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THREE FLAVONOIDS FROM *DAPHNE ODORA**

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Key Word Index—*Daphne odora*; Thymelaeaceae; biflavonoids; daphnodorins J–L.

Abstract—Three new flavonoids, daphnodorins J–L, were isolated from the roots of *Daphne odora*, and their structures established from spectral and chemical evidence. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

In the course of our studies on the chemical constituents of thymelaeaceae species we have isolated three new flavonoids, daphnodorins J–L (**1**–**3**) in addition to 11 biflavonoids, daphnodorins A–C, D_1, D_2, E–I and dihydrodaphnodorin B from the roots of *Daphne odora* Thunb. [1–6]. This paper deals with their isolation and structural elucidation.

RESULTS AND DISCUSSION

Three new flavonoids, daphnodorins J–L (**1**–**3**) were isolated from the biflavonoid fraction of an ethyl acetate root extract of *D. odora*.

Compound **1**, a pale yellow viscous oil, was assigned the molecular formula $C_{30}H_{24}O_9$ by HR-SI mass spectrometry (m/z 529.1479 $[M + H]^+$). The UV spectrum showed absorption maxima at 324 sh, 285, 226.5 and 217 nm. The IR spectrum showed absorption bands at 3402 br, 1626, 1518 and 1459 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 [δ 7.15, 6.61 (each 2H, *d*, $J = 8.5$ Hz), 7.08, 6.69 (each 2H, *d*, $J = 8.5$ Hz)], a 2,4,6-trioxyphenyl group [δ 5.80 (2H, *br s*)], a 2,8 (or 2,6)-disubstituted 5,7-dioxy-3,4-dihydrobenzopyran ring [δ 6.05 (1H, *s*), 4.95 (1H, *dd*, $J = 9.8$ and 2.1 Hz), 2.65 (2H, *m*), 2.13 (1H, *m*) and 1.76 (1H, *m*)], one pair of coupled benzylmethine [δ 6.11, 5.95 (each 1H, *d*, $J = 10.6$ Hz)] and six phenolic hydroxyl groups [δ 13.65, 9.80, 9.13, 8.30, 8.20, 8.19 (each 1H, *s*)]. These signals were closely related to those of dihydrodaphnodorin B (**4**), except for the presence of signals due to a 2,8 (or 2,6)-disubstituted 5,7-dioxy-3,4-dihydrobenzopyran ring instead of the signals due to a 2,8-disubstituted 5,7-dioxy-3-hydroxy-3,4-dihydrobenzopyran ring [δ 6.08 (1H, *s*), 4.76 (1H, *d*, $J = 6.9$ Hz), 4.27 (1H, *d*, $J = 4.8$ Hz), 3.92 (1H, *m*), 2.82 (1H, *dd*, $J = 16.0, 4.9$ Hz), 2.62 (1H, *dd*, $J = 16.0, 7.5$ Hz)]. The ^{13}C NMR spectrum of **1** (Table 1) was very similar to that of **4** except for a signal assignable to a methylene carbon instead of a signal due to methine carbon in **4**, indicating that **1** is dihydrodaphnodorin A. This presumption was confirmed by direct comparison with one of two dihydro isomers prepared from daphnodorin A (**5**) by catalytic hydrogenation with PdO in EtOH. Thus, the absolute configuration at the C-2 position in **1** was assigned as *S* from its similarity to **5**. The relative configuration between C-2″ and C-3″ was concluded to be *cis* by the NOE experiment of **1**, although the absolute stereochemistry remains to be determined.

Compound **2**, a pale yellow viscous oil, was assigned the molecular formula $C_{30}H_{22}O_9$ by HR-SI mass spectrometry (m/z 527.1339 $[M + H]^+$). The UV spectrum showed absorption maxima at 348 sh, 304 sh, 269, 228 sh and 215 nm. The IR spectrum showed absorption bands at 3381 br, 1652, 1610 and 1499 cm^{-1}, indicating the presence of hydroxyl, carbonyl groups and an aromatic ring. The ^1H NMR spectrum of **2** (Table 2) showed signals owing to four pairs of 4-oxyphenyl groups [δ 7.59, 7.58 (each 2H, *d*, $J = 8.7$ Hz) and 6.82 (4H, *d*, $J = 8.7$ Hz), 7.30, 7.28 (each 2H, *d*, $J = 8.6$ Hz) and 6.86 (4H, *d*, $J = 8.6$ Hz)], two 2,8 (or 2,6)-disubstituted 5,7-dioxy-3-hydroxy-3,4-dihydrobenzopyran rings [δ 6.00 (2H, *s*), 4.92, 4.88 (each 1H, *dd*, $J = 10.1, 1.9$ Hz), 2.69 (4H, *m*), 2.10 (2H, *m*), 1.95 (2H, *m*)], and 12 phenolic hydroxyl groups [δ 13.18, 13.17, 9.08, 9.05, 8.45, 8.43, 7.93, 7.92 (each 1H, *s*), 9.72, 7.59 (each 2H, *s*)]. This NMR profile was similar to those of the atropisomers of 5,7,4′-trihydroxyflavane 5″, 7″, 4‴-trihydroxyflavone, daphnodorin D_1 and D_2 (**6** and **7**), indicating that **2** is also a mixture of two atropisomers, i.e. it is structurally analogous

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*Part 14 of the series 'Chemical Constituents of Thymelaeaceal Species'. For part 13 see ref. [1].

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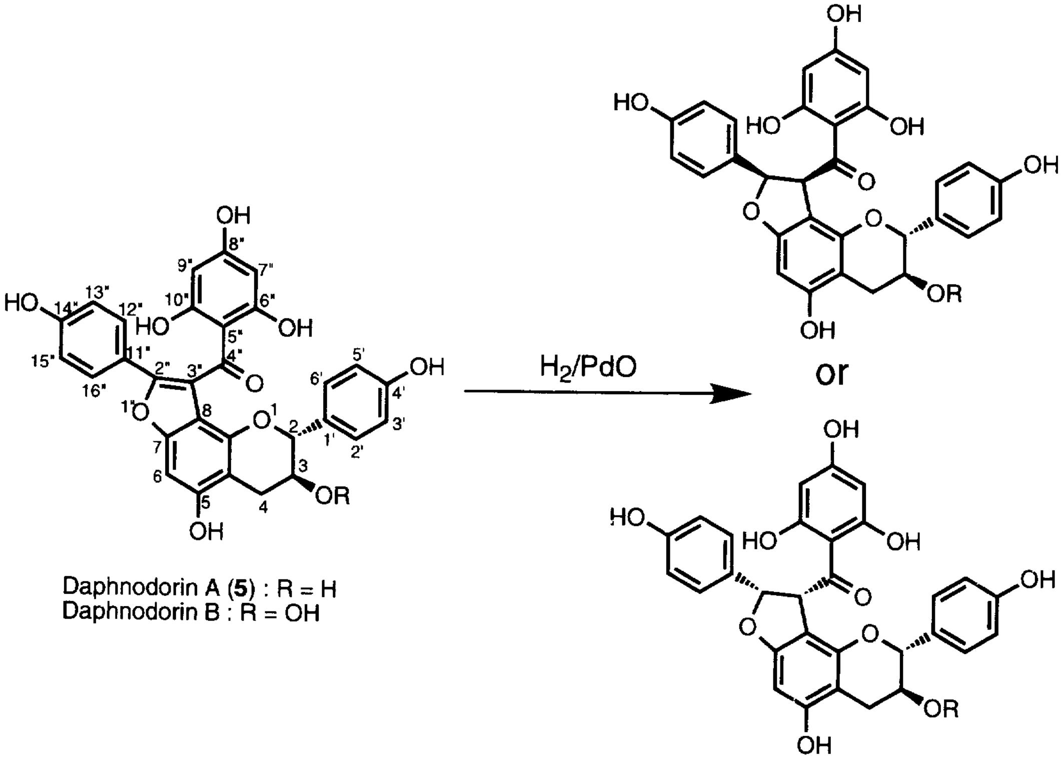
Table 1. NMR spectra data for compounds **1** and **4** (values in parentheses are coupling constants in Hz) (δ ppm, in acetone-d_6)

	H		C	
	1	**4**	**1**	**4**
2	4.95 *dd* (9.8, 2.1)	4.76 *d* (6.9)	88.7	82.4
3	2.13 *m*	3.92 *m*	31.7	69.2
(H or OH)	1.76 *m*	4.27 *d* (4.8)		
4	2.65 *m*	2.82 *dd* (16.0, 4.9)	20.3	28.3
		2.62 *dd* (16.0, 7.5)		
4a			102.8	101.2
5			152.3*	165.8*
6	6.05 *s*	6.08 *s*	90.1	90.5
7			157.3*	165.8*
8			106.7	106.6
8a			157.7*	162.0*
1′			130.5	130.3
2′,6′	7.08 *d* (8.5)	7.14 *d* (8.6)	127.7	129.0
3′,5′	6.69 *d* (8.5)	7.13 *d* (8.6)	116.1	115.5
4′			158.0*	158.0*
2″	6.11 *d* (10.6)	6.09 *d* (10.4)	78.1	88.8
3″	5.95 *d* (10.4)	5.94 *d* (10.4)	57.2	57.3
4″			202.9	202.9
5″			106.5	105.9
6″			161.8	157.8
7″	5.80 *brs*	5.76 *brs*	96.1	96.1
8″			165.6*	157.7*
9″	5.80 *brs*	5.76 *brs*	96.1	96.1
10″			157.3*	157.7*
11″			134.6	131.8
12″,16″	7.15 *d* (8.5)	6.61 *d* (8.6)	129.9	130.1
13″,15″	6.61 *d* (8.5)	6.70 *d* (8.6)	127.7	116.1
14″			158.0*	152.4*
-OH	13.65 *s*	13.64 *s*		
	9.80 *s*	9.78 *s*		
	9.13 *s*	9.14 *s*		
	8.30 *s*	8.39 *s*		
	8.20 *s*	8.25 *s*		
	8.19 *s*	8.23 *s*		

*Assignments with the same superscript may be reversed in each column.

to **6** and **7**. Methylation of **2** with diazomethane afforded a pentamethyl ether (**8**), whose ^{13}C NMR spectrum showed the down field shift of two methoxy carbon signals to δ 60.3 and 60.2, which were not observed in those of the hexamethyl ethers of **6** and **7** [7]. From the above results, it is deduced that **2** is not a C-8/C-3″-biflavonoid, but a C-6/C-3″-biflavonoid. This deduction was confirmed by the production of **2** on treatment of both **6** and **7** with HCl/MeOH. Furthermore, **2** is optically inactive.

Compound **3**, a pale yellow viscous oil was assigned the molecular formula $C_{23}H_{18}O_7$ by HR-SI mass spectrometry (m/z 407.1120 $[M + H]^+$). The UV spectrum showed absorption maxima at 351 sh, 305 sh, 295.5 and 224 nm. The IR spectrum showed absorption bands at 3447 br, 1631, 1596 and 1518 cm^{-1}, suggesting the presence of hydroxyl and carbonyl groups and an aromatic ring. The ^{1}H NMR spectrum of **3** (Table 3) showed signals assignable to two pairs of 4-oxyphenyl groups [δ 7.89, 6.74 (each 2H, *d*, $J = 8.9$ Hz), 6.82, 6.65 (each 2H, *d*, $J = 8.6$ Hz)], a 2,8 (or 2,6)-disubstituted 5,7-dioxy-3,4-dihydrobenzopyran ring [δ 6.09 (1H, *s*), 4.64 (1H, *dd*, $J = 10.2$, 2.2 Hz), 2.60 (2H, *m*), 1.90 (2H, *m*)], a chelated hydroxyl group [δ 12.57 (1H, *s*)] and three phenolic hydroxyl groups [δ 9.95, 9.24, 8.33 (each 1H, *s*)]. The ^{13}C NMR spectrum of **3** (Table 3) showed signals assignable to two carbonyl carbons at δ 199.2 and 190.6, in addition to the signals described above. On acetylation with acetic anhydride and pyridine **3** formed a tetraacetate (**9**), $C_{31}H_{26}O_{11}$. From these results, it was deduced that **3** is a 5,7,4′-trihydroxyflavan bearing a benzyl moiety, whose partial structure was confirmed by the 1,2-dinitrobenzene/formaldehyde test [8]. Thus, the structure of **3** was elucidated as shown. This structure was further supported by analyses of the long range C-H COSY spectrum of **3** (Table 4) and the MS fragmentation of **9**.



Daphnodorin A (5) : R = H
Daphnodorin B : R = OH

Daphnodorin J (1) : R = H
Dihydrodaphnodorin B (4) : R = OH

EXPERIMENTAL

General. EIMS: 70 eV. ^{1}H and ^{13}C NMR: 300 and 75.4 MHz with TMS as int. standard. CC: Merck silica gel 60 (70–230 mesh), Merck silica gel 60H and Sephadex LH-20. TLC: Merck silica gel 60 F_{254} plate (0.25 mm) and Whatman silica gel 150A PLK5F (1 mm). Spots and bands were detected by UV irradiation (254 and 365 nm).

Extraction and isolation. Air dried roots of *Daphne odora* Thunb. (4.5 kg) were collected from plants grown in the botanic garden of Osaka University of Pharmaceutical Sciences in January 1992 and for which a voucher specimen is deposited in the same university. The roots were chopped into small pieces and extracted with EtOAc (20 l × 5) under reflux. The combined EtOAc extracts were concd to dryness *in vacuo*. The residue (825 g) was subjected to CC on silica gel eluted successively with a hexane-EtOAc system of increasing polarity. The 50% EtOAc eluates, containing the biflavonoids, were concd and rechromatographed on silica gel with $CHCl_3$-MeOH (10 : 1) to give **1** (2.0 g), **2** (0.46 g) and **3** (0.2 g).

Daphnodorin J (**1**). Pale yellow amorphous powder, Gibbs test: orange. HR-SIMS *m/z* 529.1479 $[M + H]^+$ (calc. for $C_{30}H_{25}O_9$, 529.1479). UV $\lambda_{max}^{dioxane}$ nm (log ε): 324 sh (4.65), 285 (5.25), 226.5 (5.62), 217 (5.56). IR ν_{max}^{KBr} cm^{-1}: 3402 br, 1626, 1518, 1459. ORD (dioxane; *c* 0.47) $[\alpha]^{20}$ (nm); +25.0° (589), +25.4° (550), +24.6 (500), +6.7° (450), 0° (437), −70.0 (400), −285.4 (374). CD (dioxane; *c* 5.68 × 10^{-5}) $\Delta\varepsilon^{20}$ (nm): 0 (380), −5.6 (305), 0 (284), +0.8 (280), 0 (273), −0.5 (285), 0 (250). ^{1}H and ^{13}C NMR in Table 1.

Catalytic hydrogenation of **5**. A soln of **5** (100 mg) in EtOH (2 ml) was added to prereduced PdO (500 mg) in EtOH (50 ml), and the mixt. was stirred in the presence of H_2 until consumption of H_2 ceased. The catalyst was filtered off and the filtrate evapd to dryness. The product was purified by CC on Sephadex LH-20 with MeOH to give two dihydro isomers (**1a** and **1b**), of which **1a** was identified as daphnodorin J (**1**). Compound **1b**: pale yellow amorphous powder. ^{1}H NMR (Me_2CO-d_6): δ 13.65–8.18 (6H *br*), 7.12 (4H, *d*, *J* = 8.6 Hz), 6.69 (2H, *d*, *J* = 8.6 Hz), 6.58 (2H, *d*, *J* = 8.6 Hz), 6.07 (1H, *d*, *J* = 10.2 Hz), 6.06 (1H, *s*), 6.00 (1H, *d*, *J* = 10.2 Hz), 5.74 (2H, *brs*), 4.86 (1H, *d*, *J* = 9.8 Hz), 2.65 (2H, *m*), 2.13 (1H, *m*), 1.76 (1H, *m*).

Daphnodorin K (**2**). Pale yellow viscous oil. Gibbs Test: yellow. HR-SIMS *m/z* 527.1339 $[M + H]^+$ (calc. for $C_{30}H_{23}O_9$, 527.1340). UV, $\lambda_{max}^{dioxane}$ nm (log ε): 348 sh (2.81), 304 sh (3.11), 269 (4.36), 228 sh (3.53), 215 (3.70). IR ν_{max}^{KBr} cm^{-1}: 3381 br, 1652, 1610, 1499. ^{1}H and ^{13}C NMR in Table 2.

Pentamethyl ether of **2** (**8**). Pale yellow amorphous powder. HR-MS *m/z* 596.2014 $[M]^+$ (calc. for $C_{35}H_{32}O_9$, 596.2044). ^{1}H NMR ($CDCl_3$): δ 13.11 (1H, *s*), 13.07 (1H, *s*), 7.50 (2H, *d*, *J* = 8.8 Hz), 7.49 (2H, *d*, *J* = 8.8 Hz), 7.37 (2H, *d*, *J* = 8.8 Hz), 7.35 (2H, *d*, *J* = 8.8 Hz), 6.94 (4H, *d*, *J* = 8.8 Hz), 6.82 (2H, *d*, *J* = 8.8 Hz), 6.81 (2H, *d*, *J* = 8.8 Hz), 6.48 (2H, *d*, *J* = 2.2 Hz), 6.38 (2H, *d*, *J* = 2.2 Hz), 6.36 (1H, *s*),

Table 2. NMR spectral data for compounds **2**, **6** and **7** (δ ppm, in acetone-d_6)

	H			C		
	2	**6**	**7**	**2**	**6**	**7**
2	4.92, 4.88 *dd* (10.1, 1.9)	4.60 *dd* (9.6, 2.4)	4.84 *dd* (10.0, 2.1)	78.1, 77.9	78.4	78.4
3	2.69, 2.69 *m*	1.94 *m*	1.69 *m*	29.5, 29.5	31.7	30.4
4	2.10, 2.10 *m* 1.95, 1.95 *m*	2.62 *m*	2.62 *m*	20.5, 20.3	20.3	20.4
4a				102.2, 102.1^{a}	102.7	102.5
5				154.8, 154.7	165.0^{a}	165.0^{a}
6		6.08 *s*	6.10 *s*	100.8, 100.7^{a}	96.5	96.3
7				157.8, 157.6^{b}	164.6^{a}	163.9^{a}
8	6.00, 6.00 *s*			96.2, 96.1	101.2	101.0
8a				155.6, 155.5^{b}	163.9^{a}	160.7^{a}
1′				133.9, 133.9	134.5	134.4
2′,6′	7.30, 7.28 *d* (8.6)	7.14 *d* (8.6)	6.90 *d* (8.6)	128.3, 128.2	128.4	128.3
3′,5′	6.86, 6.86 *d* (8.6)	6.72 *d* (8.6)	6.65 *d* (8.6)	115.8, 115.7^{c}	116.0	116.1
4′				157.8, 157.8	160.5^{a}	159.1^{a}
2″				165.2, 165.2	159.1^{a}	157.9^{a}
3″				112.5, 112.5	114.3	114.2
4″				183.3, 183.3	183.5	183.3
4″a				105.2, 105.2	105.5	105.4
5″				163.4, 163.4	159.1^{a}	157.3^{a}
6″	6.28, 6.28 *d* (2.0)	6.23 *d* (2.1)	6.19 *d* (2.1)	99.3, 99.3	99.8	99.6
7″				164.7, 164.7	157.9^{a}	156.0^{a}
8″	6.49, 6.49 *d* (2.0)	6.39 *d* (2.1)	6.39 *d* (2.1)	94.1, 94.1	94.6	94.4
8″a				158.8, 158.8	155.8^{a}	155.8^{a}
9″				125.2, 125.2	126.2	126.1
10″,14″	7.59, 7.58 *d* (8.7)	7.42 *d* (8.8)	7.58 *d* (8.8)	131.2, 131.2	131.5	131.6
11″,13″	6.82, 6.82 *d* (8.7)	6.78 *d* (8.8)	6.84 *d* (8.8)	115.8, 115.7^{c}	116.1	116.1
12″				160.4, 160.4	155.7^{a}	155.5^{a}
-OH	13.18, 13.17 *s* 9.72, 9.72 *s* 9.08, 9.05 *s* 8.45, 8.43 *s* 7.93, 7.92 *s* 7.59, 7.59 *s*	13.35 *s* 9.51 *s* 8.86 *s* 8.22 *s* 8.20 *s* 7.61 *s*	13.29 *s* 9.54 *s* 8.95 *s* 8.25 *s* 8.22 *s* 7.69 *s*			

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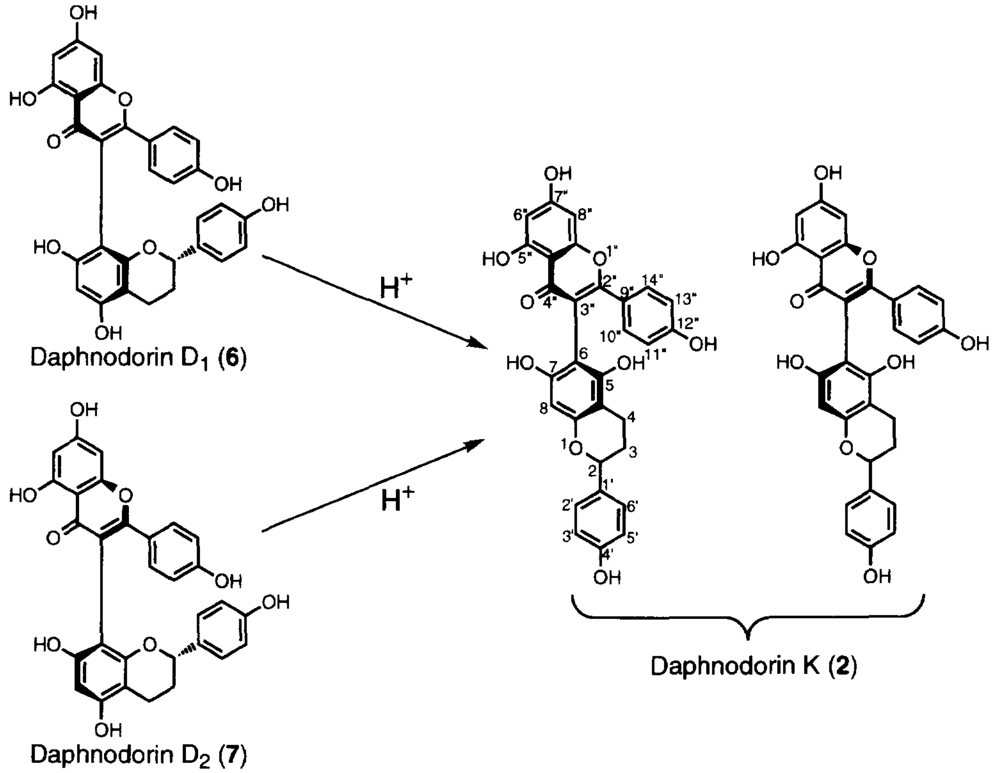
[a] [c] Assignments with the same superscript may be reversed in each column.



Daphnodorin D$_1$ (6)

Daphnodorin D$_2$ (7)

Daphnodorin K (2)

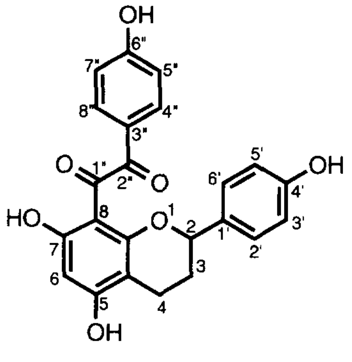
6.33 (1H, *s*), 5.00 (1H, *dd*, $J = 9.5, 2.1$ Hz), 4.95 (1H, *dd*, $J = 9.5, 2.1$ Hz), 3.89 (6H, *s*), 3.83 (6H, *s*), 3.81 (3H, *s*), 3.80 (3H, *s*), 3.64 (3H, *s*), 3.60 (3H, *s*), 3.58 (3H, *s*), 3.44 (3H, *s*), 2.80 (2H, *m*), 2.69 (2H, *m*), 2.13 (2H, *m*), 2.04 (2H, *m*). ^{13}C NMR (CDCl$_3$): δ 182.2, 182.0, 165.4 ×2, 162.4 ×4, 161.1 ×2, 159.4 ×2, 157.8 ×2, 157.4 ×2, 157.3, 157.2, 157.1 ×2, 133.6 ×2, 129.9 ×4, 127.5 ×4, 125.7 ×2, 114.0 ×2, 113.9 ×2, 113.8 ×2, 113.6 ×2, 113.5 ×2, 108.2 ×2, 108.1 ×2, 105.1 ×2, 97.8 ×2, 96.6, 96.5, 92.0 ×2, 77.9, 77.7, 60.3, 60.2, 55.9 ×2, 55.8 ×2, 55.4 ×2, 55.3 ×2, 29.4 ×2, 20.2 ×2.

Table 3. NMR spectral data for compound **3** (values in parentheses are coupling constants in Hz) (δ ppm, in acetone-d_6)

	H	C
2	4.64 *dd* (10.2, 2.2)	80.1
3	1.90 *m*	19.7
4	2.60 *m*	29.5
4a		102.7
5		166.5
6	6.09 *s*	96.3
7		166.2
8		103.6
8a		159.9
1′		131.7
2′, 6′	6.82 *d* (8.6)	128.6
3′, 5′	6.65 *d* (8.6)	115.8
4′		158.2
1″		199.2
2″		190.6
3″		126.4
4″, 8″	7.89 *d* (8.9)	116.1
5″, 7″	6.74 *d* (8.9)	132.6
6″		163.4
-OH	12.56 *s* 9.95 *s* 9.24 *s* 8.33 *s*	

Conversion of **6** *and* **7** *to* **2**. Compound **6** (124 mg) in MeOH (5 ml) was heated at 100 with 8% HCl–MeOH (5ml) for 20 min, and extracted with EtOAc. The EtOAc soln was washed with water, dried and concd to dryness and purified by prep. TLC (CHCl$_3$–MeOH 7 : 1) to afford **2** (13.8 mg). Compound **7** (60 mg) was treated in the same way as **6** to afford **2** (9.4 mg).

Daphnodorin L (**3**). Pale yellow viscous oil, Gibbs



Daphnodorin L (3)

Table 4. Long range ^{13}C–^{1}H COSY spectral data for compound **3**

C	Correlated H
4a	4, 6
5	6, 7-OH
6	7-OH
7	6, 5-OH
8	6, 7-OH
8a	4
1′	3′, 5′
2′, 6′	2, 2′, 6′
4′	2′, 6′
2″	4″, 8″
3″	5″, 7″
4″, 8″	4″, 5″, 7″, 8″
5″, 7″	4″, 5″, 7″, 8″
6″	4″, 5″, 7″, 8″

test: grey-green. HR-SIMS *m/z* 407.1121 $[M + H]^+$ (calc. for $C_{23}H_{19}O_7$, 407.1130). UV $\lambda_{max}^{dioxane}$ nm (log ε): 351 sh (3.42), 305 sh (4.14), 295.5 (4.20), 224 (4.35). IR ν_{max}^{KBr} cm^{-1} 3447 br, 1631, 1596, 1518. ORD (dioxane; *c*0.48) $[\alpha]^{20}$ (nm): −22.9 (589), −28.8 (550), −39.6 (500), −58.3 (450), −91.7 (400). CD (dioxane; *c*4.93 × 10^{-5},)$\Delta\varepsilon^{20}$ (nm): 0 (400), −4.9 (360), 0 (340), −39.3 (301), −31.9 (298), −52.9 (292), 0 (266), +4.9 (250), 0 (244). ^{1}H and ^{13}C NMR in Table 3.

Tetraacetate of **3** (**9**). Pale yellow viscous oil. HR-MS *m/z* 574.1461 $[M]^+$ (calc. for $C_{31}H_{26}O_{11}$, 574.1473), 412.1148 ($C_{22}H_{20}O_8$, 412.1157), 411.1090 ($C_{22}H_{19}O_8$, 411.1079), 163.0395 ($C_9H_7O_3$, 163.0394). IR ν_{max}^{KBr} cm^{-1} λ: 3505 br, 3069, 2361, 2345, 1769, 1678, 1600, 1510. ^{1}H NMR ($CDCl_3$): δ 7.59 (2H, *d*, $J = 8.7$ Hz), 6.95 (2H, *d*, $J = 8.7$ Hz), 6.93 (2H, *d*, $J = 8.7$ Hz), 6.84 (2H, *d*, $J = 8.7$ Hz), 6.64 (1H, *s*), 4.77 (2H, *dd*, $J = 9.7$, 3.4 Hz), 2.70 (2H, *m*), 2.09 (2H, *m*), 2.32, 2.31, 2.30, 2.92 (each 3H, *s*). ^{13}C NMR ($CDCl_3$): δ 191.8, 189.9, 169.7, 169.4, 168.6, 167.9, 158.1, 154.9, 153.8, 150.6, 150.4, 135.9, 131.2 ×2, 129.8, 127.2 ×2, 121.6 ×4, 114.3, 113.9, 110.8, 78.9, 27.9, 20.9 ×2, 20.6 ×2, 19.8.

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