Studies on the Constituents of *Ailanthus integrifolia*

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A new phenolic glycoside, 3,4,5-trimethoxyphenol-1-(6-xylopyranosyl)glucopyranoside, was isolated together with twenty known compounds identified as koaburaside, 3,4,5-trimethoxyphenol, 5,7-dihydroxychromone-7-neohesperidoside, naringin, neoeriocitrin, *p*-coumaric acid, vanillin, vanillic acid, coniferyl aldehyde, ferulic acid, *trans*-triacontyl-4-hydroxy-3-methoxycinnamate, *p*-methoxycinnamic acid, 2,6-dimethoxybenzoquinone, 2-(1-hydroxyethyl)naphtho[2,3-*b*]furan-4,9-dione, 2-acetylnaphtho[2,3-*b*]furan-4,9-dione, 2-(1-hydroxyethyl)-6-methoxynaphtho[2,3-*b*]furan-4,9-dione, 2-acetyl-6-methoxynaphtho[2,3-*b*]furan-4,9-dione, specioside, jioglutin C and rehmaglutin D from the bark of *Ailanthus integrifolia* LAMK (Simaroubaceae).

Keywords *Ailanthus integrifolia*; Simaroubaceae; iridoid; flavonoid; furanonaphthoquinone; 3,4,5-trimethoxyphenol-1-(6-xylopyranosyl)glucopyranoside

Ailanthus integrifolia LAMK is a tall tree endemic to Indonesia and belonging to the Simaroubaceae, but no detailed studies have been reported on its chemical constituents.¹⁾

In this paper we report the isolation and structural elucidation of a new phenolic glycoside (**1**) and twenty known compounds. Their structures were determined on the basis of spectral data and chemical evidence.

Results and Discussion

Compound **1** was obtained as colorless needles, mp 219–221 °C, $[\alpha]_D^{25} -31.9^\circ$. The high resolution mass spectrum (HR-MS) of **1** showed a molecular ion at m/z 478.1685 (C₂₀H₃₀O₁₃). The infrared (IR) and ultraviolet (UV) spectra of **1** indicated the presence of hydroxyl ($\nu_{\max}$ 3600–3100 cm⁻¹) and aromatic ring ($\nu_{\max}$ 1600, 1500 cm⁻¹ and $\lambda_{\max}$ 268 nm) groups. The proton nuclear magnetic resonance (¹H-NMR) spectrum showed signals of three aryl methoxyl groups [δ 3.61 (3H, s), 3.75 (6H, s)], two sugar anomeric protons [δ 4.17 (d, $J=7.3$ Hz), 4.77 (d, $J=7.3$ Hz)], and two aromatic protons [δ 6.36 (2H, s)]. The carbon-13 nuclear magnetic resonance (¹³C-NMR) spectrum showed signals of three aryl methoxyl groups [δ 55.83 (C×2), 60.01], two anomeric carbons (δ 100.86, 104.07), and six aromatic carbons [δ 153.74, 153.08 (C×2), 132.82, 94.67 (C×2)]. These data suggested **1** is a trimethoxyphenol diglycoside. On acid hydrolysis, D-glucose (Glc) and D-xylose (Xyl) were obtained as component sugars. The assignments of proton and carbon signals were confirmed by correlation spectroscopy via ¹³C–¹H long-range couplings (COLOC), ¹H-detected heteronuclear multiple-bond correlation (HMBC), and long-range selective proton decoupling (LSPD). The COLOC spectrum of **1** showed long-range correlation between δ 153.74 (C-1 of aglycone) and δ 4.77 (H-1' of Glc). The HMBC spectrum showed long-range correlations between δ 4.17 (H-1'' of Xyl) and δ 68.79 (C-6' of Glc), δ 3.60, 3.97 (H-6' of Glc) and δ 104.07 (C-1'' of Xyl), thus suggesting that the xylose unit was connected to the C-6' of glucose. Additionally, the electron impact mass spectrum (EI-MS) of **1** showed fragment ion peaks at m/z 346 [$M-Xyl$]⁺, 184 [$M-Glc-Xyl$]⁺. From the above results, **1** was characterized as 3,4,5-trimethoxy-

phenol-1-(6-xylopyranosyl)glucopyranoside.

Compounds **2**–**21** were identified as koaburaside (**2**),²⁾ 3,4,5-trimethoxyphenol (**3**),²⁾ 5,7-dihydroxychromone-7-neohesperidoside (**4**),³⁾ naringin (**5**), neoeriocitrin (**6**),⁴⁾ *p*-coumaric acid (**7**), vanillin (**8**), vanillic acid (**9**), coniferyl aldehyde (**10**), ferulic acid (**11**), *trans*-triacontyl-4-hydroxy-3-methoxycinnamate (**12**),⁵⁾ *p*-methoxycinnamic acid (**13**), 2,6-dimethoxybenzoquinone (**14**), 2-(1-hydroxyethyl)naphtho[2,3-*b*]furan-4,9-dione (**15**),⁶⁾ 2-acetylnaphtho[2,3-*b*]furan-4,9-dione (**16**),⁶⁾ 2-(1-hydroxyethyl)-6-methoxynaphtho[2,3-*b*]furan-4,9-dione (**17**),⁷⁾ 2-acetyl-6-methoxynaphtho[2,3-*b*]furan-4,9-dione (**18**),⁷⁾ specioside (**19**),⁸⁾ jioglutin C (**20**)⁹⁾ and rehmaglutin D (**21**)¹⁰⁾ respectively, on the basis of the spectral data and by comparison with the respective literature data.

Experimental

General Experimental Procedures Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Hitachi 260-30 IR spectrometer. UV spectra were recorded on a Hitachi 340 spectrometer in MeOH and CHCl₃. Optical rotations were determined on a JASCO DIP-4 digital polarimeter. EI-MS were measured on a JEOL D-300 mass spectrometer. HR-MS and FAB-MS were measured on a JEOL DX-303 mass spectrometer. ¹H-, ¹³C- and two dimensional (2D)-NMR spectra were recorded with JEOL EX-400 (400 MHz for ¹H-NMR and 100 MHz for ¹³C-NMR) spectrometers. Chemical shifts were expressed in δ (ppm) downfield from tetramethylsilane as an internal standard, and coupling constants in hertz (Hz). Silica gel 60 (Merck), Diaion HP-20 (Mitsubishi Kasei), and octadecyl silica (ODS) (Fuji Silysia Chemical, Ltd.) were used for column chromatography. HPLC was carried out on silica gel [Senshu Pak silica 3031-N, Senshu Scientific Co., Ltd., 8.0 mm × 300 mm, detector UV 254 nm, solvent system CHCl₃–MeOH (100:1)].

Extraction and Isolation Dried bark (3.0 kg) of the plant collected Indonesia in March, 1990, was extracted with CHCl₃ (30 l) and MeOH (30 l) under reflux for 3 h. The CHCl₃ and MeOH extracts were concentrated under reduced pressure to give residues of 26 and 312 g, respectively. The CHCl₃ extract was chromatographed on silica gel (500 g) with CHCl₃ as eluent containing increasing amounts of MeOH (1, 5, 10, 50 and 100%). The fractions obtained by eluting with CHCl₃ and CHCl₃–MeOH (99:1) were repeatedly chromatographed on silica gel to give **8** (3.4 mg), **10** (0.3 mg), **12** (87.0 mg), **15** (4.9 mg), **16** (16.3 mg), **17** (5.5 mg) and **18** (0.6 mg). The MeOH extract was chromatographed on Diaion HP-20 (1.5 kg) with H₂O as eluent containing increasing amounts of MeOH (10, 25, 50, 70 and 100%). The fraction obtained by eluting with H₂O–MeOH (9:1–4:1) was repeatedly chromatographed on silica gel and ODS to give **2** (8.9 mg), **20** (45.0 mg) and **21** (490.0 mg). Similarly, the fraction obtained by eluting with H₂O–MeOH (1:1) was

Chart 1

TABLE I. ¹³C-, ¹H-NMR Spectral Data and Selected Cross-Peaks from the HMBC and COLOC Experiments for Compound 1

No.	δ _C	δ _H mult. (J/Hz)	HMBC	COLOC
1	153.74			H-2, 6, H-1'
2	94.67	6.36 s		
3	153.08			H-2, OCH ₃ -3
4	132.82			H-2, 6, OCH ₃ -4
5	153.08			H-6, OCH ₃ -5
6	94.67	6.36 s		
3-OMe	55.83	3.75 s		
4-OMe	60.01	3.61 s		
5-OMe	55.83	3.75 s		
1'	100.86	4.77 d (7.3)		
2'	73.08	3.22 m	C-1', C-3'	
3'	76.43	3.27 dt (3.9, 8.8)	C-2', C-4'	H-4'
4'	69.84	3.14 dt (4.1, 8.9)	C-3', C-5', C-6'	H-3', H-5'
5'	75.58	3.53 ddd (1.9, 9.3, 7.8)	C-4'	
6'	68.79	3.97 dd (1.8, 11.0)	C-1''	
		3.60 m	C-5'	
1''	104.07	4.17 d (7.3)	C-6'	
2''	73.23	2.97 dt (4.4, 8.3)	C-1'', C-3''	H-3''
3''	76.48	3.10 dt (4.4, 8.3)	C-2'', C-4''	H-4'', H-5''
4''	69.46	3.25 m	C-3''	H-3'', H-5''
5''	65.51	3.69 dd (5.4, 11.2)	C-1'', C-3'', C-4''	
		3.01 dd (10.3, 11.2)	C-1'', C-3'', C-4''	

In DMSO-*d*₆, ¹H: 400 MHz, ¹³C: 100 MHz.

repeatedly chromatographed on silica gel and ODS to give **1** (95.0 mg), **3** (28.4 mg), **4** (90.0 mg), **5** (3.57 g), **6** (247.8 mg), **7** (41.8 mg), **9** (12.3 mg), **11** (16.0 mg), **13** (7.6 mg), **14** (0.9 mg) and **19** (81.1 mg).

3,4,5-Trimethoxyphenol-1-(6-xylopyranosyl)glucopyranoside (1) Colorless needles (H₂O–acetone), mp 219–221 °C, [α]_D²⁵ –31.9° (*c* = 1.1, MeOH). UV λ_{max}^{MeOH} nm (log ε): 220 (3.74), 268 (2.87). IR ν_{max}^{KBr} cm^{–1}: 3600–3100, 1600, 1500, 1465, 1420, 1230, 1200, 1170, 1120, 1070, 1045, 1000, 810, 615. HR-MS *m/z*: 478.1685 (Calcd for C₂₀H₃₀O₁₃, 478.1677). EI-MS *m/z* (rel. int.): 478 (M⁺, 0.3), 346 (0.03), 185 (14), 184 (100), 170 (5), 169 (42), 141 (9), 126 (5), 111 (4), 73 (11), 69 (6), 60 (5), 57 (6), 42 (6). ¹H-, ¹³C-NMR, COLOC and HMBC: see Table I.

Acid Hydrolysis of 1 Compound **1** (11 mg) was dissolved in 1 N HCl (3 ml) and heated at 90 °C for 5 h in a hot bath. The reaction mixture was extracted with AcOEt, then the AcOEt layer was evaporated to dryness *in vacuo* after being washed with H₂O. The AcOEt extract was identified as 3,4,5-trimethoxyphenol (**3**) by HPLC. The aqueous layer was neutralized with Amberlite MB-3 and evaporated to dryness *in vacuo*. The residue was trimethylsilylated with *N*-trimethylsilylimidazole (0.2 ml) at room temperature for 1 h. The reaction mixture was added to H₂O and extracted with *n*-hexane, and the *n*-hexane layer was washed with H₂O. The *n*-hexane solution was subjected to gas chromatography (GC) for identification of the sugar moiety. The TMSi derivatives were identified as D-glucose and D-xylose. The GC conditions were as follows: column, 2% SE-30 (3 mm × 1 m); column temperature, 150 °C; injection port temperature 300 °C; carrier gas, N₂ (15 ml/min).

Koaburaside (2) Colorless needles, mp 205–207 °C. [α]_D²⁰ +53.8° (*c* = 0.65, MeOH). UV λ_{max}^{MeOH} nm (log ε): 222 sh (4.06), 270 (3.02). IR ν_{max}^{KBr} cm^{–1}: 3300, 1600, 1500, 1230, 1125, 1070. EI-MS *m/z* (rel. int.): 346 (M⁺, 1.3), 185 (12), 184 (100), 169 (67).

3,4,5-Trimethoxyphenol (3) Colorless needles, mp 145–146 °C. UV λ_{max}^{MeOH} nm (log ε): 222 sh (3.87), 276 (3.09). IR ν_{max}^{KBr} cm^{–1}: 3280, 1610, 1510, 1480, 1430, 1230, 1125, 995, 820, 775. EI-MS *m/z* (rel. int.): 184 (M⁺, 34), 169 (59), 141 (32), 111 (20), 75 (100), 69 (23).

5,7-Dihydroxychromone-7-neohesperidoside (4) Colorless needles, mp

152—155°C. $[\alpha]_D^{25} -57.2^\circ$ ($c=1.0$, MeOH). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 310 (3.39), 286 (3.64), 257 (4.12), 250 (4.11), 225 (4.05). UV $\lambda_{\max}^{\text{MeOH}+\text{AlCl}_3}$ nm (log ϵ): 363 (3.36), 302 (3.66), 261 (4.21). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3400, 1660, 1620, 1070. EI-MS m/z (rel. int.): 178 (100), 150 (26), 85 (25), 43 (27). FAB-MS m/z : 487 $[\text{M}+\text{H}]^+$.

Naringin (5) Colorless needles, mp 170—172°C. $[\alpha]_D^{25} -41.4^\circ$ ($c=1.1$, MeOH). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 228 (4.38), 285 (4.18), 330 sh (3.44). UV $\lambda_{\max}^{\text{MeOH}+\text{AlCl}_3}$ nm (log ϵ): 224 (4.50), 308 (4.28), 382 (3.47). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3400, 1640, 1180, 1075. EI-MS m/z (rel. int.): 272 (63), 153 (100), 120 (83), 85 (69), 73 (44), 71 (59), 57 (65), 42 (84). FAB-MS m/z : 581 $[\text{M}+\text{H}]^+$.

Neorocitrin (6) Colorless amorphous powder, $[\alpha]_D^{20} -96.4^\circ$ ($c=1.01$, $\text{C}_5\text{H}_5\text{N}$). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 286 (4.46), 330 sh (3.67). UV $\lambda_{\max}^{\text{MeOH}+\text{AlCl}_3}$ nm (log ϵ): 308 (4.46), 380 (3.67). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3400, 1630, 1295, 1170, 1080. EI-MS m/z (rel. int.): 288 (41), 153 (100), 136 (59), 60 (45). FAB-MS m/z : 619 $[\text{M}+\text{Na}]^+$, 597 $[\text{M}+\text{H}]^+$.

p-Coumaric Acid (7) Colorless needles, mp 188—190°C. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 230 (4.01), 303 sh (4.29), 312 (4.26). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3380, 1670, 1600, 1510, 1450, 1240, 1215, 830. EI-MS m/z (rel. int.): 164 (M^+ , 100), 163 (31), 147 (49), 119 (35), 118 (27), 91 (29), 65 (24).

Vanillin (8) Colorless needles, mp 73—74°C. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 233 (4.28), 280 (4.12), 310 (4.10). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3150, 1660, 1585, 1505, 1450, 1425, 1290, 1260, 1150. EI-MS m/z (rel. int.): 152 (M^+ , 92), 151 (100), 109 (39), 81 (70), 52 (42), 51 (43).

Vanillic Acid (9) Colorless needles, mp 216—217°C. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 262 (4.07), 293 (3.77). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3480, 1670, 1595, 1515, 1300, 1200. EI-MS m/z (rel. int.): 168 (M^+ , 100), 153 (79), 125 (48), 97 (29).

Coniferyl Aldehyde (10) Colorless oil. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 222 (4.00), 238 (4.02), 305 sh (4.09), 337 (4.32). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3247, 1656, 1599, 1519, 1136. EI-MS m/z (rel. int.): 178 (M^+ , 100), 147 (48), 135 (72), 107 (81), 77 (85), 51 (70), 40 (48).

Ferulic Acid (11) Colorless needles, mp 175—176°C. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 239 (4.15), 302 sh (4.22), 325 (4.32). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3420, 1660, 1590, 1505, 1270, 1170. EI-MS m/z (rel. int.): 194 (M^+ , 100), 179 (25), 133 (22), 77 (16), 51 (16).

trans-Triacontyl-4-hydroxy-3-methoxycinnamate (12) Colorless amorphous powder. UV $\lambda_{\max}^{\text{CHCl}_3}$ nm (log ϵ): 250 sh (3.81), 300 (3.93), 326 (4.04). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3420, 2910, 1710, 1635, 1600, 1510, 1470, 1265, 1170. HR-MS m/z : 614.5303 (Calcd for $\text{C}_{40}\text{H}_{70}\text{O}_4$, 614.5256). EI-MS m/z (rel. int.): 614 (M^+ , 96), 194 (30), 120 (100), 43 (21).

p-Methoxycinnamic Acid (13) Colorless needles, mp 138—140°C. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 243 (4.28), 317 sh (4.55) and 327 (4.59). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3350, 1680, 1600, 1505, 1430, 1160, 830. EI-MS m/z (rel. int.): 178 (M^+ , 62), 147 (100), 119 (35), 91 (25).

2,6-Dimethoxybenzoquinone (14) Yellow needles, mp 215—217°C. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 285 (4.29), 372 (2.87). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 1696, 1644, 1592, 1323, 1260, 1219, 1107. EI-MS m/z (rel. int.): 168 (M^+ , 25), 80 (26), 69 (100), 53 (24).

2-(1-Hydroxyethyl)naphtho[2,3-b]furan-4,9-dione (15) Yellow needles, mp 190—192°C. $[\alpha]_D^{25} -9.3^\circ$ ($c=0.43$, CHCl_3). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 249 (4.13), 272 sh (3.67), 332 sh (3.08), 360 sh (2.91). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3346, 1683, 1594, 1539, 1364, 1218, 1194, 1100, 954. HR-MS m/z : 242.0584 (Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_4$, 242.0576). EI-MS m/z (rel. int.): 242 (M^+ , 33), 227 (100), 200 (59), 199 (45), 171 (25).

2-Acetylnaphtho[2,3-b]furan-4,9-dione (16) Yellow needles, mp 227—228°C. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 253 (4.66), 320 sh (4.56), 338

(3.80). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 1670, 1570, 1350, 1255, 1220. HR-MS m/z : 240.0437 (Calcd for $\text{C}_{14}\text{H}_8\text{O}_4$, 240.0420). EI-MS m/z (rel. int.): 240 (M^+ , 61), 225 (100), 157 (12), 113 (11) and 42 (11).

2-(1-Hydroxyethyl)-6-methoxynaphtho[2,3-b]furan-4,9-dione (17) Orange needles, mp 182—184°C. $[\alpha]_D^{25} -8.9^\circ$ ($c=0.21$, CHCl_3). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 266 (4.09), 303 sh (3.46), 340 sh (3.13), 400 (3.08). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3444, 1671, 1595, 1581, 1286, 1247. HR-MS m/z : 272.0640 (Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_5$, 272.0681). EI-MS m/z (rel. int.): 272 (M^+ , 57), 257 (100), 229 (51), 201 (20), 135 (39), 63 (13), 43 (16).

2-Acetyl-6-methoxynaphtho[2,3-b]furan-4,9-dione (18) Orange needles, mp 227—229°C. UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 248 (3.99), 282 (4.18), 400 (3.27). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 1697, 1675, 1594, 1576, 1270, 1248. EI-MS m/z (rel. int.): 270 (M^+ , 84), 255 (100), 187 (23), 75 (42), 42 (35).

Specioside (19) Colorless amorphous powder. $[\alpha]_D^{20} +195.5^\circ$ ($c=0.89$, $\text{C}_5\text{H}_5\text{N}$). UV $\lambda_{\max}^{\text{MeOH}}$ nm (log ϵ): 233 (3.88), 308 sh (4.15), 316 (4.21). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3430, 3350, 1700, 1605, 1510, 1225, 1055. EI-MS m/z (rel. int.): 200 (13), 164 (54), 147 (55), 120 (70), 91 (76), 85 (64), 81 (97), 73 (73), 57 (56), 42 (100), 38 (52), 30 (84). FAB-MS m/z : 509 $[\text{M}+\text{H}]^+$.

Jioglutin C (20) Colorless oil. $[\alpha]_D^{20} +39.2^\circ$ ($c=1.05$, $\text{C}_5\text{H}_5\text{N}$). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3428, 1125, 1042, 1022, 1005. EI-MS m/z (rel. int.): 85 (53), 59 (46), 58 (100), 42 (39), 40 (41), 31 (40), 30 (86). FAB-MS m/z : 201 $[\text{M}-\text{OCH}_3]^+$.

Rehmaglutin D (21) Colorless oil. $[\alpha]_D^{21} +60.6^\circ$ ($c=1.24$, MeOH). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1} : 3381, 1148, 1047, 1028, 962, 789. EI-MS m/z (rel. int.): 155 (18), 154 (28), 85 (18), 84 (100), 83 (36), 71 (54), 42 (19). FAB-MS m/z (rel. int.): 223 $[\text{M}+\text{H}]^+$ (6), 221 $[\text{M}+\text{H}]^+$ (17).

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