, 312.0996), 180.0420 ($C_9H_8O_4$, 180.0422), 134.0730 ($C_9H_{10}O$, 134.0730). UV $\lambda_{max}^{dioxane}$ nm (log ε): 224.0 (4.59), 283.0 (3.98). CD (dioxane; *c*3.19 $\times 10^{-5}$) $\Delta\varepsilon^{18}$ (nm): 0 (365), − 1.90 (317), 0 (307), + 4.55 (294), 0 (287), − 6.45 (278), − 1.13 (258), − 2.66 (250). ^{1}H and ^{13}C NMR in Tables 4 and 5.

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