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A SPIROBIFLAVONOID GENKWANOL B FROM *DAPHNE GENKWA**

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Key Word Index—*Daphne genkwa*; Thymelaeaceae; roots; biflavonoid; genkwanol B; flavonoid.

Abstract—A novel biflavonoid, genkwanol B, was isolated from the roots of *Daphne genkwa*. The structure of genkwanol B was determined on the basis of chemical studies and spectroscopic data, including NOESY and HMBC experiments.

INTRODUCTION

The buds and the roots of *Daphne genkwa* Sieb. et Zucc. have been used in traditional Chinese medicine [2]. In our preceding paper [3], we reported the isolation of a new spirobiflavonoid, genkwanol A (**1**) as well as daphnodorin B, umbelliferone, daphnoretin, daphnin, syringin and yuenkwanin from the root of this plant. As a result of further examination, we have now isolated another novel biflavonoid, genkwanol B (**2**), and have elucidated its structure.

RESULTS AND DISCUSSION

A methanol extract of the roots of *Daphne genkwa* Sieb. et Zucc. yielded **2** after repeated chromatographic purification. Compound **2** was isolated as pale yellow amorphous powder. Its molecular composition was found to be $C_{30}H_{22}O_{11}$, by FAB mass spectrometry (*m/z* 559 [$M^+ + 1$]). The UV spectrum showed absorption maxima at 341 sh, 298, 283, 257 and 226 nm. The IR spectrum showed absorption bands at 3413 br, 1689, 1639, 1615 and 1590 cm^{-1}, suggesting the presence of hydroxyl group, carbonyl group and aromatic ring. The ^{1}H NMR spectrum of **2** (Table 1) showed the presence of two pairs of 1,4-disubstituted benzene groups [δ7.09, 6.73 (each 2H, *d*, J=8.8 Hz), 6.59, 6.51 (each 2H, *d*, J=8.8 Hz)], 2,4,6-trioxyphenyl group [δ6.12, 6.04 (each 1H, *d*, J=2.2 Hz)], 3-hydroxy-2,5,6-trisubstituted dihydropyran [δ4.56 (1H, *d*, J=8.4 Hz), 3.35 (1H, *m*), 2.59 (1H, *dd*, J=16.9, 4.8 Hz), 2.05 (1H, *dd*, J=16.9, 8.9 Hz), 5.15 (1H, *d*, J=6.2 Hz)], four phenolic hydroxyl groups [δ11.23 (2H, *s*), 9.58 (1H, *s*), 9.34 (1H, *s*)] and an alcoholic hydroxyl group [δ6.57 (1H, *s*)]. Further, the two singlet signals were observed at 5.97 (1H, *s*) and 5.71 (1H, *s*). In the ^{13}C NMR spectrum of **2** (Table 2) two carbonyl carbon signals (δ191.07 and 186.87) and two quaternary carbon signals attached to oxygen atom (δ85.30 and 80.04) were observed in addition to the signals described above. The acetylation of **2** with acetic anhydride and pyridine afforded a pentaacetate (**3**), which gave a monomethyl ether (**4**) after methylation with methyl iodide. The methylation of **2** with diazomethane afforded a pentamethyl ether (**5**) which gave a 5-monomethyl ether (**6**) (**2** hexamethyl ether) by methylation with methyl iodide. On acetylation of **5** with acetic anhydride and pyridine a monoacetate (**7**) was obtained. Hence the hydroxyl group in **5** is situated in the C-3 position of a dihydropyran ring, while that of **3** is a tertiary hydroxyl group or sterically hindered hydroxyl group. The reduction of **6** with sodium borohydride followed by treatment with *d*-HCl gave **8** ($C_{29}H_{32}O_8$), **9** ($C_{36}H_{36}O_{11}$) and **10** ($C_{37}H_{38}O_{11}$) in addition to *p*-anisaldehyde. On the other hand, by reduction with sodium borohydride followed by treatment with water, **6** afforded **9**, **10** and **11** ($C_{37}H_{38}O_{11}$). Compound **8** was estimated to be a degradation product resulting from the elimination of *p*-anisaldehyde from **6** by mass spectrometry. In the ^{1}H NMR spectrum of **8**, one of the 4-hydroxyphenyl groups and one of the singlet signals were lacking compared with that of **6** and the remaining singlet signal was shifted to a higher field. Furthermore, one pair of doublet signal [δ6.89, 5.95 (each 1H, *d*, J=9.8 Hz)] was newly formed (Table 1). The above spectral data, the presence of two carbonyl carbon signals in the ^{13}C NMR spectrum (Table 2) and the long range C–H COSY experiment of **8** (Table 3) led to its structure as shown. The ^{13}C NMR spectra of **9** and **10** (Table 2) showed the absence of one of the carbonyl signals and the presence of an aromatic or olefinic carbon signal and a quaternary carbon signal different from that of **6** (Table 2). The ^{1}H NMR spectra of **9** and **10** (Table 1) were similar to that of **6** except that one pair of doublet signal coupled by 9.9 Hz was observed instead of a singlet (δ5.85) in **6**. Compound **10** was obtained from **9** by methylation with methyl iodide. In the ^{1}H NMR spectrum of **11** (Table 1), one of the singlet signals in **6** was shifted to higher field and coupled by 2.8 Hz with a newly formed methine proton signal attached to oxygen atom. From the above spectral data of **9**–**11**, it was concluded that **11** was formed by reduction of one carbonyl group in **6** followed by methanolysis, while **9** and **10** were obtained by elimination of a hydroxyl group formed by reduction of **6**, subsequent rearrangement of a double bond and by the introduction of one hydroxyl group or one methoxyl group. Thus, the structures of **9**–**11** have been established. The structure of **11** was further supported by the long

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Table 1. ^{1}H NMR spectral data for compounds **2**, **5**, **6**, **8**–**11** (values in parentheses are coupling constants in Hz) (in $CDCl_3$, TMS)

H	**2** (DMSO-d_6)	**5**	**6**	**8**	**9**	**10**	**11**
2	4.56 *d* (8.4)	4.60 *d* (6.7)	4.93 *d* (5.1)	4.79 *d* (7.6)	4.61 *d* (6.5)	4.55 *d* (7.3)	4.72 *d* (6.1)
3	3.55 *m*	3.70 *m*	3.51 *dt* (5.1, 4.5)	3.75 *m*	3.47 *m*	3.47 *m*	3.44 *m*
4	2.59 *dd* (16.9, 4.8)	2.72 *dd* (17.3, 5.0)	2.52 *d* (4.4)	2.52 *dd* (16.2, 5.4)	2.41 *dd* (17.0, 5.0)	2.47 *dd* (17.0, 5.2)	2.32 *d* (4.9)
	2.05 *dd* (16.9, 8.9)	2.28 *dd* (17.3, 7.5)		2.40 *dd* (16.2, 7.7)	2.21 *dd* (17.0, 6.7)	2.24 *dd* (17.0, 7.3)	
5				6.89 *d* (9.8)	5.99 *d* (9.9)	5.93 *d* (9.9)	4.86 *d* (2.8)
6	5.71 *s*	5.77 *s*	5.85 *s*	5.95 *d* (9.8)	5.74 *d* (9.9)	5.84 *d* (9.9)	5.41 d (2.8)
2′, 6′	6.59 *d* (8.8)	6.72 *d* (8.8)	6.88 *d* (8.8)	6.87 *d* (8.8)	7.06 *d* (8.8)	7.07 *d* (8.8)	6.88 *d* (8.8)
3′, 5′	6.51 *d* (8.8)	6.62 *d* (8.8)	6.72 *d* (8.8)	6.68 *d* (8.8)	6.74 *d* (8.8)	6.72 *d* (8.8)	6.70 *d* (8.8)
2″	5.97 *s*	5.83 *s*	5.91 *s*		5.32 *s*	5.38 *s*	5.73 *s*
3″				4.57 *s*			
6″	6.04 *d* (2.2)	6.09 *d* (2.2)	6.13 *d* (2.2)	6.00 *d* (2.2)	6.04 *d* (2.3)	5.98 *d* (2.3)	6.10 *d* (2.3)
8″	6.12 *d* (2.2)	6.14 *d* (2.2)	6.17 *d* (2.2)	6.08 *d* (2.2)	6.24 *d* (2.3)	6.29 *d* (2.3)	6.17 *d* (2.3)
2‴, 6‴	7.09 *d* (8.8)	7.12 *d* (8.8)	7.19 *d* (8.8)		7.19 *d* (8.8)	7.24 *d* (8.8)	7.21 *d* (8.8)
3‴, 5‴	6.73 *d* (8.8)	6.77 *d* (8.8)	6.86 *d* (8.8)		6.81 *d* (8.8)	6.82 *d* (8.8)	6.84 *d* (8.8)
–OH	11.23 *s* ×2	3.80 *br*			4.60 s		
	9.58 *s*						
	9.34 *s*						
	6.57 s						
	5.15 d (6.2)						
–OMe		3.81 *s*	3.85 *s*	3.81 *s*	3.86 *s*	3.86 *s*	3.85 *s*
		3.71 *s*	3.82 *s*	3.76 *s*	3.78 *s* ×2	3.78 *s* ×2	3.79 *s*
		3.69 *s* ×2	3.79 *s*	3.70 *s*	3.77 *s*	3.76 *s*	3.78 *s*
		3.31 *s*	3.77 *s*	3.57 *s*	3.34 *s*	3.57 *s*	3.77 *s*
			3.43 *s*	3.15 *s*	3.13 *s*	3.31 *s*	3.40 *s*
			3.20 *s*			3.11 *s*	3.20 *s*
							3.17 *s*

Assignments are based on ^{13}C–^{1}H COSY and spin decoupling measurements.

Table 2. ^{13}C NMR spectral data for compounds **2**, **5**, **6**, **8–11** (δ, ppm, in $CDCl_3$, TMS)

C	**2** (DMSO-d_6)	**5**	**6**	**8**	**9**	**10**	**11**
2	82.28	82.35	79.81	79.69	78.97	79.03	78.18
3	66.63	67.61	75.78	76.39	76.73	76.87	76.85
4	27.01	25.54	21.22	29.60	29.11	29.77	26.07
4a	109.57	110.56	110.25	105.24	106.41	105.93	110.27
5	186.87	187.48	187.49	148.10	123.14	121.27	75.00
6	100.76	102.30	102.38	118.46	124.75	125.88	99.84
7	169.10	169.33	169.30	195.17	104.97	107.31	155.98
8	85.30	84.93	84.95	80.69	90.20	91.25	85.58
8a	157.22[a]	158.05	157.90	156.12	145.33	146.52	145.73
1′	128.34	129.16	130.00	129.99	130.74	130.70	131.24
2′, 6′	127.73	127.88	127.51	127.96	127.79	128.02	127.70
3′, 5′	114.77	114.24	114.03	113.79	113.70	113.58[a]	113.82
4′	158.46[a]	160.24	159.90	159.74	159.65[a]	159.64[a]	159.63
2″	90.21	90.94	91.09		83.54	84.06	88.98
3″	80.04	86.10	86.15	82.13	91.40	91.51	85.37
4″	191.07	183.20	183.25	188.57	184.37	184.42	184.73
4″a	100.15	105.53	105.36	105.54	105.32	105.37	105.70
5″	163.82	163.35	163.26	161.82	163.22	162.96	163.16
6″	97.33	94.45	94.36	93.54	93.72	93.29	93.73
7″	168.12	167.22	167.06	166.08	166.86	166.85	166.73
8″	96.46	94.58	94.51	93.71	94.17	94.25	94.21
8″a	160.64	162.87	162.82	163.03	163.30	164.50	163.69
1‴	122.39	124.36	124.47		126.22	126.29	126.14
2‴, 6‴	130.24	130.03	130.00		130.17	130.43	129.94
3‴, 5‴	114.95	113.85	113.85		113.47	113.52[a]	113.65
4‴	158.60[a]	160.72	160.69		160.09[a]	160.15[b]	160.25
OMe		56.57	56.91 (3)	61.69 (3″)	57.49 (3)	57.64 (3)	57.20 (3)
		56.18	56.56	57.74 (3)	56.70	56.51	56.49
		55.86	56.07 (3″)	56.46	56.48	56.37	55.97
		55.58	55.73 (5″)	55.89	55.99	55.95	55.51
		55.46	55.52 (7″)	55.48	55.52	55.50	55.44
			55.47		55.40	55.40	54.87
						51.59 (7)	50.32 (5)

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.

range C–H COSY experiment (Table 3). Based on this evidence, the structure of **6** is established, a structure further supported by HR-MS (see Experimental) and the HMBC spectrum (Table 4). The determination of the relative configuration was made by analysis of the NOESY spectrum of **6** (not shown). Hence, the structure of **2** is fully substantiated.

EXPERIMENTAL

General. Mps: uncorr; EIMS: 70 eV; ^{1}H and ^{13}C NMR: 300 and 75.4 MHz, respectively, with TMS as an int. standard. CC: Merck silica gel 60 (70–230 mesh), Merck silica gel 60H, Merck RP-18 and Sephadex LH-20; TLC and prep. TLC; Merck silica gel 60F_{254} plates (0.25 mm) and Whatman silica gel 150A PLK 5F (1 mm). Spots and band were detected by UV irradiation (254 and 365 nm).

Plant material. The plants of *Daphne genkwa* Sieb. et Zucc. were cultivated and collected in the botanical garden of Osaka University of Pharmaceutical Sciences in March 1990. A voucher specimen is deposited in this University.

Extraction and isolation. Air-dried roots of *Daphne genkwa* (5.3 kg) were chopped into small pieces and extracted with MeOH (10 l × 4) under reflux. The combined MeOH extracts were concd to 2 l *in vacuo*. After removal of a ppt. by filtration, the filtrate was concd *in vacuo*. The residue was treated with *n*-hexane and the insoluble part concd *in vacuo* to give a residue (655 g), which was subjected to CC on silica gel eluted successively with $CHCl_3$–MeOH solvent mixture of increasing polarity. The 10% MeOH eluates were rechromatographed on Sephadex LH-20 with MeOH to give genkwanol B (**2**) (4.5 g).

Genkwanol B (**2**). Pale yellow amorphous powder, $C_{30}H_{22}O_{11}$, FAB-MS *m/z* 559 $[M+1]^+$, UV $\lambda_{max}^{dioxane}$ nm (log ε): 341 sh (3.55), 298 (4.16), 283 (4.13), 257 (4.25), 226 (4.50). ORD (dioxane; *c* 0.53) $[\alpha]^{24}$ (nm): −164.2° (589), −283.0° (500), −577.4° (400), −747.2° (375). CD (dioxane; *c* 2.15 × 10^{-5}) $\Delta\varepsilon^{25}$ (nm): 0 (388), +4.9 (333), 0 (324), −37.3 (300), 0 (273), +27.8 (256), +13.4 (240), +14.1 (236), +13.4 (232), +27.5 (219), 0 (210). ^{1}H and ^{13}C NMR see Tables 1 and 2.

Acetate (**3**). $C_{40}H_{32}O_{16}$, viscous oil. FD-MS *m/z* 769 $[M+1]^+$. UV $\lambda_{max}^{dioxane}$ nm (log ε): 315 (3.61), 256 (4.32), 219.5 (4.47). ORD (dioxane; *c* 0.51) $[\alpha]^{24}$ (nm): −233.3° (589), −398.0° (500), −933.3° (400), −1935.3° (360). CD (dioxane; c 1.56 × 10^{-5},) $\Delta\varepsilon^{25}$ (nm): 0 (388), +7.3 (336), 0 (328), −45.1 (308), −20.2 (280), −15.0 (270), 0 (262), +29.6 (248), +10.7 (225), +23.3 (215). ^{1}H NMR

Table 3. Long range ^{13}C–^{1}H 2D COSY spectral data for compounds **8** and **11**

C	Correlated H	
	8	**11**
2	2′, 6′	2′, 6′
3	3-OMe	3-OMe
4a	4, 6	6
5	4	5-OMe
6		5
7	5	5, 6
8	6, 3″	6
8a	5, 3″	5
1′	3′, 5′	3′, 5′
2′, 6′	2, 2′, 6′	2, 2′, 6′
3′, 5′	3′, 5′	3′, 5′
4′	2′, 6′, 4′-OMe	2′, 6′
2″		2‴, 6‴
3″	3″-OMe	3″-OMe
4″a	6″, 8″	6″, 8″
5″	5″-OMe	6″
6″	8″	8″
7″	6″, 7″-OMe	6″
8″	6″	6″
8″a	8″	8″
1‴		3‴, 5‴
2‴, 6‴		2″, 2‴, 6‴
3‴, 5‴		3‴, 5‴
4‴		2‴, 6‴
OMe-5		5
OMe-3″	3″	

Table 4. HMBC data for compound **6**

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

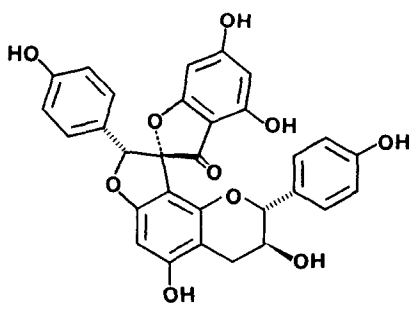
($CDCl_3$): δ7.28 (2H, *d*, J=8.8 Hz), 7.12 (2H, *d*, J=8.8 Hz), 6.98 (2H, *d*, J=8.8 Hz), 6.91 (1H, *d*, J=2.2 Hz), 6.91 (2H, *d*, J=8.8 Hz), 6.67 (1H, *d*, J=2.2 Hz), 6.02 (1H, *s*), 5.90 (1H, *s*), 5.07 (2H, *m*), 3.69 (1H, *s*), 2.62 (1H, *dd*, J=17.6, 4.7 Hz), 2.44 (1H, *dd*, J=17.6, 5.8 Hz), 2.35, 2.30, 2.28, 2.26, 1.93 (each 3H, *s*). ^{13}C NMR ($CDCl_3$): δ186.90 (*s*), 186.55 (*s*), 170.41 (*s*), 169.93 (*s*), 169. 68 (*s*), 169.33 (*s*), 168.20 (*s*), 168.13 (*s*), 161.69 (*s*), 158.13 (*s*), 156.79 (*s*), 152.04 (*s*), 151.83 (*s*), 151.23 (*s*), 133.96 (*s*), 129.52 (*d*) × 2, 128.93 (*s*), 127.04 (*d*) × 2, 122.22 (*d*) × 2, 121.95 (*d*) × 2, 112.09 (*d*), 110.55 (*s*), 109.57 (*d*), 109.05 (*s*), 103.00 (*d*), 90.10 (*d*), 85.89 (*s*), 80.75 (*s*), 79.27 (*d*), 68.42 (*d*), 22.03 (*t*), 21.39 (*q*), 21.32 (*q*) × 2, 21.06 (*q*), 21.01 (*q*).

Penta-acetate methyl ether (**4**). Pale yellow viscous oil. ^{1}H NMR ($CDCl_3$): δ7.25 (2H, *d*, J=8.8 Hz), 7.10 (2H, *d*, J=8.8 Hz), 7.03 (4H, *s*), 6.86 (1H, *d*, J=2.2 Hz), 6.61 (1H, *d*, J=2.2 Hz), 6.00 (1H, *s*), 5.92 (1H, *s*), 5.23 (1H, *m*), 5.14 (1H, *d*, J=3.9 Hz), 3.44 (3H, *s*), 2.60 (1H, *dd*, J=17.6, 4.7 Hz), 2.52 (1H, *dd*, J=17.6, 5.8 Hz), 2.32, 2.29 (each 6H, *s*), 1.89 (3H, *s*). ^{13}C NMR ($CDCl_3$): δ186.40 (*s*), 184.01 (*s*), 169.96 (*s*), 169.67 (*s*), 169.49 (*s*), 169.33 (*s*), 168.37 (*s*), 168.01 (*s*), 160.70 (*s*), 157.28 (*s*), 156.61 (*s*), 151.85 (*s*), 151.75 (*s*), 151.23 (*s*), 133.70 (*s*), 129.64 (*d*) × 2, 129.00 (*s*), 126.89 (*d*) × 2, 122.28 (*d*) × 2, 121.44 (*d*) × 2, 112.02 (*d*), 111.08 (*s*), 110.52 (*s*), 109.34 (*d*), 103.02 (*d*), 90.00 (*d*), 86.29 (*s*), 85.53 (*s*), 79.30 (*d*), 68.04 (*d*), 55.49 (*q*), 21.25 (*q*) × 2, 21.20 (*q*), 21.06 (*q*), 20.85 (*q*), 20.85 (*t*).

Pentamethyl ether (**5**). Pale yellow viscous oil. HR-MS *m/z* 628.1946 $[M]^+$ (calcd for $C_{35}H_{32}O_{11}$, 628.1942). UV $\lambda_{max}^{dioxane}$ nm (log ε): 323 sh (3.77), 293 sh (4.18), 281 sh (4.24), 256 (4.39), 227 (4.61). ORD (dioxane; *c* 0.53) $[\alpha]^{24}$ (nm): −217.0° (589), −330.2° (500), −754.7° (400), −1358.5° (358). CD (dioxane; *c* 1.91 × 10^{-5}) $\Delta\varepsilon^{25}$ (nm): 0 (385), +5.2 (335), 0 (325), −52.7 (291), 0 (270), +30.5 (255), +14.3 (240), +15.1 (237), +13.1 (232), +34.1 (221), 0 (210). ^{1}H and ^{13}C NMR see Tables 1 and 2.

Hexamethyl ether (**6**) Pale yellow viscous oil. HR-MS *m/z* 642.2095 $[M]^+$ (calcd for $C_{36}H_{34}O_{11}$, 642.2098); 462.1675 ($C_{27}H_{26}O_7$, 462.1676); 298.0832 ($C_{17}H_{14}O_5$, 298.0840); 180.0417 ($C_9H_8O_4$, 180.0421); 164.0833 ($C_{10}H_{12}O_2$, 164.0836). UV $\lambda_{max}^{dioxane}$ nm (log ε): 321 sh (3.78), 292 sh (4.17), 281 sh (4.23), 257 (4.38), 227.5 (4.60). ORD (dioxane; *c* 0.56) $[\alpha]^{24}$ (nm): −262.5° (589), −425.0° (500), −975.0° (400), −1750.0° (358). CD (dioxane; *c* 1.87 × 10^{-5}) $\Delta\varepsilon^{25}$ (nm): 0 (387), +5.7 (335), 0 (325), −63.2 (291), 0 (271), +37.3 (255), +18.6 (240), +19.5 (235), +16.2 (231), +35.3 (221), +24.3 (215). ^{1}H and ^{13}C NMR see Tables 1 and 2.

Pentamethyl ether acetate (**7**). Prisms, mp 166–167°, HR-MS *m/z* 670.2018 $[M]^+$ (calcd for $C_{37}H_{34}O_{12}$, 670.2047). ^{1}H NMR ($CDCl_3$): δ7.12 (2H, *d*, J=8.8 Hz), 6.90 (2H, *d*, J=8.8 Hz), 6.79 (2H, *d*, J=8.8 Hz), 6.67 (2H, *d*, J=8.8 Hz), 6.06 (1H, *d*, J=2.2 Hz), 6.03 (1H, *d*, J=2.2 Hz), 5.86 (1H, *s*), 5.79 (1H, *s*), 5.14 (1H, *m*), 5.02 (1H, *d*, J=3.4 Hz), 3.76, 3.74, 3.72, 3.69, 3.43 (each 3H, *s*), 2.50 (1H, *dd*, J=17.6, 4.1 Hz), 2.38 (1H, *dd*, J=17.6, 4.4 Hz), 1.80 (3H, *s*). ^{13}C NMR ($CDCl_3$): δ186.99 (*s*), 183.25 (*s*), 170.24 (*s*), 169.35 (*s*), 167.13 (*s*),



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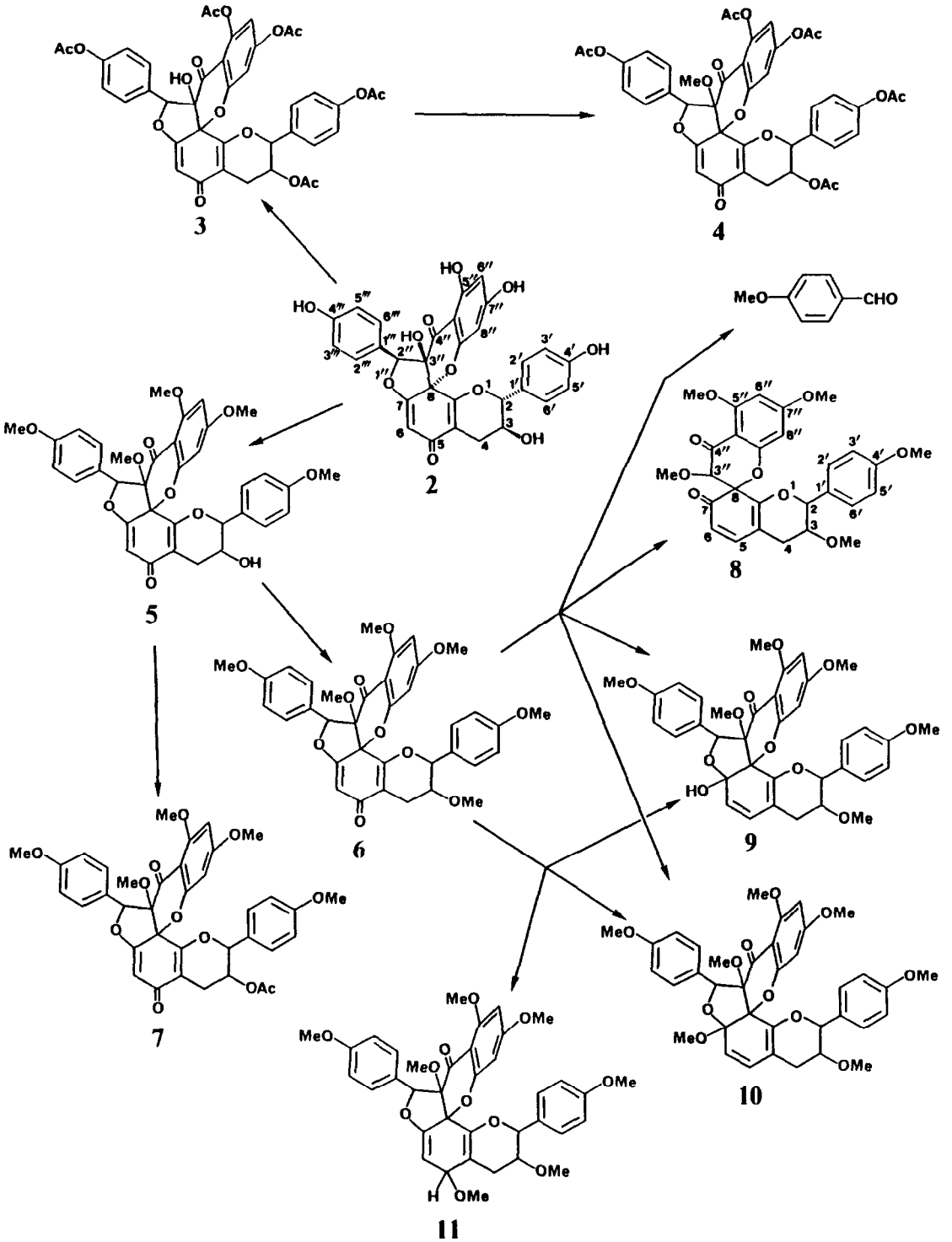

163.17 (*s*), 162.70 (*s*), 160.75 (*s*), 160.17 (*s*), 157.56 (*s*), 129.87 (*d*) × 2, 128.83 (*s*), 127.26 (*d*) × 2, 124.39 (*s*), 114.27 (*d*) × 2, 113.89 (*d*) × 2, 110.25 (*s*), 105.05 (*s*), 102.53 (*d*), 94.50 (*d*), 94.45 (*d*), 91.25 (*d*), 86.15 (*s*), 84.90 (*s*), 79.17 (*d*), 68.39 (*d*), 56.53 (*q*), 56.04 (*q*), 55.60 (*q*), 55.53 (*q*), 55.48 (*q*), 20.95 (*q*), 20.84 (*t*).

Reduction of compound **6** *followed by treatment of* 2 M HCl. A mixture of **6** (500 mg) in tetrahydrofuran (15 ml) and $NaBH_4$ (500 mg) in EtOH (15 ml) was stirred and allowed to stand at room temp. overnight. The reaction mixture was acidified with 2 M HCl, then extracted with EtOAc. EtOAc soln was dried and concd *in vacuo*. The residue was purified by CC on silica gel (hexane–EtOAc, 2:3) to give *p*-anisaldehyde (10 mg), **8** (40 mg), **9** (100 mg) and **10** (100 mg). Compound **8**: yellow viscous oil, HR-MS *m/z* 508.2095 $[M]^+$ (calcd for $C_{29}H_{32}O_8$, 508.2095). UV λ_{max}^{MeOH} nm

(log ε): 392 (3.28), 276 (3.88), 223 (4.37). CD (MeOH; c 2.36 $\times 10^{-5}$) $\Delta\varepsilon^{25}$ (nm): 0 (380), −8.3 (318), 0 (287), +9.1 (267), 0 (242), −3.2 (233), 0 (231), +18.6 (216), +5.1 (205). ^{1}H and ^{13}C NMR see Tables 1 and 2. Compound **9**: pale yellow viscous oil. HR-MS m/z 644.2193 $[M]^+$ (calcd for $C_{36}H_{36}O_{11}$, 644.2254). UV $\lambda_{max}^{dioxane}$ nm (log ε): 360 sh (3.27), 322 sh (3.63), 282 (4.18), 227 (4.55). ORD (dioxane; c 0.47) $[\alpha]^{24}$ (nm): −204.3° (589), −331.9° (500), −823.4° (400). CD (dioxane; c 1.55 × 10^{-5}) $\Delta\varepsilon^{25}$ (nm): 0 (382), −2.3 (347), −1.2 (326), −12.1 (303), 0 (287), +1.0 (284), 0 (281), −5.7 (270), −2.0 (240), −9.2 (230), 0 (222). ^{1}H and ^{13}C NMR see Tables 1 and 2. Compound **10**: pale yellow viscous oil, $C_{37}H_{38}O_{11}$, EI-MS m/z 659 $[M+1]^+$. UV λ_{max}^{MeOH} nm (log ε): 328 sh (3.68), 294 (4.16), 281 sh (4.10), 227 (4.47). CD (MeOH; c 2.13 × 10^{-5}) $\Delta\varepsilon^{25}$ (nm): 0 (380), −2.6 (349), −1.3 (332), −14.7 (309), 0 (298), +4.8 (291), 0 (285), −7.6 (270), −4.3 (250), −1.4 (239), −10.3 (230), 0 (222), +7.1 (214), 0 (208). ^{1}H and ^{13}C NMR see Tables 1 and 2.

Reduction of compound **6** *followed by treatment with* H_2O. A mixture of **6** (500 mg) in tetrahydrofuran (15 ml) and $NaBH_4$ (500 mg) in EtOH (15 ml) was stirred and allowed to stand at room temp. overnight. The reaction mixture was diluted with H_2O and extracted with EtOAc. The EtOAc soln was dried and concd *in vacuo*. The residue was purified by CC on silica gel ($CHCl_3$–MeOH, 30:1) and RP-18 (80%-MeOH) to give **9** (20 mg), **10** (100 mg) and **11** (120 mg). Compound **11**: pale yellow viscous oil, $C_{37}H_{38}O_{11}$, EI-MS m/z 659 $[M+1]^+$. UV λ_{max}^{MeOH} nm (log ε): 325 sh (3.55), 294 (4.12), 280 sh (4.00), 228 (4.55). CD (MeOH; c 1.82 × 10^{-5}) $\Delta\varepsilon^{25}$ (nm): 0 (370), −13.6 (322), −11.3 (305), −12.1 (296), −1.8 (266), −18.9 (237), 0 (230), +46.5 (219), 0 (205). ^{1}H and ^{13}C NMR see Tables 1 and 2.

Methylation of compound **9**. Compound **9** (40 mg) in $CHCl_3$ (2 ml) was reacted with CH_3I (1 ml) and Ag_2O (500 mg) under reflux for 5 hr. The reaction mixture was purified with CC on RP-18 (80%-MeOH) to give **10** (12 mg).

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