Two New Endiandric Acid Analogs, a New Benzopyran, and a New Benzenoid from the Root of *Beilschmiedia erythrophloia*

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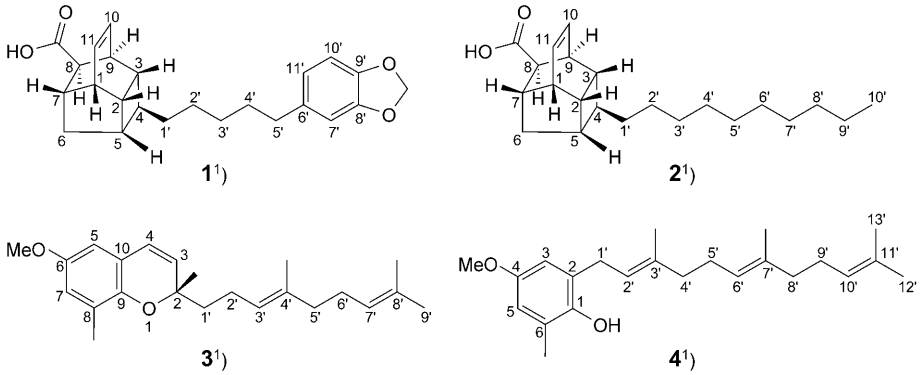
Phytochemical investigation of the root of *Beilschmiedia erythrophloia* led to the isolation and structural elucidation of two new endiandric acid analogs, endiandric acids I and J (**1** and **2**, resp.), a new benzopyran, dehydrooligandrol methyl ether (**3**), and a new benzenoid, farnesylol (**4**), together with six known compounds. Their structures were established on the basis of extensive 1D- and 2D-NMR analyses in combination with HR-MS experiments.

Introduction. – The genus *Beilschmiedia* (Lauraceae), comprising *ca*. 200 species, is widely distributed throughout tropics regions, with only 2 species occurring in Taiwan, *B. erythrophloia* HAY. and *B. tsangii* MERR. [1]. Endiandric acids [2], benzopyrans [2], arylpropanoids [2], aporphines [3], bisbenzylisoquinolines [4], and flavonoids [5] are widely distributed in plants of the genus *Beilschmiedia*. Several constituents have shown biological activities such as antibacterial [2] and antimalarial [4] activities. In our recent study, several cytotoxic and antitubercular compounds were isolated from the leaves [6] and the stems [7] from Formosan *B. tsangii*.

B. erythrophloia HAY. is an evergreen tree, distributed in Indochina, south China, Hainan Island, Ryukyus, and throughout Taiwan [1]. The chemical constituents and biological properties of this plant have never been investigated. Recently, over 1,000 species of Formosan plants have been screened for *in vitro* antimycobacterial activities, and *B. erythrophloia* has been found to be one of the active species. We describe herein the isolation and structural elucidation of two new endiandric acid analogs, endiandric acids I and J (**1** and **2**, resp.), a new benzopyran, dehydrooligandrol methyl ether (**3**), and a new benzenoid, farnesylol (**4**), together with six known compounds, from the AcOEt-soluble fraction of the root of *B. erythrophloia*. The structural elucidations of these new compounds were based on spectroscopic analyses.

Results and Discussion. – The AcOEt-soluble fraction of the MeOH extract was fractionated by a combination of SiO_2 and *RP-18* columns, as well as preparative HPLC to yield ten compounds, the structures of which were elucidated by 1D- and 2D-NMR spectra and comparison with literature data.



Compound **1** was obtained as an optically inactive yellowish oil. $[\alpha]_D^{25} = 0$ ($c = 0.39$, $CHCl_3$). The molecular formula was determined as $C_{24}H_{28}O_4$ on the basis of the $[M + Na]^+$ peak at m/z 403.1882 (calc. 403.1885 for $C_{24}H_{28}NaO_4^+$) in its HR-ESI-MS. The UV absorptions (λ_{max} 234 and 286 nm) confirmed the presence of a benzenoid nucleus [8]. The bands at 2600–3300, 1701, and 1039 and 938 cm^{-1} in the IR spectrum revealed the presence of a OH group, C=O, and O–CH_2–O groups, respectively. Eleven indices of hydrogen deficiency (IHD) were determined from the molecular formula, ^{13}C-NMR (*Table 1*), and DEPT spectra. Based on further spectral evidences, the structure of **1** was elucidated as (1*RS*,1a*SR*,3*RS*,3a*RS*,6*RS*,6a*SR*,6b*SR*,7*SR*)-1-[5-(1,3-benzodioxol-5-yl)pentyl]-1,1a,2,3,3a,6,6a,6b-octahydro-3,6-methanocyclobut[*cd*]indene-7-carboxylic acid, designated as endiandric acid I [9], which was further confirmed by ^{13}C-NMR, COSY (*Fig. 1*), NOESY (*Fig. 1*), HSQC, and HMBC (*Fig. 1*) experiments and comparison with the spectroscopic data of endiandric acid C [2][10].

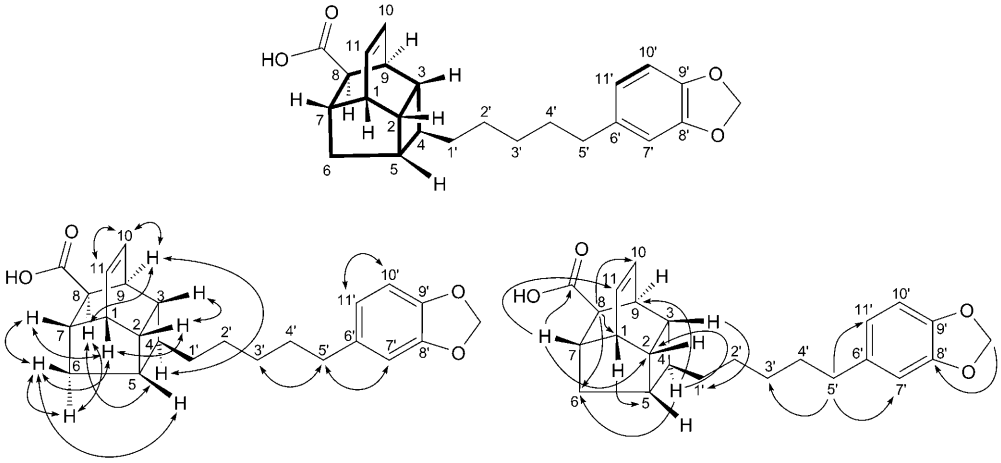


Fig. 1. *Significant COSY* (—), *NOESY* (↔), *and HMBC* (→) *correlations of* **1**[1])

[1]) Arbitrary numbering. For systematic name, see *Exper. Part*.

Table 1. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$, 400 and 100 MHz, resp.) *of* **1** *and* **2**[1]). δ in ppm, J in Hz.

	1		**2**	
	δ(C)	δ(H)	δ(C)	δ(H)
H–C(1)	41.8	2.66–2.71 (*m*)	41.8	2.69 (*ddd*, *J* = 7.2, 4.8, 2.0)
H–C(2)	40.1	2.35 (*dt*, *J* = 8.8, 5.6)	40.1	2.35 (*dt*, *J* = 8.4, 5.6)
H–C(3)	39.5	1.59–1.67 (*m*)	39.6	1.61–1.66 (*m*)
H–C(4)	39.4	1.59–1.67 (*m*)	39.4	1.61–1.66 (*m*)
H–C(5)	40.2	2.22 (*t*, *J* = 6.4)	40.2	2.23 (br. *t*, *J* = 6.8)
H_α–C(6)		1.51–1.53 (*m*)		1.54 (*d*, *J* = 12.6)
H_β–C(6)	38.5	1.96 (*ddd*, *J*= 12.8, 7.6, 5.6)	38.5	1.90 (*ddd*, *J* = 12.6, 7.6, 5.6)
H–C(7)	38.3	2.50–2.56 (*m*)	38.2	2.54 (*t*, *J* = 5.2)
H–C(8)	48.9	2.86 (*d*, *J* = 3.6)	48.9	2.87 (*d*, *J* = 4.0)
H–C(9)	35.0	3.02 (br. *s*)	35.0	3.02 (*dt*, *J* = 7.2, 4.8)
H–C(10)	131.3	6.22 (*ddd*, *J* = 10.4, 8.0, 1.6)	131.3	6.23 (*ddd*, *J* = 10.0, 8.0, 2.0)
H–C(11)	131.9	6.23 (*ddd*, *J* = 10.4, 8.0, 1.6)	131.9	6.23 (*ddd*, *J* = 10.0, 8.0, 2.0)
CH_2(1′)	36.2	1.42–1.50 (*m*)	36.3	1.43–1.50 (*m*)
CH_2(2′)	27.1	1.21–1.30 (*m*)	27.3	1.26 (br. *s*)
CH_2(3′)	29.1	1.21–1.30 (*m*)	29.4–29.7	1.26 (br. *s*)
CH_2(4′)	31.7	1.54–1.58 (*m*)	29.4–29.7	1.26 (br. *s*)
CH_2(5′)	35.6	2.52 (*t*, *J* = 7.6)	29.4–29.7	1.26 (br. *s*)
C(6′) or CH_2(6′)	136.7	–	29.4–29.7	1.26 (br. *s*)
H–C(7′) or CH_2(7′)	108.8	6.67 (*d*, *J* = 1.6)	29.4–29.7	1.26 (br. *s*)
C(8′) or CH_2(8′)	147.4	–	31.9	1.26 (br. *s*)
C(9′) or CH_2(9′)	145.4	–	22.7	1.26 (br. *s*)
H–C(10′) or Me(10′)	108.0	6.72 (*d*, *J* = 7.6)	14.1	0.88 (*t*, *J* = 6.6)
H–C(11′)	121.0	6.62 (*dd*, *J* = 7.6, 1.6)	–	–
OCH_2O	100.7	5.91 (*s*)	–	–
C=O	180.0	–	180.1	–

The ^{1}H-NMR spectrum of **1** (*Table 1*) showed signals of one methylenedioxyphenyl group at δ(H) 5.91 (*s*, OCH_2O), 6.67 (*d*, *J* = 1.6, H–C(7′)[1]), 6.72 (*d*, *J* = 7.6, H–C(10′)), and 6.62 (*dd*, *J* = 7.6, 1.6, H–C(11′)), two *cis*-form mutually-coupled vinyl H-atoms at δ(H) 6.22 (*ddd*, *J* = 10.4, 8.0, 1.6, H–C(10)) and 6.23 (*ddd*, *J* = 10.4, 8.0, 1.6, H–C(11)), and five CH_2 groups (δ(H) 1.42–1.50 (*m*, CH_2(1′)), 1.21–1.30 (*m*, CH_2(2′, 3′)), 1.54–1.58 (*m*, CH_2(4′)), 2.52 (*t*, *J* = 7.6, CH_2(5′))). In the ^{13}C-NMR spectrum, beside the signals corresponding to the above-mentioned H-atoms, there are still ten tertiary C-atoms including the two vinyl C-atoms C(10) (δ(C) 131.3) and C(11) (δ(C) 131.9) composing the remaining structure of **1**, which was very similar to that of endiandric acid C [2][10]. By the ^{1}H,^{1}H-COSY (*Fig. 1*) and HSQC data, a nine contiguous structural sequence was derived from correlations from H–C(1) (δ(H) 2.66–2.71; δ(C) 41.8) to H–C(11) (δ(H) 6.23; δ(C) 131.9), from H–C(11) to H–C(10) (δ(H) 6.22; δ(C) 131.3), from H–C(10) to H–C(9) (δ(H) 3.02; δ(C) 35.0), from H–C(9) to H–C(3) (δ(H) 1.59–1.67; δ(C) 39.5), from H–C(3) to H–C(2) (δ(H) 2.35; δ(C) 40.1), from H–C(2) to H–C(5) (δ(H) 2.22; δ(C) 40.2), from H–C(5) to and CH_2(6) (δ(H) 1.51–1.53, 1.96; δ(C) 38.5)), and from H–C(6) to H–C(7) (δ(H) 2.50–2.56; δ(C) 38.3)), in accord with the presence of a spin system corresponding to a

CH(1)–CH(11)–CH(10)–CH(9)–CH(3)–CH(2)–CH(5)–CH_2(6)–CH(7) moiety (*Fig. 1*).

The HMBC data (*Fig. 1*) made it possible to establish the full connectivity within the molecule. Correlations between the H-atom signal at δ(H) 2.50–2.56 (H–C(7)[1])) and the C-atom signal at δ(C) 131.9 (C(11)) revealed that C(1) (δ(C) 41.8) connected with C(7) (δ(C) 38.3), and the correlations from H–C(7) to C(2) (δ(C) 40.1) and from H–C(1) (δ(H) 2.66–2.71) to C(5) (δ(C) 40.2) established a five-membered ring of C(1)–C(2)–C(5)–C(6)–C(7) and a six-membered ring of C(1)–C(2)–C(3)–C(9)–C(10)–C(11). The other six-membered ring was composed of C(1)–C(7)–C(8)–C(9)–C(10)–C(11), ascertained by the ^{1}H,^{13}C-NMR long-range correlations between the H-atom signal at δ(H) 2.86 (H–C(8)) and the C-atom signals at δ(C) 41.8 (C(1)), and 131.3 (C(10)) in the HMBC spectrum. Finally, the correlations between the H-atom signal at δ(H) 1.59–1.67 (H–C(4)) and the C-atom signals at δ(C) 40.1 (C(2)), 38.5 (C(6)), and 35.0 (C(9)) confirmed the existence of a four-membered ring (C(2)–C(3)–C(4)–C(5)). A C=O group in the molecule was indicated by the band at 1701 cm^{-1} in the IR spectrum and confirmed by the signal at δ(C) 180.0 in the ^{13}C-NMR spectrum. HMBC Correlations between the C=O group (δ(C) 180.0) and both H–C(7) (δ(H) 2.50–2.56) and H–C(8) (δ(H) 2.86) established the position of the COOH group at C(8). Finally, the HMBC correlations of H–C(5)/C(1′), H–C(3)/C(1′) and H–C(5′)/C(7′/11′) indicated that the endiandric acid main skeleton and the (methylenedioxy)phenyl moiety were linked by five methylenes (CH_2(1′–5′)) at C(4) and C(6′), respectively. Complete ^{1}H and ^{13}C assignments (*Table 1*) were achieved through a combination of COSY, HSQC, HMBC, and NOESY experiments. The full assignments of the C-atom resonances based on HSQC and HMBC techniques were shown in *Table 1*.

The relative configuration of **1** was derived by a NOESY spectrum (*Fig. 1*) in combination with biogenetic considerations [11] and comparison with endiandric acid C [10], the relative configuration of which was based on an X-ray crystallographic analysis. According to the NOESY spectrum, the H–C(9) was α-oriented, which was confirmed by the NOE H–C(10)/H–C(9). NOEs for H–C(9)/H–C(4) and H–C(8) indicated that H–C(4) and H–C(8) were on the same side of the molecular plane, tentatively assumed as α-orientation. On the other hand, the NOE cross peaks H–C(3)/H–C(2), H–C(2)/H–C(1) and H–C(5), H–C(5)/H–C(6β), and H–C(6β)/H–C(7) demonstrated the *cis*-β-orientation of the H-atoms H–C(1), H–C(2), H–C(3), H–C(5), and H–C(7). Besides, no detectable NOESY effect could be observed between H–C(4) and H–C(5), and between H–C(7) and H–C(8), just as in endiandric acid C [11], and thus the α-orientation of H–C(4) and H–C(8) was confirmed. Thus, the relative configuration of H–C(1), H–C(2), H–C(3), H–C(4), H–C(5), H–C(7), H–C(8), and H–C(9) was assigned as (1*RS*,2*RS*,3*RS*,4*SR*,5*SR*,7*SR*,8*RS*,9*SR*)[1]), as in endiandric acid C [10]. In view of the optical inactivity, **1** was concluded to be racemic, the same as endiandric acid C [10][11].

Compound **2** was obtained as colorless needles with $[\alpha]_D^{25} = 0$ ($c = 0.44$, $CHCl_3$). The HR-ESI-MS exhibited a *quasi*-molecular ion peak at *m*/*z* 353.2455 ($[M+Na]^+$) corresponding to the molecular formula of $C_{22}H_{34}O_2$ and indicating six degrees of unsaturation. The IR spectrum of **2** displayed absorbtions for a OH group (3300–

3500 cm^{-1}), and a C=O group (1701 cm^{-1}), and the ^{1}H-NMR (*Table 1*), ^{13}C-NMR (*Table 1*), HMBC, COSY, and NOESY data confirmed the structure as (1*RS*,1a*SR*,3*R-S*,3a*RS*,6*RS*,6a*SR*,6b*SR*,7*SR*)-1-decyl-1,1a,2,3,3a,6,6a,6b-octahydro-3,6-methanocyclobut[*cd*]indene-7-carboxylic acid, named endiandric acid J.

The ^{1}H-NMR spectrum of **2** was similar to that of endiandric acid I (**1**), except that a decyl group (δ(H) 0.88 (*t*, J = 6.6, H–C(10′))[1]), 1.26 (br. *s*, H–C(2′–9′)), 1.43–1.50 (*m*, H–C(1′))) in **2** replaced the 5-(1,3-benzodioxol-5-yl)pentyl moiety in the C(4) position of **1**. Ten tertiary C-atoms including two *cis*-form vinyl C-atom signals at δ(C) 131.3 (C(10)), δ(C) 131.9 (C(11)) and a secondary C-atom (C(6)) composed the endiandric acid skeleton. The COOH group was also attached to C(8) (δ(C) 48.9), according to the HMBC ^3J correlation between C=O and both H–C(7) (δ(H) 2.54) and H–C(9) (δ(H) 3.02). A decyl group was located at C(4), confirmed by the HMBC correlations from H–C(1′) (δ(H) 1.43–1.50) to C(3) (δ(C) 39.6), H–C(5) (δ(H) 2.23) to C(1′) (δ(C) 36.3), and H–C(4) (δ(H) 1.61–1.66) to C(2′) (δ(C) 27.3). Because of the optical inactivity, **2** was also proposed to be racemic.

Compound **3** was isolated as colorless oil with $[\alpha]_D^{25} = -28.0$ (c = 0.72, $CHCl_3$). The HR-ESI-MS data determined the molecular formula to be $C_{23}H_{32}O_2$ (*m*/*z* 363.2303 ($[M + Na]^+$; calc. 363.2300)). The UV absorptions of **3** at 232 and 269 nm suggested the presence of a benzenoid nucleus [8]. The IR spectrum suggested the presence of an aromatic ring in the molecule at 1594 and 1468 cm^{-1}. The ^{1}H- and ^{13}C-NMR (*Table 2*), HMBC (*Fig. 2*), COSY (*Fig. 2*), and NOESY (*Fig. 2*) spectra were compatible with the structure of **3** as (2*S*)-2-[(3*E*)-4,8-dimethylnona-3,7-dien-1-yl]-6-methoxy-2,8-dimethyl-2*H*-1-benzopyran, named dehydrooligandrol methyl ether.

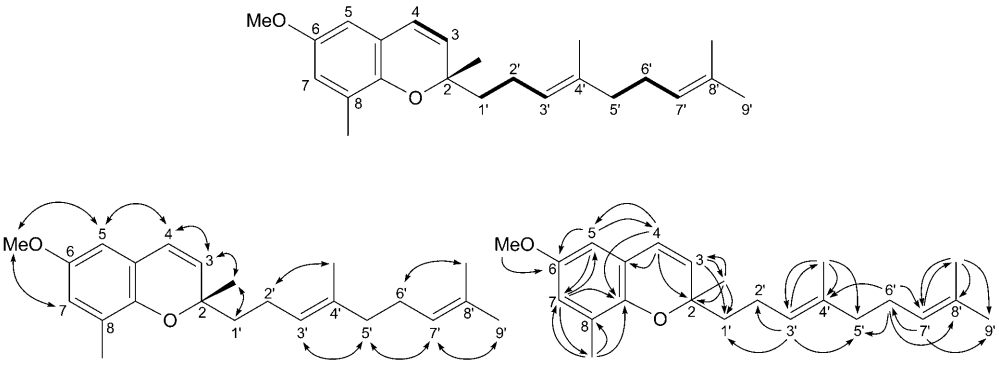


Fig. 2. *Significant COSY* (—), *NOESY* (↔), *and HMBC* (→) *correlations of* **3**[1])

The ^{1}H- and ^{13}C-NMR spectra (*Table 2*) of **3** were similar to those of oligandrol [2], also isolated in this study, except that a MeO group (δ(H) 3.73 (*s*, MeO–C(6))) and the C=C bond (δ(H) 5.58 (*d*, J = 9.6, H–C(3)[1])) and δ(H) 6.29 (*d*, J = 9.6, H–C(4))) of **3** replaced a OH group at C(6) and C(3)–C(4) (δ(H) 1.76 (*t*, J = 6.7, H–C(3)) and 2.73 (*t*, J = 6.7, H–C(4))) of oligandrol. Compound **3** showed laevorotatory optical activity with $[\alpha]_D^{25} = -28.0$ (c = 0.72, $CHCl_3$). With regard to the (*R*)-configuration of

Table 2. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$, 400 and 100 MHz, resp.) *of* **3** *and* **4**[1]). δ in ppm, J in Hz.

	3		**4**	
	δ(C)	δ(H)	δ(C)	δ(H)
C(1)	–	–	146.7	–
HO–C(1)	–	–	–	4.78 (*s*)
C(2)	77.8	–	125.4	–
Me(2)	25.9	1.36 (*s*)	25.7	1.67 (*s*)
H–C(3)	130.6	5.58 (*d*, *J* = 9.6)	112.9	6.53 (*d*, *J* = 3.0)
H–C(4) or C(4)	123.1	6.29 (*d*, *J* = 9.6)	153.0	–
MeO–C(4)	–	–	55.6	3.74 (*s*)
H–C(5)	108.8	6.38 (*d*, *J* = 3.0)	114.0	6.57 (*d*, *J* = 3.0)
C(6)	152.9	–	127.2	–
MeO–C(6) or Me(6)	55.6	3.73 (*s*)	16.0	2.22 (*s*)
H–C(7)	116.0	6.55 (*d*, *J* = 3.0)	–	–
C(8)	126.2	–	–	–
Me(8)	15.6	2.16 (*s*)	–	–
C(9)	145.0	–	–	–
C(10)	121.1	–	–	–
CH_2(1′)	40.8	1.65–1.70 (*m*)	30.5	3.33 (*d*, *J* = 7.2)
CH_2(2′) or H–C(2′)	22.6	2.12 (*td*, *J* = 8.4, 2.0)	121.6	5.30 (br. *t*, *J* = 7.2)
H–C(3′) or C(3′)	124.3	5.11 (*t*, *J* = 6.6)	138.8	–
Me(3′)	–	–	16.2	1.79 (*s*)
C(4′) or CH_2(4′)	135.2	–	39.7	1.96–2.17 (*m*)
Me(4′)	15.9	1.57 (*s*)	–	–
CH_2(5′)	39.7	1.93–1.97 (*m*)	26.3	1.96–2.17 (*m*)
CH_2(6′) or H–C(6′)	26.7	2.01–2.05 (*m*)	123.6	5.08 (br. *t*, *J* = 7.2)
H–C(7′) or C(7′)	124.1	5.08 (*t*, *J* = 6.6)	135.6	–
Me(7′)	–	–	16.2	1.59 (*s*)
C(8′) or CH_2(8′)	131.3	–	39.7	1.96–2.17 (*m*)
Me(9′) or CH_2(9′)	25.7	1.67 (*s*)	26.7	1.96–2.17 (*m*)
Me(10′) or H–C(10′)	17.7	1.58 (*s*)	124.3	5.08 (br. *t*, *J* = 7.2)
C(11′)	–	–	131.3	–
Me(12′)	–	–	25.7	1.67 (*s*)
Me(13′)	–	–	17.7	1.59 (*s*)

(+)-plastochromanol-8 [12] ($[\alpha]_D^{25} = -14.0$, $CHCl_3$), the absolute configuration at C(2) could be tentatively proposed as (*S*).

Compound **4** was obtained as colorless oil. The HR-ESI-MS data indicated the molecular formula to be $C_{23}H_{34}O_2$, based on the $[M+Na]^+$ ion signal at *m*/*z* 365.2459 (calc. 365.2456). The UV absorptions of **4** at 232, 270, and 294 nm suggested the presence of a benzenoid nucleus [8]. The IR spectrum showed absorption bands for a OH group at 3476 cm^{-1}, and an aromatic ring at 1601 and 1479 cm^{-1}. The ^{1}H- and ^{13}C-NMR (*Table 2*), COSY (*Fig. 3*), NOESY (*Fig. 3*), HSQC, and HMBC (*Fig. 3*) experiments confirmed the structure as 4-methoxy-2-methyl-6-[(2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl]phenol, and designated farnesylol. Compound **4** was first isolated from a natural source, though it has ever been synthesized [13].

The ^{1}H-NMR data (*Table 2*) of **4** revealed two aromatic H-atoms in *meta* position at δ(H) 6.53 (*d*, *J* = 3.0, H–C(3)[1])) and δ(H) 6.57 (*d*, *J* = 3.0, H–C(5)) corroborated

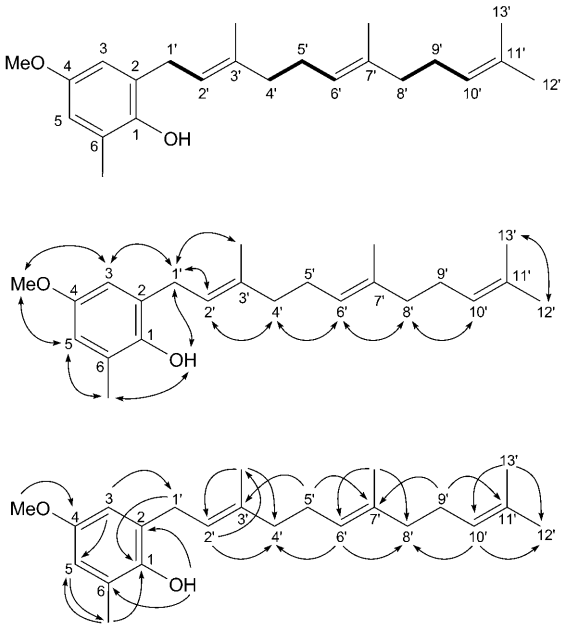


Fig. 3. *Significant COSY* (—), *NOESY* (↔), *and HMBC* (→) *correlations of* **4**[1])

by ^{13}C-NMR signals at δ(C) 112.9 (C(3)) and 114.0 (C(5)) (*Table 2*). A OH group (δ(H) 4.78 (*s*)), a Me group (δ(H) 2.22 (*s*)), and a MeO group (δ(H) 3.74 (*s*)) located at the aromatic ring were determined by ^{13}C-NMR signals at C(1) (δ(C) 146.7), C(4) (δ(C) 153.0), and C(6) (δ(C) 127.2), and the HMBC correlations of MeO–C(4)/C(4), Me–C(6)/C(6), C(5) and C(1), and HO–C(1)/C(2) and C(6). The ^{13}C-NMR spectrum indicated that there were 15 C-atoms in the terpenyl side-chain, which was elucidated as a 2-(3,7,11-trimethyldodeca-2,6,10-trienyl) group from the presence of five CH_2 H-atoms at δ(H) 3.33 (*d*, J = 7.2, CH_2(1′)), 1.96–2.17 (*m*, CH_2(4′), CH_2(5′), CH_2(8′), CH_2(9′)), three vinylic H-atoms at δ(H) 5.30 (br. *t*, J = 7.2, H–C(2′)), 5.08 (br. *t*, J = 7.2, H–C(6′), H–C(10′)), and four allylic Me H-atoms at δ(H) 1.59 (*s*, Me(7′)), 1.59 (*s*, Me(13′)), 1.67 (*s*, Me(12′)), 1.79 (*s*, Me(3′)). The location of the terpenyl substituent at C(2) was confirmed by the correlation between H–C(1′) and H–C(3)/HO–C(1) in the NOESY spectrum (*Fig. 3*). The full assignment of this terpenyl side chain was further confirmed by COSY (*Fig. 3*), HSQC, and HMBC (*Fig. 3*) spectra. The correlations of H–C(3)/MeO–C(4), MeO–C(4)/H–C(5), and Me–C(6)/H–C(5) were also observed in the NOESY experiment (*Fig. 3*) and further supported the positions of the substituents of the aromatic moiety.

The known isolates, *i.e.*, oligandrol [2], oligandrol methyl ether [2], caryophyllene oxide [14], β-sitostenone [15], and a mixture of β-sitosterol [15] and stigmasterol [15], were readily identified by comparison with literature data.

Until now, endiandric acid analogs were only found in four species of *Beilschmiedia* [2] and one species of *Endiandra* genus [16]. Interestingly, we have not detected endiandric acids in the leaves [6] and stems [7] of *B. tsangii*, the second species of the

genus *Beilschmiedia* growing in Taiwan in previous investigations. For the sake of better understanding the distribution of endiandric acid analogs, the roots of *B. tsangii* are worth examining for the presence of these secondary metabolites.

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Experimental Part

General. TLC: silica gel *60* F_{254} precoated plates (*Merck*). Column chromatography (CC): silica gel *60* (SiO_2; 70–230 or 230–400 mesh, *Merck*) or *Spherical C18* (20–40 μm) (*Silicycle*). HPLC: *Spherical C18* column (250 × 10 mm, 5 μm; *Waters*); *LDC-Analytical-III* apparatus; UV-VIS detector (*SPD-10A*, *Shimadzu*); MeCN/H_2O 10:1 as mobile phase, flow rate 1.0 ml/min. M.p.: *Yanaco* micro-melting point apparatus; uncorrected. Optical rotation: *Jasco DIP-370* polarimeter; in $CHCl_3$. UV Spectra: *Jasco UV-240* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Perkin-Elmer-2000* FT-IR spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H-, ^{13}C-, and 2D-NMR Spectra: *Varian-Gemini-200*, *Varian-Unity-Plus-400* and *Varian-Mercury-400* spectrometers; δ in ppm rel. to Me_4Si, *J* in Hz. GC-MS: *Trace GC/POLARIS Q Thermo Finnigan*; in *m/z* (rel. %). EI-MS: *VG-Biotech Quatro-5022* mass spectrometer; in *m/z* (rel. %). ESI- and HR-ESI-MS: *Bruker APEX-II* mass spectrometer; in *m/z*.

Plant Material. The roots of *B. erythrophloia* were collected from Mudan, Pingtung County, Taiwan, in February 2005 and identified by *I.-S. C.*, College of Pharmacy, Kaohsiung Medical University. A voucher specimen (Chen 1187) has been deposited with the Herbarium of the Faculty of Pharmacy, College of Pharmacy, Kaohsiung Medical University, Kaohsiung, Taiwan, R.O.C.

Extraction and Isolation. Air-dried root of *B. erythrophloia* (7.5 kg) were sliced and extracted with cold MeOH (3 × 30 l, 3 d each) at r.t. The extract was concentrated under reduced pressure and was partitioned with AcOEt/H_2O (1:1, *v/v*) to afford an AcOEt-soluble fraction (160 g), a H_2O-soluble fraction (100 g) and an insoluble fraction (43 g).

The AcOEt fraction (100 g) was subjected to CC (2 kg SiO_2, 230–400 mesh; hexane/AcOEt gradient) to give 13 fractions: *Fr. 1–Fr. 13*. *Fr. 5* (2.66 g) was subjected to CC (40 g, SiO_2, 230–400 mesh; hexane/AcOEt gradient) to obtain 11 subfractions: *Fr. 5.1–Fr. 5.11*. *Fr. 5.7* (41 mg) was subjected to *RP-C18* CC (10 g), eluting with Me_2CO and H_2O (20:1) to obtain 15 subfractions: *Fr. 5.7.1–Fr. 5.7.15*. *Fr. 5.7.14* (10 mg, Me_2CO/H_2O 20:1) was subjected to RP-HPLC (MeCN/H_2O 10:1) to afford **6** (5.0 mg, r.t. 15.2 min). *Fr. 6* (1.0 g) was purified by *RP-C18* CC (20 g), eluting with Me_2CO and H_2O (3:1), to obtain 4 fractions: *Fr. 6.1–Fr. 6.4*. *Fr. 6.1* (40.0 mg) was subjected to *RP-C18* CC (10 g), eluting with MeCN and H_2O (20:1), to obtain **7** (6.0 mg) and **8** (5.0 mg). *Fr. 6.3* (40.0 mg) was subjected to CC (10 g, SiO_2, 230–400 mesh; hexane/AcOEt 40:1) to afford **3** (3.0 mg) and **4** (2.5 mg). *Fr. 6.4* (22.0 mg) was subjected to CC (10 g, SiO_2, 230–400 mesh; hexane/AcOEt 40:1) to afford **5** (3.6 mg). *Fr. 10* (20 g) was subjected to CC (400 g, SiO_2, 230–400 mesh; hexane/Me_2CO gradient) to obtain 7 fractions: *Fr. 10.1–Fr. 10.7*. *Fr. 10.3* (2.0 g) was subjected to CC (50 g, SiO_2, 230–400 mesh; CH_2Cl_2 gradient) to obtain 5 fractions: *Fr. 10.3.1–Fr. 10.3.5*. *Fr. 10.3.2* (20.0 mg) was subjected to CC (400 mg, SiO_2, 230–400 mesh; hexane/Me_2CO 4:1) to afford **1** (2.6 mg). *Fr. 10.3.4* (70 mg) was subjected to CC (1.5 g, SiO_2, 230–400 mesh; hexane/Me_2CO 5:1) to afford a mixture of **9** and **10** (50.0 mg). *Fr. 10.6* (3.5 g) was subjected to *RP-C18* CC (10.0 g), eluting with Me_2CO and H_2O (20:1) to obtain **2** (1.7 mg).

Endiandric Acid I (=*(1*RS,*1a*SR,*3*RS,*3a*RS,*6*RS,*6a*SR,*6b*SR,*7*SR*)-1-[5-(1,3-Benzodioxol-5-yl)pentyl]-1,1a,2,3,3a,6,6a,6b-octahydro-3,6-methanocyclobut[*cd*]indene-7-carboxylic Acid*; **1**). Yellowish oil. $[\alpha]_D^{25} = 0$ ($c = 0.39$, $CHCl_3$). UV (MeOH): 234 (4.05), 286 (3.95). IR (neat): 2600–3300 (CO*OH*), 1701 (C=O), 1039, 938 (OCH_2O). ^{1}H- and ^{13}C-NMR: see *Table 1*. ESI-MS: 381 ($[M+H]^+$). HR-ESI-MS: 403.1882 ($[M+Na]^+$, $C_{24}H_{28}NaO_4^+$; calc. 403.1885).

Endiandric Acid J (=*(1*RS,*1a*SR,*3*RS,*3a*RS,*6*RS,*6a*SR,*6b*SR,*7*SR*)-1-Decyl-1,1a,2,3,3a,6,6a,6b-octahydro-3,6-methanocyclobut[*cd*]indene-7-carboxylic Acid*; **2**). Colourless needles. M.p. 130–135°. $[\alpha]_D^{25} = 0$ ($c = 0.44$, $CHCl_3$). IR (neat): 3300–3500 (CO*OH*), 1701 (C=O). ^{1}H- and ^{13}C-NMR: see *Table 1*. ESI-MS: 353 ($[M+Na]^+$). HR-ESI-MS: 353.2455 ($[M+Na]^+$, $C_{22}H_{34}NaO_2^+$; calc. 353.2456).

Dehydrooligandrol Methyl Ether (=*(2*S*)-2-[(3*E*)-4,8-Dimethylnona-3,7-dien-1-yl]-6-methoxy-2,8-dimethyl-2*H*-1-benzopyran*; **3**). Colorless oil. $[\alpha]_D^{25} = -28.0$ ($c = 0.72$, $CHCl_3$). UV (MeOH): 232 (3.88), 269 (3.29). IR (neat): 1594, 1468 (C=C). ^{1}H- and ^{13}C-NMR: see *Table 2*. ESI-MS: 363 ($[M+Na]^+$). HR-ESI-MS: 363.2303 ($[M+Na]^+$, $C_{23}H_{32}NaO_2^+$; calc. 363.2300).

Farnesylol (=*4-Methoxy-2-methyl-6-[(2*E*,6*E*)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl]phenol*; **4**). Yellowish oil. UV (MeOH): 232 (3.95), 270 (3.34), 294 (3.25). IR (neat): 3476 (OH), 1601, 1479 (C=C). ^{1}H- and ^{13}C-NMR: see *Table 2*. ESI-MS: 365 ($[M+Na]^+$). HR-ESI-MS: 365.2459 ($[M+Na]^+$, $C_{23}H_{34}NaO_2^+$; calc. 365.2456).

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