Isolation and Characterisation of l,l'-binaphthalene-2,2'-diol, A New Biaryl Natural Product from *Sesbania grandiflora* Root

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Abstract: This study aimed to isolate and characterise purified compound from the root of *Sesbania grandiflora.* The root of *Sesbania grandiflora* provided a new natural compound: l,l'-binaphthalene-2,2'-diol (**1**) together with two known isoflavanoids (**2**-**3**). Complete ^{1}H- and ^{13}C-NMR data of compounds isolated were reported. The structures were determined through various spectroscopic methods notably 1D- and 2D-NMR, UV, IR and HRESIMS.

Keywords: *Sesbania grandiflora*, l,l'-binaphthalene-2,2'-diol, biaryl natural product.

INTRODUCTION

Leguminosae is a family of the pea and/or bean plants. They are used as crops, forages, and green manures. Their wide variety of natural products lead to the production of flavors, drugs, poison, and dyes [1]. *Sesbania grandiflora* (L.) Pers. is a Leguminosaous plant belongs to subfamily Papilionoideae. *Sesbania grandiflora* is a small erect, fast-growing, and sparsely branched tree. They are native to tropical Asia and widespread in Malaysia, Indonesia, Philippine, and India. The Malay names of this plant are *turi* and *geti* [1].

Various phytochemical studies of crude leaves, flowers, and aerial parts of this plant showed the presence of sterol, saponin, and tannins [2]. These chemical constituents are well known for their potential health benefits and have been reported to posses valuable biological activities such as antibacterial and antifungal [3], antioxidant [4-6], antiurolithiatic [6], anticonvulsant and anxiolytic [7], and hepatoprotection activity [8].

Phytochemical studies on the flowers and the seeds of this plant reported the isolation of kaempferol-3-rutinoside, oleanolic acid, cyanidin, leucocyanidin and galactomannan [9]. Even though *S. grandiflora* was extensively studied by other researchers for its phytopharmacological potentials especially on leaves, flowers, and aerial parts of the plant, no phytochemical studies have been performed on the root of *S. grandiflora*. We report herein, the isolation and structural elucidation of a new natural compound: l,l'-binaphthalene-2,2'-diol (**1**) along with two known isoflavanoids (**2**-**3**) from the roots of *S. grandiflora*.

MATERIALS AND METHODS

General Experimental Procedures

TLC: Silica gel 60 F254 precoated plates (Merck). Column chromatography (CC): silica gel 60 (70–230 or 230–400 mesh, Merck). M.p.: Stuart Scientific SMP1 apparatus; uncorrected. Optical rotation: Jasco DIP-370 polarimeter; in MeOH. UV Spectra: Perkin-Elmer Lambda 25 spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: Perkin-Elmer-2000 FT-IR spectrophotometer; with KBr pellets at 25^{o}; in cm^{-1}. ^{1}H-, ^{13}C- and 2D-NMR spectra: Bruker Avance-300, Bruker Avance-400 and Bruker Avance-500 spectrometers; δ in ppm rel. to Me_4Si, *J* in Hz. FAB- and HR-ESI-MS: Finnigan MAT95 and TOF MS-EI mass spectrometers; in *m/z*.

Plant Material

The roots of *Sesbania grandiflora* were collected from the village of Sidosari, in South Lampung, Indonesia, in September 2008. The identity of the plant specimen was authenticated by Dr. Harry Wiriadinata and a voucher specimen of this collection (No. N-III) was deposited at the Bogoriense Herbarium, Bogor, Indonesia.

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Extraction and Isolation

Dried and powdered roots (1 kg) of *S. grandiflora* were extracted three times with MeOH at room temperature for one week. The extract was concentrated under reduced pressure, and was partitioned with *n*-hexane to afford hexane-soluble fraction (*Fr. A*, 1.9 g) and the MeOH-soluble fraction. The MeOH-soluble fraction was suspended in H_2O and partitioned sequentially with $CHCl_3$, EtOAc, and acetone, yielding three corresponding fractions respectively, $CHCl_3$-soluble fraction (*Fr. B*, 0.9 g), EtOAc-soluble fraction (*Fr. C*, 2.3 g), and acetone-soluble fraction (*Fr. D*, 1.7 g). Based on the similarity shown in TLC analysis, *Fr. C* and *Fr. D* were combined and then it was further called *Fr. C* (4 g). The rest of MeOH-soluble fraction (*Fr. E*, 0.9 g) was chromatographed over silica gel column using *n*-hexane and *n*-hexane-EtOAc by gradually increasing the polarity gradient to obtain 5 major fractions: *Fr. E1-E5*. *Fr. E3* (60 mg) was selected to further fractionated by column chromatography (2 g SiO_2, 70-230 mesh; cyclohexane:EtOAc 90 : 10) to obtain 6 subfractions: *Fr. E3.1- Fr. E3.6. Fr. E3.4* (8 mg) was purified by column chromatography (250 mg SiO_2, 70-230 mesh; cyclohexane:aceton 95 : 5) to give compound **1** (1.2 mg; R_f 0.24). *Fr. C* was separated by extensive centrifugal TLC (SiO_2, *n*-hexane/EtOAc gradient) to obtain 7 major fractions: *Fr. C1-C7*. *Fr. C2* (290 mg) was subjected to further fractionated by centrifugal TLC (SiO_2, $CHCl_3$:MeOH 95 : 5) to afford 8 subfractions: *Fr. C2.1- Fr. C2.8. Fr. C2.6* (180 mg) was subjected to purify further by CC (7.2 g SiO_2, 70-230 mesh; hexane/EtOAc 95 : 5) to give 10 subfractions: *Fr. C2.6.1- Fr. C2.6.10. Fr. C2.6.7* (40 mg) was further purified by prep. TLC (SiO_2, hexane/$CHCl_3$/MeOH 5 : 99 : 1) to afford **2** (20 mg; R_f 0.25). *Fr. C3* (250 g) was separated by centrifugal TLC (SiO_2, $CHCl_3$/MeOH gradient) to afford 7 subfractions: *Fr. C3.1- Fr. C3.7. Fr. C3.4* (95 mg) was purified by prep. TLC (SiO_2, toluene:EtOAc 99 : 1) to provide **3** (7 mg; R_f 0.47).

RESULTS

l, l'-binaphthalene-2,2'-diol (1)

Colourless solid. M.p. 205-206°C. UV (MeOH): 229 (4.85), 277 (3.94), 336 (3.79). IR (KBr): 3485, 3402, 2955, 2923, 2852, 1617, 1596, 1461, 1380, 1216, 1175, 1146, 826,750. ^{1}H- and ^{13}C-NMR (Table **1**). TOF MS-EI [M]: 286.0675, indicating $C_{20}H_{14}O_2$

Isovestitol (2)

Amorphous powder. M.p. 166-167°C. $[\alpha]^{20}_D$ = -66.6 (c = 0.1, MeOH). UV (MeOH): 207 (4.58), 227 (4.09), 284 (3.70). IR (KBr): 3361, 2941, 1624, 1593, 1455, 1269, 1142. ^{1}H- and ^{13}C-NMR (Table **2**). FAB-MS: 273.1 ($[M+H]^+$, $C_{16}H_{16}O_4^+$).

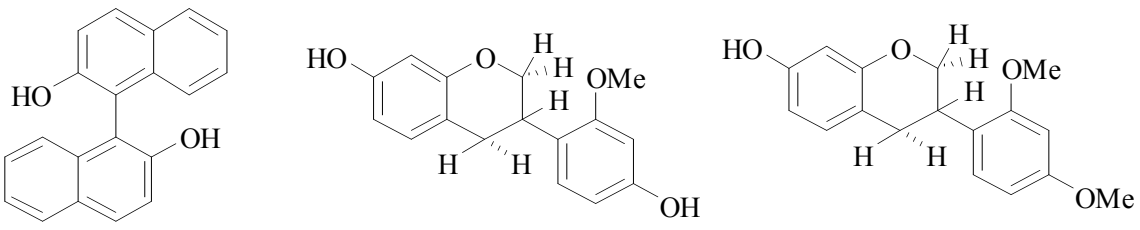
Sativan (3)

Amorphous powder. M.p. 124-126°C. UV (MeOH): 208 (4.69), 228 (4.32), 283 (3.92). IR (KBr): 3365, 2938, 1614, 1591, 1506, 1461, 1279, 1208, 1160, 1115. ^{1}H- and ^{13}C-NMR (Table **2**). HR-ESI-MS, 285.1119 ($[M-H]^+$, $C_{17}H_{18}O_4^+$; calc. 285.1132).

DISCUSSION

The crude methanol extract of *S. grandiflora* root was subjected to column chromatography over silica gel to obtain three compounds, **1-3**. Compound **1** was isolated as a colourless solid. The molecular formula of **1** was determined as $C_{20}H_{14}O_2$ ([M] m/z 286.0675) from the TOF MS-EI mass spectrum. This compound was found to be an aromatic on the basis of its characteristic spectral data; λ_{max} 229, 277, and 336 nm in the UV spectrum and a set of aromatic proton signals in the ^{1}H-NMR spectrum.

This compound has characteristic absorption bands at 229 and 278 nm with a longer wavelength at 336 nm than simple phenol. This absorption bands indicated the presence of a phenolic chromophore. The IR



1 **2** **3**

Figure 1: Molecular structures of compounds **1**, **2**, and **3**.

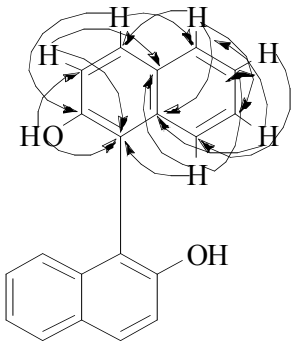


Figure 2: HMBC correlation of compound **1**.

absorption at a number of wavelength 3485 indicated hydroxyl group; at 2955 for CH aliphatic and at 1617-1146 for C=C double bond of aromatic rings. These absorption bands were suggested as a phenolic compound.

The ^{1}H-NMR spectrum of compound **1** contained seven proton signals, six protons lied in the shift range appropriate for aromatics and one signal was evidently a hydroxyl group. The typical coupling constants (8, 7, and 1.3 Hz) indicated a naphtalene ring system. Two naphtalene rings were deduced after judging the molecular weight which accounted for seven out of the total fourteen double-bond equivalents.

Table 1: ^{1}H- and ^{13}C-NMR Data of 1. At 500 MHz in $CdCl_3$; δ in ppm, *J* in Hz

Position	1	
	δ^{1}H	δ^{13}C
1/1'		110.9
2/2'		152.8
3/3'	7.32, *d* (9)	117.8
4/4'	7.91, *d* (9)	131.4
4a/4a'		129.5
5/5'	7.83, *d* (8)	128.4
6/6'	7.30, *ddd* (1.3; 7; 8)	124.0
7/7'	7.24, *ddd* (1.3; 7; 8)	127.5
8/8'	7.08, *d* (8)	124.2
8a/8a'		133.4
HO-2/2'	4.9, *s*	

The six signals in the ^{1}H-NMR spectrum of compound **1** showed first that it was disubtituted naphtalene ring. The positions of the subtituents followed from the coupling constants of the doublets at 7.91 and 7.32 ppm with ortho coupling (9 Hz), belongs to AM system of the naphtyl ring A. There were two threefold doublets at 7.30 and 7.24 ppm as the remaining fragment of the naphtyl ring B. Each of the threefold doublets exhibited two *ortho* couplings (8.0

Table 2: ^{1}H- and ^{13}C-NMR Data of 2-3. At 400 MHz for ^{1}H- and 300 MHz for ^{13}C- in Aceton-d_6; δ in ppm, *J* in Hz

Position	2		3	
	δ^{1}H	δ^{13}C	δ^{1}H	δ^{13}C
5	6.90, *d* (8.2)	130.49	6.90, *d* (8.2)	130.47
6	6.38, *dd* (8.2 & 2.4)	108.28	6.38, *dd* (8.2 & 2.5)	108.00
7		157.03		157.08
8	6.29, *d* (2.4)	103.99	6.29, *d* (2.5)	103.21
9		156.23		155.59
10		113.83		113.00
1'		120.49		122.11
2'		159.64		158.71
3'	6.51, *d* (2.5)	102.08	6.59, *d* (2.5)	98.88
4'		155.64		160.33
5'	6.43, *dd* (8.5 & 2.5)	105.24	6.50, *dd* (8.4 & 2.5)	105.04
6'	7.06, *d* (8.5)	128.24	7.10, *d* (8.4)	127.92
1				
2	H_α, 3.99, *t* (10)	70.01	H_α, 3.95, *t* (10)	70.07
	H_β, 4.25, *br d* (10; 3; & 2)		H_β, 4.20, *ddd* (10; 3; & 2)	-
3	3.49, *m* (8; 5; & 3)	33.69	3.47, *m*	31.97
4	H_α, 2.81, *dd* (10; 5 & 2)	32.19	H_α, 2.78, *br d* (7; 5 & 2)	30.68
	H_β, 2.98, *dd* (16, 5)		H_β, 2.81, *br d* (7; 5 & 2)	
2'-OCH_3	3.73, *s*, 3H	54.89	3.80, *s*, 3H	55.07
4'-OH	8.14, *br s*			
4'-OCH_3			3.86, *s*, 3H	55.36
7-OH	8.59, *br s*		8.15, *br s*	

and 7.0 Hz) and one *meta* coupling (1.3 Hz) which were characteristics for the naphtyl ring.

The connection between two naphtyl rings only occured once at 110.9 ppm which belong to quaternary carbon atom. The ^{13}C-NMR spectrum of compound **1** was interpreted by the assistance of DEPT spectra and showed 10 signals for one unit structure of naphtyl rings. These signals were distributed into six methine carbon and four quarternary carbon atoms. Further assignment was done by Heteronuclear Multiple Quantum Coherence (HMQC) and Heteronuclear Multiple Bond Correlation (HMBC) spectra (Figure **2**).

Based on the spectroscopy data which were observed including 1D and 2D NMR (see Table **1**), the structure of compound **1** was established as l,l'-binaphthalene-2,2'-diol or 1,1'-bi-2-naphthol. It was fully characterised here for the first time as a new natural product, but it was previously reported as a synthetic compound [10].

The structure of known natural products, isovestitol (**2**) and sativan (**3**) were also characterized and confirmed in this work.

CONCLUSION

We conclude that the root of *Sesbania grandiflora* contains a new natural product compound: l,l'-binaphthalene-2,2'-diol. To the knowledge of the authors, l,l'-binaphthalene-2,2'-diol was isolated here for the first time from a natural source, it has been previously reported as a synthetic compound. This study indicates that *S. grandiflora* root could be used as a potential natural source for future development and utilization of *S. grandiflora.*

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