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°. The high resolution mass spectrum (HR-MS) of **1** showed a molecular ion at *m/z* 478.1685 ($C_{20}H_{30}O_{13}$). The infrared (IR) and ultraviolet (UV) spectra of **1** indicated the presence of hydroxyl (ν_{max} 3600—3100 cm^{-1}) and aromatic ring (ν_{max} 1600, 1500 cm^{-1} and λ_{max} 268 nm) groups. The proton nuclear magnetic resonance (^{1}H-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 (^{13}C-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* ^{13}C–^{1}H long-range couplings (COLOC), ^{1}H-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-trimethoxyphenol-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 $CHCl_3$. 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. ^{1}H-, ^{13}C- and two dimensional (2D)-NMR spectra were recorded with JEOL EX-400 (400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-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 $CHCl_3$–MeOH (100 : 1)].

Extraction and Isolation Dried bark (3.0 kg) of the plant collected Indonesia in March, 1990, was extracted with $CHCl_3$ (30 l) and MeOH (30 l) under reflux for 3 h. The $CHCl_3$ and MeOH extracts were concentrated under reduced pressure to give residues of 26 and 312 g, respectively. The $CHCl_3$ extract was chromatographed on silica gel (500 g) with $CHCl_3$ as eluent containing increasing amounts of MeOH (1, 5, 10, 50 and 100%). The fractions obtained by eluting with $CHCl_3$ and $CHCl_3$–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 H_2O as eluent containing increasing amounts of MeOH (10, 25, 50, 70 and 100%). The fraction obtained by eluting with H_2O–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 H_2O–MeOH (1 : 1) was

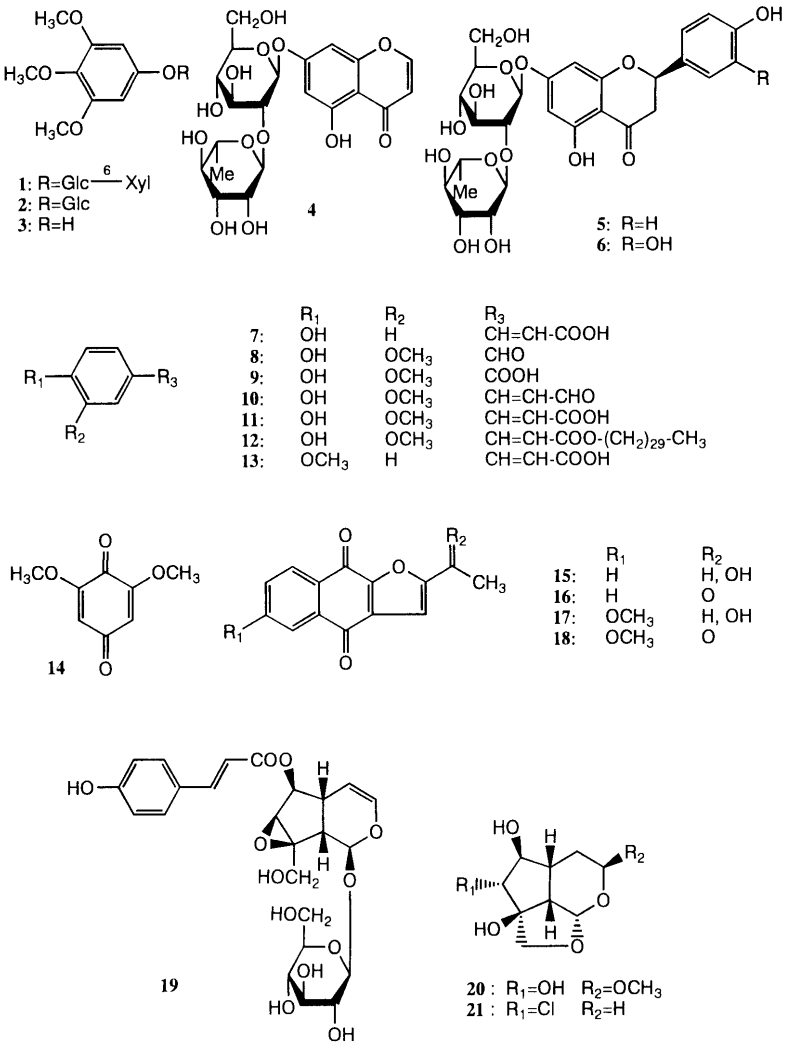

Chart 1

TABLE I. ^{13}C-, ^{1}H-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, ^{1}H: 400 MHz, ^{13}C: 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 (H_2O–acetone), mp 219—221 °C, $[\alpha]_D^{25}$ −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 $C_{20}H_{30}O_{13}$, 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). ^{1}H-, ^{13}C-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 H_2O. 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 H_2O and extracted with *n*-hexane, and the *n*-hexane layer was washed with H_2O. 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, N_2 (15 ml/min).

Koaburaside (2) Colorless needles, mp 205—207 °C. $[\alpha]_D^{20}$ +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° (c=1.0, MeOH). UV λ_{max}^{MeOH} nm (log ε): 310 (3.39), 286 (3.64), 257 (4.12), 250 (4.11), 225 (4.05). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 363 (3.36), 302 (3.66), 261 (4.21). IR ν_{max}^{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 $[M+H]^+$.

Naringin (5) Colorless needles, mp 170—172 °C. $[\alpha]_D^{25}$ −41.4° (c=1.1, MeOH). UV λ_{max}^{MeOH} nm (log ε): 228 (4.38), 285 (4.18), 330 sh (3.44). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 224 (4.50), 308 (4.28), 382 (3.47). IR ν_{max}^{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 $[M+H]^+$.

Neoeriocitrin (6) Colorless amorphous powder, $[\alpha]_D^{20}$ −96.4° (c=1.01, C_5H_5N). UV λ_{max}^{MeOH} nm (log ε): 286 (4.46), 330 sh (3.67). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 308 (4.46), 380 (3.67). IR ν_{max}^{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 $[M+Na]^+$, 597 $[M+H]^+$.

***p*-Coumaric Acid (7)** Colorless needles, mp 188—190 °C. UV λ_{max}^{MeOH} nm (log ε): 230 (4.01), 303 sh (4.29), 312 (4.26). IR ν_{max}^{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 λ_{max}^{MeOH} nm (log ε): 233 (4.28), 280 (4.12), 310 (4.10). IR ν_{max}^{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 λ_{max}^{MeOH} nm (log ε): 262 (4.07), 293 (3.77). IR ν_{max}^{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 λ_{max}^{MeOH} nm (log ε): 222 (4.00), 238 (4.02), 305 sh (4.09), 337 (4.32). IR ν_{max}^{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 λ_{max}^{MeOH} nm (log ε): 239 (4.15), 302 sh (4.22), 325 (4.32). IR ν_{max}^{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 $\lambda_{max}^{CHCl_3}$ nm (log ε): 250 sh (3.81), 300 (3.93), 326 (4.04). IR ν_{max}^{KBr} cm^{-1}: 3420, 2910, 1710, 1635, 1600, 1510, 1470, 1265, 1170. HR-MS m/z: 614.5303 (Calcd for $C_{40}H_{70}O_4$, 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 λ_{max}^{MeOH} nm (log ε): 243 (4.28), 317 sh (4.55) and 327 (4.59). IR ν_{max}^{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 λ_{max}^{MeOH} nm (log ε): 285 (4.29), 372 (2.87). IR ν_{max}^{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° (c=0.43, $CHCl_3$). UV λ_{max}^{MeOH} nm (log ε): 249 (4.13), 272 sh (3.67), 332 sh (3.08), 360 sh (2.91). IR ν_{max}^{KBr} cm^{-1}: 3346, 1683, 1594, 1539, 1364, 1218, 1194, 1100, 954. HR-MS m/z: 242.0584 (Calcd for $C_{14}H_{10}O_4$, 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 λ_{max}^{MeOH} nm (log ε): 253 (4.66), 320 sh (4.56), 338 (3.80). IR ν_{max}^{KBr} cm^{-1}: 1670, 1570, 1350, 1255, 1220. HR-MS m/z: 240.0437 (Calcd for $C_{14}H_8O_{14}$, 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° (c=0.21, $CHCl_3$). UV λ_{max}^{MeOH} nm (log ε): 266 (4.09), 303 sh (3.46), 340 sh (3.13), 400 (3.08). IR ν_{max}^{KBr} cm^{-1}: 3444, 1671, 1595, 1581, 1286, 1247. HR-MS m/z: 272.0640 (Calcd for $C_{15}H_{12}O_5$, 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 λ_{max}^{MeOH} nm (log ε): 248 (3.99), 282 (4.18), 400 (3.27). IR ν_{max}^{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° (c=0.89, C_5H_5N). UV λ_{max}^{MeOH} nm (log ε): 233 (3.88), 308 sh (4.15), 316 (4.21). IR ν_{max}^{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 $[M+H]^+$.

Jioglutin C (20) Colorless oil. $[\alpha]_D^{20}$ +39.2° (c=1.05, C_5H_5N). IR ν_{max}^{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 $[M-OCH_3]^+$.

Rehmaglutin D (21) Colorless oil. $[\alpha]_D^{21}$ +60.6° (c=1.24, MeOH). IR ν_{max}^{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 $[M+H]^+$ (6), 221 $[M+H]^+$ (17).

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