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Chemical Studies on the Heartwood of *Cassia garrettiana* CRAIB. III. Structures of Two New Polyphenolic Compounds

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Two new polyphenols, cassigarol A and cassigarol B, have been isolated from the heartwood of *Cassia garrettiana* CRAIB. (Thai drug "sa mae sarn," Leguminosae). The structures of cassigarol A and cassigarol B were determined by means of chemical studies and spectral and X-ray analyses.

Keywords——*Cassia garrettiana*; Leguminosae; polyphenol; cassigarol A; cassigarol B; stilbene dimer; X-ray analysis

The Thai drug "sa mae sarn" is the heartwood of *Cassia garrettiana* CRAIB. (Leguminosae) and has been used as a mild cathartic in folk medicine. Previous studies on this plant have led to the isolation and identification of anthraquinones, a stilbene, bibenzyls and flavonoids.[1,2] In a continuation of our chemical investigation of this drug, two new phenolic compounds, cassigarol A (**1**) and B (**2**) were isolated. This paper deals with the structure elucidation of compounds **1** and **2**.

Cassigarol A (**1**), $C_{28}H_{24}O_8$, a pale brown viscid oil, optically inactive, gave a grayish purple coloration with Gibb's reagent. The ultraviolet (UV) spectrum of **1** showed the absorption maximum at 284 nm. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **1** (Table I) showed the presence of a 6-monosubstituted 2,4-dioxyphenyl group [δ 6.09 (d, J=2.3 Hz) and 6.05 (d, J=2.3 Hz)], a 6-monosubstituted 3,4-dioxyphenyl group [δ 6.27 (s) and 6.15 (s)], a 3,4-dioxyphenyl group [δ 6.70 (d, J=7.9 Hz), 6.62 (d, J=2.0 Hz) and 6.52 (dd, J=2.0, 7.9 Hz)], a 3,5-dioxyphenyl group [δ 6.04 (d, J=2.3 Hz) and 5.99 (t, J=2.3 Hz)] and two pairs of adjacent benzyl methine and benzyl methylene group [δ 4.58 (dd, J=7.0, 9.0 Hz), 3.18 (dd, J=9.0, 14.0 Hz), 3.05 (dd, J=7.0, 14.0 Hz) and 3.78 (dd, J=4.0, 13.0 Hz), 3.64 (dd, J=13.0, 16.0 Hz), 2.52 (dd, J=4.0, 16.0 Hz)] in addition to eight phenolic hydroxyl groups (δ 8.98, 8.94, 8.94, 8.87, 8.79, 8.64, 8.42, 8.37). The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **1** (Table I) showed two methine carbon signals, two methylene carbon signals, six phenolic carbon signals assigned to a total of 8 atoms, eight nonsubstituted aromatic carbon signals (a total of 10 atoms) and five substituted aromatic carbon signals (a total of 6 atoms). The acetylation and the methylation of **1** afforded an octaacetate (**3**), $C_{44}H_{40}O_{16}$, colorless crystals, mp 189—190 °C and an octamethyl ether (**4**), $C_{36}H_{40}O_8$, pale yellow viscid oil, whose NMR data are given in Table I and the experimental section. From these NMR data and the findings that this plant contains piceatannol (3,4,3′,5′-tetrahydroxystilbene) in large quantities and that fragments corresponding to $[C_{19}H_{19}O_4]^+$ and $[C_{27}H_{29}O_6]^+$ were observed in the high resolution mass spectrum (HR-MS) of **4**, it was assumed that **1** is a stilbene dimer, **1a** or **1b**, having a 10, 11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene skeleton like that of hopeaphenol[3] or balanocarpol.[4] The degradation of **4** with CrO_3 in 85% HOAc gave 3,5-dimethoxybenzaldehyde (**5**) and a compound (**6**), $C_{24}H_{22}O_8$, orange needles, mp 116—118 °C, whose infrared (IR) absorption

TABLE I. NMR Data for Compounds **1** (in DMSO-d_6) and **4** (in $CDCl_3$)

	1			**4**		
	^{13}C-NMR	^{1}H-NMR	J (Hz)	^{13}C-NMR	^{1}H-NMR	J (Hz)
1	119.9	6.15 s		116.1	6.26 s	
2	143.2			147.4[b]		
3	143.2			146.8[b]		
4	118.5	6.27 s		115.6	6.37 s	
4a	141.0			141.6[c]		
5	43.1	4.58 dd	7.0, 9.0	44.5	4.88 dd	7.5, 9.0
5a	120.9			123.7		
6	154.3			157.4		
7	100.2	6.09 d	2.3	97.9	6.28 d	2.3
8	155.5			159.0		
9	107.6	6.05 d	2.3	106.4	6.39 d	2.3
9a	131.7[a]			133.2[d]		
10	42.4	3.64 dd	13.0, 16.0	43.4	3.71 dd	13.0, 14.5
		2.52 dd	4.0, 16.0		2.84 dd	4.0, 14.5
11	48.8	3.78 dd	4.0, 13.0	49.8	4.18 dd	4.0, 13.0
11a	141.0			142.0[c]		
α	45.1	3.18 dd	9.0, 14.0	45.2	3.39 dd	9.0, 13.5
		3.05 dd	7.0, 14.0		3.28 dd	7.5, 13.5
1′	132.8[a]			133.5[d]		
2′	107.1	6.04 d	2.3	107.6	6.25 d	2.3
3′	157.7			160.4		
4′	100.2	5.99 t	2.3	96.7	6.29 t	2.3
5′	157.7			160.4		
6′	107.1	6.04 d	2.3	107.6	6.25 d	2.3
1″	142.2			143.4		
2″	115.5	6.62 d	2.0	111.4	6.75 d	2.3
3″	145.1			149.2		
4″	142.9			146.3		
5″	115.6	6.70 d	7.9	111.6	6.87 d	8.0
6″	118.7	6.52 dd	2.0, 7.9	120.4	6.78 dd	2.3, 8.0
OH (OMe)		8.98 s		56.2	3.90 s	
		8.94 s		56.0	3.87 s	
		8.94 s		55.9	3.80 s	
		8.87 s		55.8	3.70 s	
		8.79 s		55.7	3.70 s	
		8.64 s		55.3	3.69 s	
		8.42 s		55.2	3.67 s	
		8.37 s		55.1	3.52 s	

a—*d*) Assignments may be reversed. Assignments of the carbon signals were based on ^{13}C–^{1}H COSY data.

bands at 1670 and 1640 cm^{-1} and UV absorption maxima at 206.5, 237.0, 265.0 and 404.0 nm suggested the presence of a benzoquinonyl group.[5] The ^{1}H-NMR spectrum of **6** (Table II) showed the presence of a 3,4-dioxyphenyl group [δ 6.78 (d, J=8.0 Hz), 6.73 (dd, J=2.3, 8.0 Hz) and 6.68 (d, J=2.3 Hz)], 2-oxy-1,4-benzoquinon-5-yl group [δ 6.50 (d, J=1.0 Hz) and 5.90 (s)], 2-oxy-1,4-benzoquinon-6-yl group [δ 6.35 (ddd, J=1.0, 1.5, 2.3 Hz) and 5.83 (d, J=2.3 Hz)] and adjacent methine and methylene groups [δ 4.40 (ddd, J=1.0, 8.0, 9.0 Hz), 3.05 (ddd, J=1.0, 9.0, 15.0 Hz), 2.97 (ddd, J=1.5, 8.0, 15.0 Hz)] in addition to four methoxyl groups (δ 3.84, 3.84, 3.81 and 3.80). In this NMR spectrum, spin–spin coupling was observed between the C-6 proton signal (6.50) of the 2-oxy-1,4-benzoquinon-5-yl group and a methine

TABLE II. NMR Data for Compound **6** in $CDCl_3$

	^{13}C-NMR	^{1}H-NMR	*J* (Hz)		^{13}C-NMR	^{1}H-NMR	*J* (Hz)
1	182.3			1″	131.4		
2	158.4			2″	111.5	6.68 d	2.3
3	107.9	5.90 s		3″	149.2		
4	186.5			4″	148.4		
5	144.0			5″	111.5	6.78 d	8.0
6	130.2	6.50 d	1.0	6″	120.1	6.73 dd	2.3, 8.0
α	41.4	4.40 ddd	1.0, 8.0, 9.0	OMe	56.3	3.84	
β	32.5	3.05 ddd	1.0, 9.0, 15.0		56.0	3.84	
		2.97 ddd	1.5, 8.0, 15.0		55.9	3.81	
1′	181.7				55.9	3.80	
2′	158.8						
3′	107.2	5.83 d	2.3				
4′	186.9						
5′	134.3	6.35 ddd	1.0, 1.5, 2.3				
6′	151.1						

Assignments of the carbon signals were based on ^{13}C–^{1}H COSY and ^{13}C–^{1}H long-range coupling experiments.

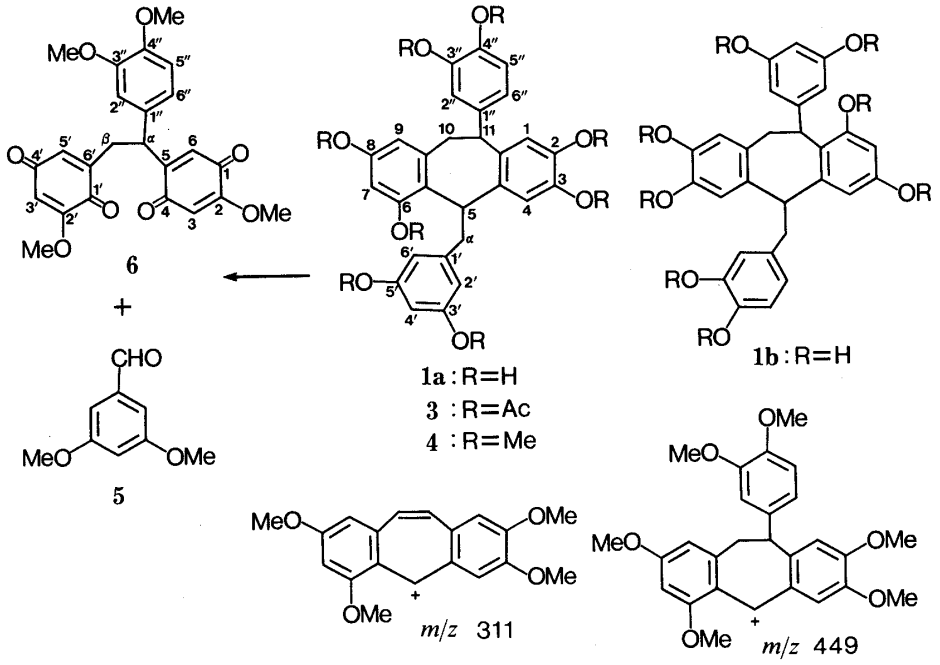


Fig. 1

proton signal (4.40), and between the C-5 proton signal (6.35) of the 2-oxy-1,4-benzoquinon-6-yl group and methylene proton signals (3.05 and 2.97). In the ^{13}C-NMR spectrum the characteristic signals of benzoquinonyl groups were also observed (Table II).[6] From these results, the structure of **6** was decided as formula **6**.

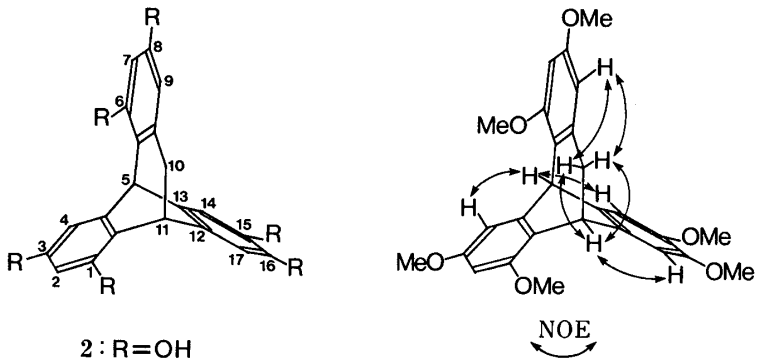
On the basis of these findings, the structure of **1** was established to be **1a**.

Cassigarol B (**2**), $C_{21}H_{16}O_6$, a pale brown viscid oil, optically inactive, gave a grayish purple coloration with Gibb's reagent. The UV spectrum of **2** showed absorption maxima at 208.5 and 280.5 nm. The ^{1}H-NMR spectrum of **2** (Table III) showed the presence of two 6-monosubstituted 2,4-dioxyphenyl groups [δ 6.04 (d, J=2.0 Hz), 6.11 (d, J=2.0 Hz) and 6.02

TABLE III. NMR Data for Compounds **2** (in DMSO-d_6) and **8** (in $CDCl_3$)

	2			**8**		
	^{13}C-NMR	^{1}H-NMR	J (Hz)	^{13}C-NMR	^{1}H-NMR	J (Hz)
1	155.5[a]			156.0[d]		
2	99.6	6.04 d	2.0	96.3	6.29 d	2.3
3	153.3[a]			158.5[d]		
4	103.2	6.11 d	2.0	102.2	6.53 d	2.3
4a	147.9			147.8		
5	41.1	5.05 s		42.0	5.52 s	
5a	120.3			123.1		
6	155.2[a]			156.3[d]		
7	99.5	6.02 d	2.0	96.5	6.23 d	2.3
8	153.2[a]			159.0[d]		
9	108.7	5.72 d	2.0	107.9	6.02 d	2.3
9a	132.8			134.1		
10	36.2	2.80 d	3.0	36.3	3.14 d	3.6
11	35.4	4.19 t	3.0	36.4	4.57 t	3.6
11a	117.9			121.5		
12	136.9[b]			137.4[e]		
13	136.0[b]			137.2[e]		
14	112.4	6.57 s		109.3	6.87 s	
15	142.5[c]			147.0[f]		
16	142.2[c]			147.2[f]		
17	113.4	6.69 s		110.0	6.93 s	
OH (OMe)		9.12 s		56.2	3.90 s	
		9.10 s		56.2	3.85 s	
		8.86 s		55.5	3.84 s	
		8.73 s		55.5	3.83 s	
		8.53 s		55.4	3.77 s	
		8.47 s		55.1	3.65 s	

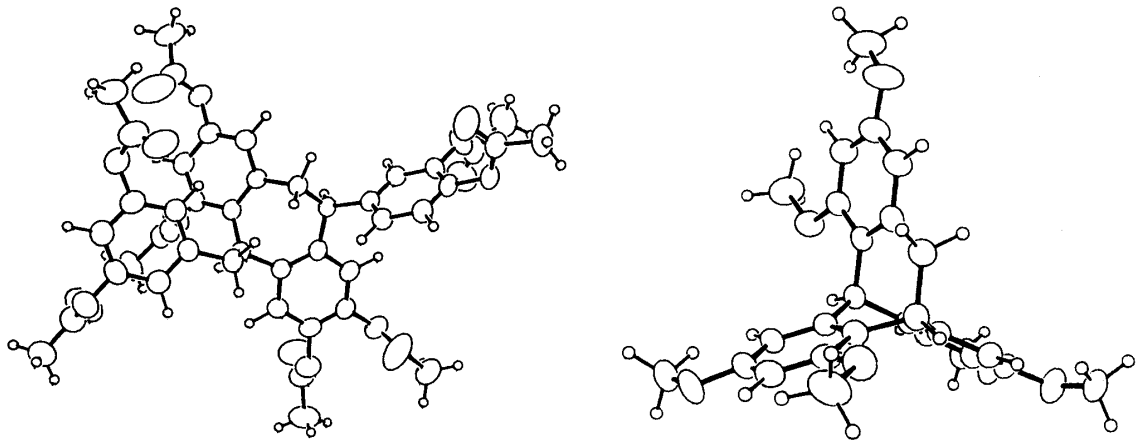
a—*f*) Assignments may be reversed. Assignments of the carbon signals were based on ^{13}C–^{1}H COSY data.



2 : R=OH
7 : R=OAc
8 : R=OMe

Fig. 2

(d, J=2.0 Hz), 5.72 (d, J=2.0 Hz)], a 2,4,5-trisubstituted phenyl group [δ 6.57 (s), 6.69 (s)], a benzyl methine [δ 5.05 (s)], a pair of adjacent benzyl methine and benzyl methylene groups [δ 4.19 (t, J=3.0 Hz), 2.80 (2H, d, J=3.0 Hz) and six hydroxyl groups (δ 9.12s, 9.10s, 8.86s, 8.73s, 8.53s, 8.47s). The ^{13}C-NMR spectrum of **2** (Table III) showed a methylene carbon



3 8

Fig. 3

TABLE IV. Crystal Data for Compounds **3** and **8**

	3	**8**
Formula	$C_{44}H_{40}O_{16}\cdot CHCl_3$	$C_{27}H_{28}O_6$
M_r	944.17	448.52
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Cell dimensions		
$a=$(Å)	12.518 (3)	31.505 (9)
$b=$(Å)	8.385 (2)	8.761 (1)
$c=$(Å)	44.239 (21)	17.722 (5)
$\beta=$(°)	93.80 (6)	110.27 (3)
$V=$(Å^3)	4633 (3)	4588 (6)
Z	4	8
D_x (Mg/m^3)	1.354	1.299
μ (cm^{-1})	23.99	7.058
F (000)	1960	1904

signal, two methine carbon signals, six phenolic carbon signals, six nonsubstituted aromatic carbon signals and six substituted aromatic carbon signals. The acetylation and the methylation of **2** gave a hexaacetate (**7**), $C_{33}H_{28}O_{12}$, pale yellow viscid oil and a hexamethyl ether (**8**), $C_{27}H_{28}O_6$, colorless fine crystals, mp 173—174 °C, whose NMR data are given in Table III and in the experimental section. Nuclear Overhauser effect (NOE) experiments among two benzyl methine protons, benzyl methylene protons and the aromatic protons of **8** were undertaken. When the benzylmethine proton at δ 5.52 was irradiated, NOE was observed at two aromatic protons at δ 6.53 (17.5%) and δ 6.87 (14.1%) and the irradiation of the benzylmethine proton at δ 4.57 resulted in NOE enhancement of an aromatic proton signal at δ 6.93 (15.1%). When the benzylmethylene proton at δ 3.14 was irradiated, NOE was observed at an aromatic proton signal at δ 6.02 (23.6%) and a methine proton signal at δ 4.57 (14.5%). From these results, the structure of **2** was established to be formula **2** (Fig. 2).

Further, the structures of **1** and **2** were supported by the results of X-ray analyses of **3** and **8**. The ORTEP drawings and the crystal data of **3** and **8** are given in Fig. 3 and Table IV.

Since **1** and **2** were detected in the cold methanol extract by chromatography, it can be presumed that these compounds were originally contained in this crude drug. However, it is doubtful whether they are natural products because of their optical inactivity.

Experimental

All melting points were measured on a Büchi melting point apparatus and are uncorrected. The UV spectra were recorded with a Shimadzu UV-200S spectrometer, and the IR spectra with a Hitachi EPI-G2 spectrometer. The MS were taken with a Hitachi M-80 spectrometer and JEOL JMS-HX100 spectrometer. The ^{1}H- and ^{13}C-NMR spectra were taken with a Varian XL-300 spectrometer with tetramethylsilane as an internal standard. Column chromatography was carried out on Merck Silica gel 60 F_{254} (70—230 mesh) and Sephadex LH-20. For thin layer chromatography (TLC) and preparative TLC, Merck Silica gel 60 F_{254} plates (0.25 mm) and Whatman linear-K silica gel PLK 5F (concentrating zone, 1 mm) were employed and the developed spots were detected under a UV lamp (253.6 and 365 nm).

Isolation of the Compounds——The dried and crushed lignum of *Cassia garrettiana* (10 kg) was extracted 3 times by refluxing with MeOH (20 l) for 5 h (for each extraction). The MeOH extract (1080 g) was chromatographed on silica gel (4.6 kg) with a mixture of hexane–EtOAc, and the eluate was collected in fractions (400 ml/fraction): fr. 1–111 (3 : 1), fr. 112–193 (2 : 1) and fr. 193–496 (1 : 1) (figures in parentheses show the solvent ratio in v/v). Fr. 212–364 (138 g), containing polyphenols, was rechromatographed on polyamide (MeOH) followed by Sephadex LH 20 (MeOH) to give cassigarol A (**1**) (16.3 g) and cassigarol B (**2**) (1.8 g).

Cassigarol A (1)——Pale brown viscid oil. Optically inactive. Gibb's test: grayish purple, UV λ_{max}^{MeOH} nm (log ε): 284.0 (4.03). *Anal.* Calcd for $C_{28}H_{24}O_8 \cdot 3/2H_2O$: C, 65.23; H, 5.23. Found: C, 65.15; H, 5.49. FAB-MS *m/z*: 489 $(M+H)^+$. ^{1}H- and ^{13}C-NMR data are summarized in Table I.

Acetylation of 1——A solution of **1** (3.0 g) in a mixture of Ac_2O (30 ml) and AcONa (3.0 g) was heated for 3 h under reflux. The reaction mixture was treated in the usual way to afford **3** (2.8 g). **3**: Colorless fine crystals, mp 189—190 °C. EI-MS *m/z*: 826 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 1750, 1600, 1500. ^{1}H-NMR (in $CDCl_3$) δ: 7.22 (1H, d, J=8.3 Hz), 7.09 (1H, dd, J=8.3, 2.3 Hz), 7.08 (1H, d, J=2.3 Hz), 6.91 (1H, d, J=2.3 Hz), 6.79 (1H, t, J=2.3 Hz), 6.76 (1H, d, J=2.3 Hz), 6.73 (1H, s), 6.67 (1H, s), 6.62 (2H, d, J=2.3 Hz), 4.32 (1H, dd, J=7.5, 6.3 Hz), 4.31 (1H, dd, J=13.1, 4.0 Hz), 3.90 (1H, dd, J=14.8, 13.1 Hz), 3.52 (1H, dd, J=13.2, 7.5 Hz), 3.34 (1H, dd, J=13.2, 6.3 Hz), 2.94 (1H, dd, J=14.8, 4.0 Hz), 2.31 (6H, s), 2.27 (9H, s), 2.24 (3H, s), 2.21 (3H, s), 2.17 (3H, s). ^{13}C-NMR (in DMSO-d_6) δ: 169.2 (s) × 3, 169.1 (s), 168.6 (s), 168.5 (s), 168.4 (s) × 2, 150.8 (s) × 2, 149.3 (s), 148.3 (s), 146.5 (s), 142.3 (s), 142.2 (s), 141.3 (s), 140.8 (s) × 2, 140.0 (s), 139.2 (s), 138.4 (s), 130.3 (s), 127.7 (d), 127.0 (d), 126.8 (d), 124.2 (d), 123.6 (d), 121.0 (d), 120.0 (d) × 2, 114.8 (d), 114.0 (d), 47.9 (d), 45.5 (t), 42.8 (d), 40.3 (t), 20.7 (q) × 3, 20.4 (q), 20.3 (q) × 2, 20.2 (q), 20.1 (q).

Methylation of 1——**1** (3.0 g) was methylated with $(CH_3)_2SO_4$ (20 g) and K_2CO_3 (15 g) in dry acetone in the usual way. The product was purified by chromatography on silica gel with $CHCl_3$ to afford **4** (2.4 g). **4**: Pale yellow viscid oil, HR-MS *m/z*: $C_{36}H_{40}O_8$ (M^+); Calcd 600.2721, Found 600.2740. $C_{27}H_{29}O_6$; Calcd 449.1962, Found 449.1959. $C_{19}H_{19}O_4$; Calcd 311.1281, Found 311.1266. ^{1}H- and ^{13}C-NMR data are summarized in Table I.

Oxidation of 4——A solution of **4** (1 g) in AcOH (20 ml) was added dropwise with stirring to a mixture of dry CrO_3 (1.5 g), AcOH (35 ml) and H_2O (5 ml) at 5—10 °C and the whole was stirred for 7 h. The reaction mixture was diluted with H_2O, treated with $NaHCO_3$ and extracted with EtOAc. The EtOAc extract was dried and concentrated *in vacuo*. The product was purified by chromatography on silica gel with hexane–AcOEt (1 : 2) to give compound **5** (13.8 mg), which was identical with an authentic commercial sample of 3,5-dimethoxybenzaldehyde, and compound **6** (26.5 mg). **6**: Orange needles, mp 116—118 °C. HR-MS *m/z*: $C_{24}H_{22}O_8$ (M^+); Calcd 438.1313, Found 438.1317. $C_{16}H_{15}O_5$; Calcd 287.0918, Found 287.0901. UV λ_{max}^{MeOH} nm (log ε): 206.5 (4.69), 237.0 (4.32), 265.0 (4.54), 404.0 (3.24). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1670, 1640, 1600, 1510. ^{1}H- and ^{13}C-NMR data are summarized in Table II.

Cassigarol B (2)——Pale brown viscid oil, HR-MS *m/z*: $C_{21}H_{16}O_6$ (M^+); Calcd 364.0945, Found 364.0945. Gibb's test: grayish purple, UV λ_{max}^{MeOH} nm (log ε): 208.5 (4.47), 280.5 (3.72), optically inactive. ^{1}H and ^{13}C-NMR data were summarized in Table III.

Acetylation of 2——A solution of **2** (40 mg) in a mixture of Ac_2O (10 ml) and AcONa (2 g) was heated for 3 h under reflux. The reaction mixture was treated in the usual way to afford **7** (33.6 mg). **7**: Pale yellow viscid oil, EI-MS *m/z*: 616 (M^+). UV λ_{max}^{EtOH} nm (log ε): 213.0 (4.67), 269.0 (3.87). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1610, 1590, 1500. ^{1}H-NMR (in $CDCl_3$) δ: 7.22 (1H, s), 7.04 (1H, s), 6.88 (1H, d, J=2.3 Hz), 6.80 (1H, d, J=2.3 Hz), 6.66 (1H, d, J=2.3 Hz), 6.55 (1H, d, J=2.3 Hz), 5.05 (1H, s), 4.30 (1H, t, J=3.5 Hz), 3.21 (2H, m), 2.50 (3H, s), 2.38 (3H, s), 2.26 (6H, s), 2.25 (3H, s), 2.20 (3H, s). ^{13}C-NMR (in $CDCl_3$) δ: 169.3 (s), 168.9 (s), 168.8 (s), 168.2 (s) × 2, 168.1 (s), 149.3 (s), 149.2 (s), 147.0 (s), 146.8 (s), 144.9 (s), 140.8 (s), 140.4 (s), 140.3 (s), 138.2 (s), 137.3 (s), 129.3 (s), 128.9 (s), 122.6 (d), 121.1 (d), 120.8 (d), 116.9 (d), 114.3 (d), 113.7 (d), 43.7 (d), 37.6 (d), 35.3 (t), 21.1 (q), 21.0 (q) × 2, 20.9 (q), 20.6 (q) × 2.

Methylation of 2——**2** (40 mg) was treated in the same way as **1**. The product was purified by chromatography on silica gel (hexane : AcOEt = 2 : 1) to afford **8** (31.8 mg). **8**: Off-white fine crystals, mp 173—174 °C. UV λ_{max}^{EtOH} nm (log ε): 282.5 (3.93). IR ν_{max}^{Nujol} cm^{-1}: 1600, 1590, 1510. ^{1}H- and ^{13}C-NMR data are summarized in Table III.

X-Ray Analysis of 3 and 8——Single crystals of **3** and **8** were grown by the slow evaporation of a hexane–$CHCl_3$ solution. The unit cell dimensions were determined and refined on an AFC-5 (Rigaku Denki Co.) with graphite-monochromated Cu-K_α radiation. A crystal of **3** was sealed in a glass capillary with a small amount of the mother solution, because this crystal included chloroform molecules. The crystal data for both compounds are given in Table

IV. The intensity data were collected with a θ–2θ scan mode at 6 °/min, and the scan angles of $(1.70+0.15\tan\theta)°$ and $(1.10+0.15\tan\theta)°$ were applied for **3** and **8**, respectively. The structures of both compounds were solved by the direct method using the MULTAN 80 programs. The structures were refined by the blockdiagonal least-squares methods minimizing $\Sigma w|F_O-F_C|$, where $w=1/(\sigma(F_O)^2+a\,F_O+b\,F_O^2)$. Anisotropic temperature factors were applied for non-hydrogen atoms. The hydrogen atoms on the stereochemically ideal position were calculated and included in the structure factor calculation with isotropic temperature factors. The final R-value of 0.1104 for 5327 reflections and the constant $a=0.24269$ and $b=0.00494$ were obtained for **3**. For **8**, the R-value 0.0928 for 3923 reflections and $a=0.32730$ and $b=0.00091$ were obtained.

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References and Notes

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