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Chemical Constituents of Stem Bark of *Shorea faguetiana*

(Juzuk Kimia Kulit Batang *Shorea faguetiana*)

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ABSTRACT

A phytochemical investigation on the acetone extract of the stem bark of Shorea faguetiana *was conducted. The isolation of the chemical compounds was carried out by different chromatographic techniques and their structures were elucidated by spectroscopic methods including UV, IR, NMR and MS, and also by comparison with the literature. Five oligostilbenes were isolated and identified as (-)-ε-viniferin, (-)-α-viniferin, (-)-laevifonol, (-)-ampelopsin E and (-)-hopeaphenol.*

Keywords: (-)-Ampelopsin E; (-)-α-Viniferin; Dipterocarpaceae; (-)-ε-Viniferin; (-)-Hopeaphenol; (-)-Laevifonol; Oligostilbenes; Shorea faguetiana

ABSTRAK

Kajian kimia terhadap ekstrak aseton kulit batang Shorea faguetiana *telah dilakukan. Pemisahan sebatian kimia dijalankan dengan menggunakan berbagai teknik kromatografi dan struktur telah ditentukan menggunakan kaedah spektroskopi seperti UL, IM, RMN dan SJ, serta membandingkan data yang diperoleh dengan data kepustakaan. Lima oligostilbena telah dipisahkan dan dikenal pasti sebagai (-)-ε-viniferin, (-)-α-viniferin, (-)-laevifonol, (-)-ampelopsin E dan (-)-hopeafenol.*

Kata kunci: (-)-Ampelopsin E; (-)-α-Viniferin; Dipterocarpaceae; (-)-ε-Viniferin; (-)-Hopeafenol; (-)-Laevifonol; Oligostilbena; Shorea faguetiana

Introduction

The Dipterocarpaceae is a relatively large family of tropical plants consisting of 16 genera and approximately 600 species (Cronquist 1981). *Shorea* is the largest and most economically important genus of this family of which 59 species are found in Peninsular Malaysia and at least 167 species in Borneo and Sumatra. This genus is widely distributed in the Southeast Asia region, especially in Malaysia and Indonesia (Symington 1974). In Peninsular Malaysia, *Shorea* is also known as *Balau*, *Meranti Pa'ang, Meranti Damar Hitam* and *Meranti Merah* (Burkill 1966). The *Shorea* wood is used for planks, building construction, furniture and plywood industry (Henye 1987). The resin is used for varnish glues, torch fuel, medicine for diarrhoea, skin diseases, dysentery, gonorrhoea (Misra & Ahmad 1997) and cosmetics (Westphal & Battermann 2010). Phytochemical studies of *Shorea* species showed that this genus is a source of oligostilbenes such as resveratrol dimers, trimers, tetramers, hexamers, heptamers and octamers (Ito 2011; Lin & Yao 2006). These compounds exhibited a variety of significant bioactivities including anti-bacterial (Nitta et al. 2002), anti-fungal (Bokel et al. 1988; Kusuma & Tachibana 2007), anti-babesial (Subeki et al. 2005), anti-tumour (Jang et al. 1997; Saroyobudiono et al. 2008) and anti-HIV (Dai et al. 1998). *Shorea faguetiana*, which falls under the Yellow Meranti group, is a species of *Shorea* in the Dipterocarpaceae family. The local name is *Damar Siput, Damar Hitam* (Malaysia); *Kalo, Mon Kai* (Thailand) and *Karambuku Lahung, Bangkirai Guruk* (Indonesia). Although *Shorea* plants are found abundantly in Malaysia and Indonesia, the phytochemical studies on these plants by the locals are still limited to only a few species. Previous phytochemical studies of the Yellow Meranti were done on *S. gibbosa* and *S. multiflora* by researchers from Indonesia. A new oligostilbene derivative, diptoindonesin F, along with five known oligostilbenes of (-)-ampelopsin A, **(-)-**α-viniferin, (-)-ampelopsin E, (-)-vaticanol B and (-)-hemsleyanol D were isolated from the bark extract of *S. gibbosa* (Saroyobudiono et al. 2008). Meanwhile, (-)-ampelopsin A, (-)-balanocarpol, (-)-α-viniferin, (-)-vaticanol G and (-)-hopeaphenol were successfully isolated from *S. multiflora* (Noviany 2002). The chemical constituents of *S. faguetiana* have not been investigated and reported previously. Thus, the objective of this research was to isolate and characterize oligostilbenes from the acetone extract of the stem bark of *S. faguetiana*. The distribution of these secondary metabolites from *S. faguetiana* in relation to other plants will also be described.

Materials and Methods

Plant material

The stem bark of *S. faguetiana* was collected from Hutan Belum, Perak, Malaysia and a voucher specimen (WYA 141) was deposited at the Herbarium of Universiti Kebangsaan Malaysia (UKMB). This species was identified by a Universiti Kebangsaan Malaysia botanist, Mr. Sani Miran.

Extraction and isolation

The dried powdered stem bark of *Shorea faguetiana* (500 g) was macerated with acetone at room temperature. The filtrate was concentrated using rotary evaporator to yield a brownish extract (30 g, 6.0%). A portion (15 g) of the extract was fractionated by vacuum liquid chromatography eluted with increasing polarity of *n*-hexane-EtOAc. The eluents showing the same profile on thin layer chromatography (TLC) chromatogram were combined to give five fractions (A-E). Further purification of fraction A (150 mg) by radial chromatography using $CHCl_3$-MeOH (9:1) afforded compound **1** (2.0 mg). Purification of fraction B (706 mg) by Sephadex LH-20 column chromatography using MeOH afforded compound **2** (8.0 mg). Fraction C (282 mg) was fractionated with radial chromatography ($CHCl_3$-MeOH 8.5:1.5) to give compound **3** (5.0 mg). Purification of fraction D (80 mg) by Sephadex LH-20 column chromatography and over preparative TLC (*n*-hexane-EtOAc 3:7) afforded compound **4** (5.0 mg). Fraction E (200 mg) was purified with radial chromatography (*n*-hexane-$CHCl_3$-MeOH 1.5:8.0:0.5) to give compound **5** (7.0 mg).

Compound identification

^{1}H and ^{13}C-APT NMR spectra were recorded in acetone-d_6 using JEOL ECP400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). UV spectra were recorded on Shimadzu UV-160 (200-400 nm). IR spectra were recorded on a Perkin Elmer GX FTIR spectrometer using NaCl discs. Normal and flash column chromatography were carried out on Kieselgel 60 (cat. no. 9385). Melting points were measured by Stuart SMP10 melting point apparatus and were uncorrected. Optical rotations were recorded on JASCO DIP-370 digital polarimeter (589 nm). TLC was performed on pre-coated silica gel (Merck, Kieselgel 60 F_{254} 0.25 mm; cat. no. 5554) and detected by UV light (254 nm) or by $CeSO_4$ spraying reagent followed by heating. ESIMS was recorded on a LC-ToFMS spectrometer.

(-)-ε-Viniferin (**1**): Yellow amorphous powder (2.0 mg), mp: 185°C (Muhtadi Hakim et al. 2005: 190°C), optical rotation $[\alpha]_D^{20}$ -40° in MeOH (c = 0.1), UV λ_{max} (MeOH) nm: 229, 325. IR (NaCl) ν_{max} cm^{-1}: 3366, 2920, 1606, 1441, 1241, 1168, 830. ESIMS *m/z* 455 $[M+H]^+$ $C_{28}H_{22}O_6$. ^{1}H NMR δ 7.44 (2H, d, *J*=8.5 Hz, H-2a/H-6a), 7.21 (2H, d, *J*=8.3 Hz, H-2b/H-6b), 7.07 (1H, d, *J*=16.6 Hz, H-8b), 6.98 (1H, d, *J*=16.6 Hz, H-7b), 6.85 (2H, d, *J*=8.5 Hz, H-3a/H-5a), 6.82 (2H, d, *J*=8.3 Hz, H-3b/H-5b), 6.68 (1H, d, *J*=2.0 Hz, H-14b), 6.58 (1H, d, *J*=2.0 Hz, H-12b), 6.22 (1H, d, *J*=2.2 Hz, H-12a), 6.15 (2H, d, *J*=2.2 Hz, H-10a/H-14a), 5.36 (1H, d, *J*=4.8 Hz, H-7a), 4.36 (1H, d, *J*=4.8 Hz, H-8a). ^{13}C-APT NMR δ 162.4 (C-11b), 159.9 (C-11a/13a), 159.7 (C-13b), 158.2 (C-4b), 158.2 (C-4a), 147.6 (C-9a), 136.3 (C-9b), 133.6 (C-1a), 130.2 (C-8b), 129.9 (C-1b), 128.6 (C-2b/6b), 127.9 (C-2a/6a), 123.1 (C-7b), 119.8 (C-10b), 116.4 (C-3b/5b), 116.1 (C-3a/5a), 106.9 (C10a/14a), 104.2 (C-14b), 102.1 (C-12a), 96.8 (C-12b), 93.9 (C-7a), 57.1 (C-8a).

(-)-α-Viniferin (**2**): Brown amorphous powder (8.0 mg), mp: 230°C (Muhtadi Hakim et al. 2005: 235°C), optical rotation $[\alpha]_D^{20}$ -33° in MeOH (c = 0.1), UV λ_{max} (MeOH) nm: 285. IR (NaCl) ν_{max} cm^{-1}: 3369, 1615, 1515, 1484, 1440, 1362, 1243, 1161, 1171, 1113, 1071, 831. ESIMS *m/z* 679 $[M+H]^+$ $C_{42}H_{30}O_9$. ^{1}H NMR δ 7.22 (2H, d, *J*=8.6 Hz, H-2b/6b), 7.04 (2H, d, *J*=7.7 Hz, H-2c/6c), 7.02 (2H, d, *J*=8.2 Hz, H-2a/6a), 6.78 (2H, d, *J*=8.4 Hz, H-3b/5b), 6.76 (2H, d, *J*=8.6 Hz, H-3c/5c), 6.71 (1H, d, *J*=1.8 Hz, H-14a), 6.70 (2H, d, *J*=8.6 Hz, H-3a/5a), 6.58 (1H, d, *J*=1.8 Hz, H-14c), 6.23 (1H, d, *J*=1.8 Hz, H-12a), 6.22 (1H, d, *J*=2.0 Hz, H-12b), 6.20 (1H, d, *J*=2.0 Hz, H-12c), 6.05 (1H, br s, H-7a), 5.98 (1H, d, *J*=2.0 Hz, H-14b), 5.95 (1H, d, *J*=10.0 Hz, H-7c), 4.90 (1H, d, *J*=6.2 Hz, H-7b), 4.67 (1H, d, *J*=10.0 Hz, H-8c), 4.61 (1H, d, *J*=6.2 Hz, H-8b), 3.95 (1H, br s, H-8a). ^{13}C-APT NMR δ 161.9 (C-11c), 161.6 (C-11a), 161.0 (C-11b), 160.7 (C-13c), 159.5 (C-13a), 159.5 (C-13b), 158.5 (C-4b), 158.3 (C-4a), 157.9 (C-4c), 141.3 (C-9a), 139.8 (C-9b), 138.7 (C-9c), 132.6 (C-1b), 132.0 (C-1a), 132.0 (C-1c), 128.8 (C-6b), 128.8 (C-2b), 128.3 (C-6a), 128.3 (C-2a), 128.2 (C-6c), 128.2 (C-2c), 120.9 (C-10a), 119.7 (C-10c), 118.9 (C-10b), 116.2 (C-5c), 116.2 (C-3c), 116.2 (C-5b), 116.2 (C-3b), 115.8 (C-5a), 115.8 (C-3a), 106.3 (C-14a), 105.9 (C-14c), 105.9 (C-14b), 98.1 (C-12a), 97.0 (C-12b), 96.6 (C-12c), 95.7 (C-7b), 90.1 (C-7c), 86.4 (C-7a), 55.8 (C-8b), 52.9 (C-8c), 46.4 (C-8a).

(-)-Laevifonol (**3**): Dark yellow gum (5.0 mg), mp: 240°C (Muhtadi Hakim et al. 2007: 242°C), optical rotation $[\alpha]_D^{20}$ -224° in MeOH (c = 0.1), UV λ_{max} (MeOH) nm: 283. IR (NaCl) ν_{max} cm^{-1}: 3367, 1788, 1641, 1517, 1453, 1338, 1260, 1161, 1126, 1030, 836. ESIMS *m/z* 629 $[M+H]^+$ $C_{34}H_{28}O_{12}$. ^{1}H NMR δ 7.16 (1H, d, *J*=2.2 Hz, H-14a), 6.96 (2H, d, *J*=8.4 Hz, H-2b/6b), 6.74 (2H, d, *J*=8.8 Hz, H-3b/5b), 6.74 (2H, d, *J*=8.8 Hz, H-3a/5a), 6.16 (1H, d, *J*=2.2 Hz, H-12a), 6.15 (1H, t, *J*=2.2 Hz, H-12b), 5.90 (2H, d, *J*=2.2 Hz, H-14b), 5.27 (1H, d, *J*=11.0 Hz, H-7a), 5.04 (1H, d, *J*=7.7 Hz, H-7b), 4.41 (1H, br s, H-4c), 4.22 (1H, br s, H-5c), 4.06 (1H, dd, *J*=10.0, 3.5 Hz, H-6c), 3.98 (1H, dd, *J*=10.0, 3.5 Hz, H-6c), 3.29 (1H, d, *J*=11.0 Hz, H-8a), 3.24 (1H, d, *J*=7.7 Hz, H-8b). ^{13}C-APT NMR δ 171.8 (C-1c), 160.9 (C-11a), 159.6 (C-13b), 159.6 (C-11b), 158.8 (C-4a), 158.4 (C-13a), 158.0 (C-4b), 145.7 (C-9b), 132.2 (C-1b), 131.7 (C-1a), 129.8 (C-9a), 128.8 (C-6b), 128.8

(C-2b), 128.0 (C-6a), 128.0 (C-2a), 122.8 (C-3c), 118.6 (C-10a), 115.8 (C-5a), 115.8 (C-3a), 115.5 (C-5b), 115.5 (C-3b), 110.5 (C-14a), 106.9 (C-14b), 106.9 (C-10b), 102.1 (C-12b), 96.8 (C-12a), 94.0 (C-7b), 89.8 (C-7a), 88.9 (C-4c), 80.9 (C-2c), 75.0 (C-6c), 74.5 (C-5c), 56.6 (C-8b), 56.0 (C-8a).

(-)-Ampelopsin E (**4**): White amorphous powder (5.0 mg), mp: 180°C (Haryoto 2008: 232°C), optical rotation $[\alpha]_D^{20}$ -94° in MeOH (c = 0.1). UV λ_{max} (MeOH) nm: 285. IR (NaCl) ν_{max} cm^{-1}: 3367, 2947, 1655, 1451, 1114. ESIMS *m/z* 681 $[M+H]^+$ $C_{42}H_{32}O_9$. ^{1}H NMR δ 7.24 (2H, d, *J*=8.4 Hz, H-2a/H-6a/H-2c/H-6c), 6.93 (2H, d, *J*=8.6 Hz, H-2b/H-6b), 6.84 (4H, d, *J*=8.4 Hz, H-3a/H-5a/H-3c/H-5c), 6.66 (1H, d, *J* =16.0 Hz, H-7b), 6.62 (2H, d, *J*=8.6 Hz, H-3b/H-5b), 6.59 (1H, d, *J*=16.0 Hz, H-8b), 6.45 (1H, s, H-12b), 6.24 (4H, d, *J*=2.0 Hz, H-10a/H-14a/H-10c/H-14c), 6.16 (2H, t, *J*=2.0 Hz, H-12a/H-12c), 5.42 (2H, d, *J*=5.0 Hz, H-7a/H-7c), 4.54 (2H, d, *J*=5.0 Hz, H-8a/H-8c). ^{13}C-APT NMR δ 162.5 (C-11b/13b), 159.7 (C-11a/13a/11c/13c), 158.3 (C-4a/4c), 158.1 (C-4b), 147.1 (C-9a/9c), 133.7 (C-8b), 133.6 (C-1a/1c), 133.2 (C-1b), 129.0 (C-9b), 128.2 (C-2b/6b), 127.8 (C-2a/6a/2c/6c), 122.0 (C-7b), 120.0 (C-10b/14b), 116.0 (C-3a/5a/3c/5c), 115.9 (C-3b/5b), 106.7 (C-10a/14a/10c/14c), 102.9 (C-12a/12c), 93.9 (C-7a/7c), 91.2 (C-12b), 57.8 (C-8a/8c).

(-)-Hopeaphenol (**5**): White amorphous powder (7.0 mg), mp: 292°C (Zuraida 2005: 292-295°C), optical rotation $[\alpha]_D^{20}$ -396° in MeOH (c = 0.1). UV λ_{max} (MeOH) nm: 282. IR (NaCl) ν_{max} cm^{-1}: 3411, 2950, 1645, 1453. ESIMS *m/z* 907 $[M+H]^+$ $C_{52}H_{42}O_{12}$. ^{1}H NMR δ 7.12 (2H, d, *J*=8.4 Hz, H-2a/H-6a), 6.89 (2H, d, *J*=8.4 Hz, H-2b/H-6b), 6.77 (2H, d, *J*=8.4 Hz, H-3a/H-5a), 6.54 (2H, d, *J*=8.4 Hz, H-3b/H-5b), 6.53 (1H, br s, H-12a), 6.29 (1H, br s, H-14a), 5.80 (1H, br s, H-7b), 5.73 (1H, d, *J*=12.4 Hz, H-7a), 5.71 (1H, d, *J*=2.2 Hz, H-12b), 5.14 (1H, d, *J*=2.2 Hz, H-14b), 4.21 (1H, d, *J*=12.4 Hz, H-8a), 3.93 (1H, s, H-8b). ^{13}C-APT NMR δ 159.2 (C-11b), 158.8 (C-11a), 158.5 (C-4a), 157.2 (C-13a), 157.1 (C-13b), 155.6 (C-4b), 142.4 (C-9a), 140.5 (C-9b), 135.2 (C-1b), 130.9 (C-1a), 130.3 (C-2a/6a), 129.3 (C-2b/6b), 121.1 (C-10a), 118.6 (C-10b), 116.0 (C-3a/5a), 115.2 (C-3b/5b), 111.3 (C-14b), 106.4 (C-14a), 101.1 (C-12a), 95.2 (C-12b), 49.8 (C-8a), 48.2 (C-8b), 41.3 (C-7b).

Results and Discussion

The acetone extract of the stem bark of *Shorea faguetiana* was subjected to several chromatographic techniques (vacuum liquid chromatography, flash column chromatography, radial chromatography and preparative TLC) to yield (-)-ε-viniferin (**1**), (-)-α-viniferin (**2**), (-)-laevifonol (**3**), (-)-ampelopsin E (**4**) and (-)-hopeaphenol (**5**).

(-)-ε-Viniferin (**1**) was isolated as a yellow amorphous powder. The mass spectrum showed a molecular ion peak $[M+H]^+$ at m/z 455 which corresponded to the molecular formula $C_{28}H_{22}O_6$. The UV spectrum of this compound in MeOH exhibited absorptions (λ_{max} 229 nm, *sh*; 325 nm) typical for stilbenoid chromophore, which showed batochromic shift on addition of NaOH. The IR spectrum gave absorptions at 3366 cm^{-1} (hydroxyls); 2920 cm^{-1} (aliphatic); 1606, 1441 cm^{-1} (aromatics) and 1241, 1168 cm^{-1} (oxyaryls). The ^{1}H NMR spectrum showed the proton signals for one unit of *trans*-4-hydroxystyryl at δ 7.21 (2H, d, *J*=8.3 Hz, H-2b/6b) and 6.82 (2H, d, *J*=8.3 Hz, H-3b/5b) including two doublet signals at 6.98 (1H, *J*=16.6 Hz, H-7b) and 7.07 (1H, *J*=16.6 Hz, H-8b). These signals suggested the presence of *trans*-stilbene skeleton in this compound. The signals of protons in 4-hydroxyphenyl were shown at δ 7.44 (2H, d, *J*=8.5 Hz, H-2a/6a) and δ 6.85 (2H, d, *J*=8.5 Hz, H-3a/5a). In addition, signals at δ 6.68 (1H, d, *J*=2.0 Hz, H-14b) and 6.58 (1H, d, *J*=2.0 Hz, H-12b) were attributable to *meta*-coupled aromatic protons on a 1,2,3,5-tetrasubstituted benzene ring. The presence of protons on 3,5-dihydroxyphenyl was shown by doublet signals at δ 6.15 (*J*=2.2 Hz) and δ 6.22 (*J*=2.2 Hz) for H10a/14a and H-12a. In addition, a pair of aliphatic protons at δ 5.36 (1H, d, *J*=4.8 Hz, H-7a) and 4.36 (1H, d, *J*=4.8 Hz, H-8a) were assigned to a 2,3-dihydrobenzofuran moiety with *trans* configuration. The ^{13}C-APT NMR spectrum indicates 21 signals representing 28 carbons which consist of six oxyaryl carbons between δ 158.2 and 162.4. There were seven signals of quaternary carbons at δ119.8 (C-10b), 129.9 (C-1b), 133.6 (C-1a), 136.3 (C-9b), 147.6 (C-9a), 159.7 (C-13b) and 162.4 (C-11b); plus two signals at δ 158.2 and 159.9 which were attributable to two carbons 4a/4b and two symmetric carbons 11a/13a. Further analysis revealed seven signals of methine carbons: C-8a (δ 57.1), 8b (123.1), 7a (93.9), 7b (130.2), 12a (96.8), 12b (102.1) and 14b (104.2). There were also five symmetric methine carbon signals: δ 128.6 (2b/6b), 127.9 (2a/6a), 116.4 (3b/5b), 116.1 (3a/5a) and 106.9 (10a/14a). The ^{1}H and ^{13}C spectra of (-)-ε-viniferin (**1**) were very similar to those of ε-viniferin that were reported in the literature by Li et al. (1996).

(-)-α-Viniferin (**2**) was obtained as a brown amorphous powder (8.0 mg), optical rotation $[\alpha]_D^{20}$ -33° in MeOH. The UV spectrum showed absorption at λ_{max} 285 nm in MeOH suggesting the presence of non-conjugated phenolic chromophore. The IR spectrum showed the presence of hydroxyls (3369 cm^{-1}), aromatics (1615, 1515, 1484, 1440 cm^{-1}), oxyaryls (1362, 1243, 1171, 1113, 1071 cm^{-1}) and 1,4-disubstituted benzenes (831 cm^{-1}). The compound revealed a molecular ion peak $[M+H]^+$ at *m/z* 679 in the MS which corresponded to molecular formula $C_{42}H_{30}O_9$. The ^{1}H and ^{13}C-APT NMR spectra showed typical signals of a trimer stilbenoid. The ^{1}H NMR spectrum of **2** showed signals for six pairs of protons which represented three units of 4-hydroxyphenyls at δ 7.02 (2H, d, *J*=8.2 Hz, H-2a/6a), 6.70 (2H, d, *J*=8.6 Hz, H-3a/5a), 7.04 (2H, d, *J*=7.7 Hz, H-2c/6c), 6.78 (2H, d, *J*=8.4 Hz, H-3b/5b), 7.22 (2H, d, *J*=8.6 Hz, H-2b/6b) and 6.76 (2H, d, *J*=8.6 Hz, H-3c/5c). In addition, the presence of three units of

1,2,3,5-tetrasubstituted benzenes were shown by six *meta*-coupled doublets at δ 6.71 (1H, d, *J*=1.8 Hz, H-14a), 6.58 (1H, d, *J*=1.8 Hz, H-14c), 6.23 (1H, d, *J*=1.8 Hz, H-12a), 6.22 (1H, d, *J*=2.0 Hz, H-12b), 6.20 (1H, d, *J*=2.0 Hz, H-12c) and 5.98 (1H, d, *J*=2.0 Hz, H-14b). The remaining signals of aliphatic protons at δ 6.05 (1H, br s, H-7a), 3.95 (1H, br s, H-8a), 4.90 (1H, d, *J*=6.2 Hz, H-7b), 4.61 (1H, d, *J*=6.2 Hz, H-8b), 5.95 (1H, d, *J*=10.0 Hz, H-7c) and 4.67 (1H, d, *J*=10.0 Hz, H-8c) indicated the presence of three units of *trans*-2,3-dihydrobenzofurans. The ^{13}C-APT spectrum exhibited 36 signals that represented 42 carbons which consist of six pairs of equivalent carbons at 2a/6a, 3a/5a, 2b/6b, 3b/5b, 2c/6c, 3c/5c at δ 128.3, 115.8, 128.8, 116.2, 128.2, 116.2; nine oxyaryl carbons at δ 158.3, 161.6, 159.5, 158.5, 161.0, 159.5, 157.9, 161.9, 160.7; six aliphatic carbons at δ 86.4, 46.4, 95.7, 55.8, 90.1, 52.9; nine quaternary carbons at δ 132.3, 141.3, 120.9, 132.6, 139.8, 118.9, 132.0, 138.7,119.7 and six aromatic carbons in three units of 1,2,3,5-tetrasubstituted benzenes at δ 98.1, 106.3, 97.0, 108.6, 96.6, 105.9. Both ^{1}H and ^{13}C NMR spectral data were consistent to a trimer stilbenoid. These assignments were similar in comparison with literature data of α-viniferin which was isolated from *Dipterocarpus hasseltii* (Muhtadi Hakim et al. 2006).

(-)-Laevifonol (**3**) was isolated as a dark yellow gum (5.0 mg) which has optical rotation $[\alpha]_D^{20}$ -224° in MeOH. The UV spectrum showed absorption at λ_{max} 283 nm in MeOH which is characteristic of phenol rings. The IR spectrum indicated the presence of hydroxyls (3367 cm^{-1}), carbonyl (1788 cm^{-1}), aromatics (1641, 1517, 1453 cm^{-1}), oxyaryls (1338, 1260, 1161,1126, 1030 cm^{-1}) and 1,4-disubstituted benzenes (836 cm^{-1}). The mass spectrum showed a molecular ion peak $[M+H]^+$ at *m/z* 629 which corresponded to the molecular formula $C_{34}H_{28}O_{12}$. The ^{1}H-NMR spectrum showed the presence of four pairs of AX aromatic protons at δ 6.74 (2H, d, *J*=8.8 Hz, H-3a/5a), 6.74 (2H, d, *J*=8.8 Hz, H-2b/6b), 6.74 (2H, d, *J*=8.8 Hz, H-3b/5b) and 6.96 (2H, d, *J*=8.4 Hz, H-2a/6a); a pair of AX_2 aliphatic protons at δ 5.90 (2H, d, *J*=2.2 Hz, H-10b/14b) and 6.15 (1H, t, *J*=2.2 Hz, H-12b); a pair of *meta* coupled aromatic protons at δ 6.16 (1H, d, *J*=2.2 Hz, H-12a) and 7.16 (1H, d, *J*=2.2 Hz, H-14a); and eight aliphatic proton at δ 3.24 (1H, d, *J*=7.7 Hz, H-8b), 3.29 (1H, d, *J*=11.0 Hz, H-8a), 3.98 (1H, dd, *J*=10.0, 3.5 Hz, H-6c), 4.06 (1H, dd, *J*=10.0, 3.5 Hz, H-6c), 4.22 (1H, br s, H-5c), 4.41 (1H, br s, H-4c), 5.04 (1H, d, *J*=7.7 Hz, H-7b) and 5.27 (1H, d, *J*=11.0 Hz, H-7a). The above two benzylic protons signals of H-8b and H-7b are characteristic for *trans*-2,3-diaryltetrahydrofuran moiety. The ^{13}C-APT NMR spectrum exhibited 28 signals that represent 34 carbons, which consist of one carbonyl (δ 171.8), six oxyaryl carbons (δ 158.0,158.4, 158.8, 159.6, 159.6, 180.9), nine aliphatic carbons (δ 56.0, 56.3, 74.5, 75.0, 80.9, 88.9, 89.8, 94.0, 122.8) and 18 aromatic carbons (δ 96.8, 102.1, 106.9, 106.9, 110.5, 115.5, 115.5, 115.8, 115.8, 118.6, 128.0, 128.0,128.8, 128.8, 129.8, 131.7, 132.3, 145.7). Based on the analysis of the ^{1}H and ^{13}C-APT NMR spectral data, this compound consists of two fragments of an ε-viniferin and bicyclic ascorbic acid moieties attached to C-7 and C-8 of the dimer stilbene skeleton. Further evidence for the structure came from comparison of (-)-laevifonol NMR spectral data from *Shorea semini*s (Aminah et al. 2002).

(-)-Ampelopsin E (**4**) was isolated as a white amorphous powder. The compound revealed a molecular ion peak $[M+H]^+$ at m/z 681 in the mass spectrum which was analysed for the molecular formula $C_{42}H_{32}O_9$. This compound had a maximum absorption at 285 nm in the UV spectrum which indicated the presence of non-conjugated phenolic chromophore. The IR spectrum disclosed the absorption bands due to the hydroxyls (3367 cm^{-1}), aliphatic (2947 cm^{-1}), aromatics (1655 and 1451 cm^{-1}) and oxyaryls (1114 cm^{-1}). The ^{1}H-NMR spectrum showed the signals for dihydrobenzofuran moiety bearing 3,5-dihydroxyphenyl and 4-hydroxyphenyl groups which were observed at δ 4.54 (2H, d, *J*=5.0 Hz, H-8a/8c), 5.42 (2H, d, *J*=5.0 Hz, H-7a/7c), 6.16 (2H, t, *J*=2.0 Hz, H-12a/12c), 6.24 (4H, d, *J*=2.0 Hz, H-10a/14a/10c/14c), 6.84 (4H, d, *J*=8.4 Hz, H-3a/5a/3c/5c) and 7.24 (4H, d, *J*=8.4 Hz, H-2a/6a/2c/6c). The spectrum also revealed the presence of a 4-hydroxyphenyl group at δ 6.62 (2H, d, *J*=8.6 Hz, H-3b/5b) and 6.93 (2H, d, *J*=8.6 Hz, H-2b/6b); an isolated aromatic hydrogen at 6.45 (1H, s, H-12b) and a *trans* double bond 6.59 (1H, d, *J*=16.0 Hz, H-8b) and 6.66 (1H, d, *J*=16.0 Hz, H-7b).The ^{13}C-APT NMR spectrum exhibited 20 signals representing highly symmetrical 42 carbons which consists of four signals for nine oxyaryl carbons at δ 158.1 (C-4b), 158.3 (C-4a/4c), 159.7 (C-11a/13a/11c/13c), 162.5 (C-11b/13b); five signals for eight quaternary carbons at δ 120 (C-10b/14b), 129.0 (C-9b), 133.2 (C-1b), 133.6 (C-1a/1c), 147.1 (C-9a/9c); seven signals for 19 aromatic methine carbons at δ 91.2 (C-12b), 102.9 (C-12a/12c), 106.7 (C-10a/14a/10c/14c), 115.9 (C-3b/5b), 116.0 (C-3a/5a/3c/5c), 127.8 (C-2a/6a/2c/6c), 128.2 (C-2b/6b); and four signals for six aliphatic carbons at 57.8 (C-8a/8c), 93.9 (C-7a/7c), 122.0 (C-7b), 133.7 (C-8b). The ^{1}H and ^{13}C spectra of (-)-ampelopsin E (**4**) were very similar to those of the published data from *Ampelopsis brevipedunculata* (Oshima & Ueno 1993).

(-)-Hopeaphenol (**5**) was isolated as a white amorphous powder. The mass spectrum showed a molecular ion peak $[M+H]^+$ at m/z 907 which was analysed for the molecular formula $C_{52}H_{42}O_{12}$. The UV spectrum of **5** exhibited absorption at 282 nm typical for phenol chromophore. The IR spectrum showed absorptions for hydroxyls (3411 cm^{-1}), aliphatic (2950 cm^{-1}) and aromatics (1645 and 1453 cm^{-1}). Since the (-)-hopeaphenol consists of two symmetrical sides with 28 carbons each, the NMR analysis for the molecule would be done on one side only (left-side). The ^{1}H NMR spectrum showed two rings of *para* substituted phenyl at δ 7.12 (2H, d, *J*=8.4 Hz, H-2a/6a), 6.89 (2H, d, *J*= 8.4 Hz, H-2b/H-6b), 6.77 (2H, d, *J*= 8.4 Hz, H-3a/H-5a), 6.54 (2H, d, *J*=8.4 Hz, H-3b/H-5b); two rings of *meta*-coupled aromatic protons for 1,2,3,5-tetrasubstituted benzene rings at 6.53 (1H, br s, H-12a), 6.29 (1H, br s, H-14a), 5.71 (1H, d, *J*= 2.2 Hz, H-12b), 5.14 (1H, d, *J*=2.2 Hz, H-14b); five hydroxyl protons at 7.47, 8.05, 8.26, 8.54, 8.57 and four

aliphatic protons at 5.80 (1H, br s, H-7b), 5.73 (1H, d, *J*= 12.4 Hz, H-7a), 4.21 (1H, d, *J*=12.4 Hz, H-8a), 3.93 (1H, br s, H-8b). The presence of the above signals at δ 5.73 (1H, d, *J*=12.4 Hz, H-7a) and 4.21 (1H, d, *J*=12.4 Hz, H-8a) are characteristic for a 2,3-diarylbenzofuran moiety with *trans*-configuration. The ^{13}C-APT NMR spectrum exhibited 24 signals representing 28 carbons, which consists of six oxyaryl carbon signals at δ 155.6 (C-4b), 157.1 (C-13b), 157.2 (C-13a), 158.5 (C-4a), 158.8 (C-11a), 159.2 (C-11b); four aliphatic carbon signals at 41.3 (C-7b), 48.2 (C-8b), 49.8 (C-8a), 88.3 (C-7a) and 14 aromatic carbon signals at δ 95.2 (C-12b), 101.1 (C-12a), 106.4 (C-14a), 111.3 (C-14b), 115.2 (C-3b/5b), 116.0 (C-3a/5a), 118.6 (C-10b), 121.1 (C-10a), 129.3 (C-2b/6b), 130.3 (C-2a/6a), 130.9 (C-1a),135.2 (C-1b), 140.5 (C-9b), 142.4(C-9a). Based on the ^{1}H and ^{13}C spectral data and comparison with the previous report by Ito et al. (2000), this compound was identified as (-)-hopeaphenol.

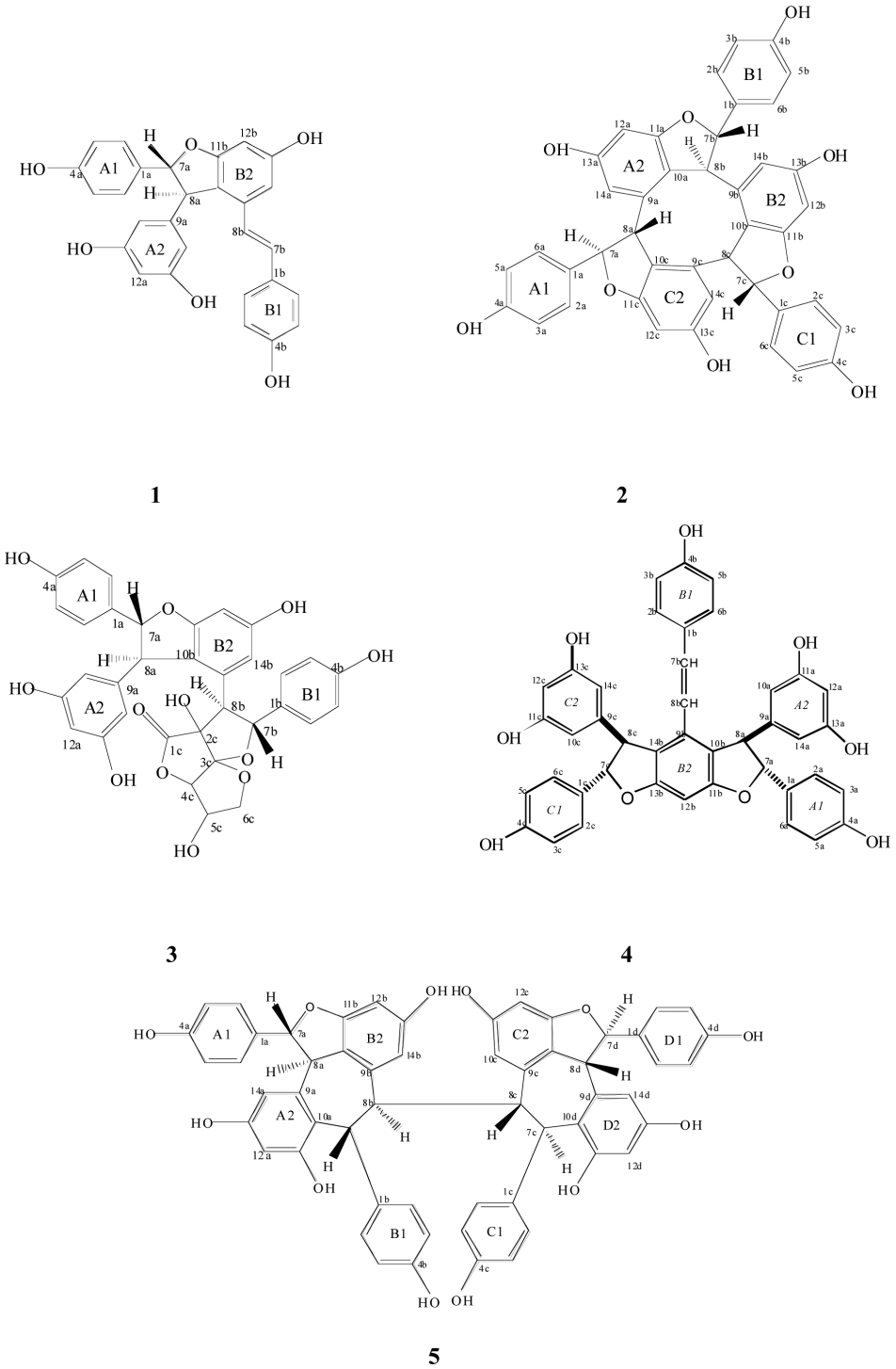

FIGURE 1. Compounds from stem bark of *Shorea faguetiana*

(-)-ε-Viniferin (**1**) and (-)-α-viniferin (**2**), a dimer and trimer of resveratrol, are frequently isolated from many species of *Shorea*, *Hopea*, *Vatica, Dryobalanops* and *Dipterocarpus*. Compound **1** is the main precursor in the biogenesis of the oligostilbenes reported earlier from *Vitis heyneana* (Li et al. 1996). Meanwhile compound **2** has been found in the most of Dipterocarpceae species such as *S. seminis*, *S hemsleyana*, *S. gibbosa*, *S. ovalis*, *H. sangal*, *H. exalata*, *H. dryobalanoides*, *V. rassak*, *D. aromatica*, *Diptercarpus verrucosus* and have been reported as a chemical marker for the family Dipterocarpaceae (Muhtadi Hakim et al. 2005). (-)-Laevifonol (**3**), a unique oligostilbene formed from condensation between **1** and ascorbic acid was first isolated from *S. laeviforia* (Hirano et al. 2003). It was recently reported to be present in *D. aromatica* (Wibowo et al. 2011) and *V. odorata* (Latip et al. 2011). (-)-Ampelopsin E (**4**) is a stilbene trimer which was first reported in *Ampelopsis brevipedunculata* (Vitaceae) (Oshima & Ueno 1993). This compound was also found in *Shorea gibbosa* from Yellow Meranti group (Saroyobudiono et al. 2008). The presence of (-)-hopeafenol (**5**) is very common in *Shorea* species. Previous studies have reported the isolation of this compound from several species such as *S. hemsleyana* (Ito et al. 2000), *S. seminis* (Aminah et al. 2002), *S. balangeran* (Tukiran Achmad et al. 2005), *S. robusta* (Varshney & Dayal 2006) and *S. ovalis* (Hadi & Noviany 2009). It is also usually available in other genus such as *Hopea*, *Dipterocarpus*, *Neobalanocarpus*, *Vatica* and also reported as a chemical marker for the family Dipterocarpaceae (Tukiran Achmad et al. 2005).

Conclusion

Five resveratrol oligomers of (-)-ε-viniferin (**1**), (-)-α-viniferin (**2**), (-)-laevifonol (**3**), (-)-ampelopsin E (**4**) and (-)-hopeaphenol (**5**) were successfully isolated from the acetone extract of *S. faguetiana*. The isolation work was carried out by means of various chromatographic techniques. The structures of compounds **1**-**5** were established on the basis of their spectral data, including UV, IR, NMR, MS and comparison with the literature data. To the best of our knowledge, this is the first report of oligostilbenes from *S. faguetiana*.

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