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Phytochemical Studies on Magnoliae Flos (I) Isolation of Lignans from the Flower Buds of *Magnolia biondii*†

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Abstract – The 12 compounds were isolated from MeOH extract of *Magnolia biondii* and their structures were identified as seven lignans, two phenolics, one coumarin, and two flavonoid compounds, respectively. Among these constituents, tiliroside (**3**), kaempferol-7-methyl ether (**4**), 4-hydroxybenzoic acid (**5**), vanilic acid (**6**), and scopoletin (**9**) were isolated from *Magnolia biondii* for the first time.
Keywords – Magnoliae Flos, *Magnolia biondii*, Isolation, Identification

Introduction

The Magnoliae Flos is described as a flower buds of *Magnolia biondii* Pampanini, *Magnolia denudate* Desrousseaux, *Magnolia kobus* De Candolle and *Magnolia sprengeri* Pampanini in the Korean Herbal Pharmacopoeia (KHP). Lignans such as biondnoid I, fargesin, aschantin, magnolin, veraguensin, galgravin, fargesone B, lariciresinol, licarin B, and burchellin (Ma, *et al*., 1996; Li, *et al*., 2005), flavonoids (Tsuruga, *et al*., 1991), alkaloids (Talapatra, *et al*., 1982; Nakano, 1956; Kimura, *et al*., 1983; Watanabe, *et al*., 1981), and terpenoids (Du, *et al*., 2001) were reported in the previous research. On the quantitative analysis of the aromatic components, and the constituent of *M. biondii* by GC/MS (Chen, *et al*., 1994; Chen and Feng, 2003), the biondnoid I component of *M. biondii* by HPLC analysis method (Yu, *et al*., 2004), the magnolin and fargesone as lignin of *M. Flos* by RP-HPLC (Fang, *et al*., 2002; Xu, *et al*., 2003), and the volatile oil by supercritical CO_2 extract method (Zang, *et al*., 2005) were reported. Pharmacological studies on this drug described neuromuscular blocking action (Kimura, *et al*., 1983), inotropic activity (Kimura, *et al*., 1989), anti-inflammatory (Kimura, *et al*., 1985; Wang, *et al*., 2000; Wang, *et al*., 2005; Lim and Park, 2005), central dopaminergic activity (Watanabe, *et al*., 1981), anti-allergy (Tsuruga, *et al*., 1991), anti-allergy rhinitis (Chen, *et al*., 2006), anti-angiogenic (Kobayashi, *et al*., 1996), platelet activating factor (PAF) receptor antagonist activity (Pan, *et al*., 1987), cholesterol acyltransferase (ACAT) inhibitory activity (Kwon, *et al*., 1999), apoptosis inducement (Kim, *et al*., 2003), and vasorelaxant activity (Yin, *et al*., 2005) effects.

In this study, we isolated and identified 12 compounds from the flower buds of *Magnolia biondii* on the basis of various spectroscopic data.

Experimental

Plant Material – The flower buds of *M. biondii* (10 kg) were collected in April 2007 and identified by Prof. Je Hyun Lee, Dongguk University.

Extraction and isolation – The samples of *M. biondii* (10 kg) were refluxed with MeOH for 5 h at 60 °C. The MeOH extract was evaporated using rotary vacuum evaporator and partitioned successively between H_2O and hexane (156.6 g), CH_2Cl_2 (458.9 g), EtOAc (26.4 g), and n-BuOH (59.4 g) and the remaining H_2O (153.0 g). The CH_2Cl_2 fraction (65.0 g) was fractionated by column chromatography over a silica gel (0.063 - 0.200 mm) column with hexane:EtOAc (gradient) and CH_2Cl_2 : MeOH (gradient) to obtain 18 fractions. The fraction 5 of them was recrystallized from MeOH to yield compound **1** and

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the fraction 7 was chromatographed on a silica gel (below 0.063 mm) column with hexane : $CHCl_3$: EtOAc (200 : 95 : 5) to afford subfractions 7-1 to 7-3. Subfraction 7-3 dissolved in MeOH of these was fractionated by Sephadex LH-20 column with 50% MeOH to afford subfraction 7-3-2, which was further chromatographed on a RP-18 column to obtain compound **4**. The fraction 8 was fractionated on a silica gel (below 0.063 mm) column with hexane : $CHCl_3$: EtOAc (15 : 10 : 1) to afford subfractions 8-1 to 8-4. Compound **3** was obtained from subfraction 8-4 by a RP-18 column. The fraction 10 was chromatographed on a silica gel (below 0.063 mm) column using hexane : $CHCl_3$: MeOH (10 : 90 : 1) to afford subfraction 10-1, followed rechromatography with hexane : $CHCl_3$: MeOH (10 : 90 : 1) to give subfraction 10-1-2, which was recrystallized from MeOH to obtain compound **2**. A mixture of fractions 13 and 14 was fractionated on a silica gel (below 0.063 mm) column to give subfractions 13 and 14-1, and 13 and 14-6. Each of two subfractions was recrystallized to afford compounds **6** and **7**. The fraction 15 was fractionated by a silica gel (below 0.063 mm) column with hexane:$CHCl_3$:EtOAc (30 : 10 : 1) afford subfractions 15-1 to 15-7. The subfraction 15-5 was rechromatographed on a sephadex LH-20 to afford compound **5** and compound **10** was obtained from subfraction 15-7 using a RP-18 column. The EtOAc fraction (26.4 g) was fractionated by column chromatography over a silica gel (0.063 - 0.200 mm) column with CH_2Cl_2 : MeOH (gradient) to obtain 12 fractions. The fraction 4 of them was fractionated by a silica gel (below 0.063 mm) column with CH_2Cl_2 : MeOH (98 : 2→97 : 3) to afford subfractions 4-1 to 4-7. The subfraction 4-6 was further chromatographed on a RP-18 column with MeOH : H_2O (4 : 6→8 : 2) to obtain compounds**11** and **8** was afforded from subfraction 4-7 using a sephadex LH-20 column. The fraction 5 was fractionated into seven subfractions and subfraction 5-4 was rechromatographed on a sephadex LH-20 column to afford compound **9** from subfraction 5-4-2. Finally, the fraction 11 was refractionated on a sephadex LH-20 column to give 11-4, which was recrystallized to obtain compound **12**.

Fargesin (1) – $C_{21}H_{22}O_6$; mp130 - 131 °C; IR V_{max} (KBr) 1592, 1441, 1272, 1245, 1141, 1083, 1030 cm^{-1}; UV λ_{max}MeOH nm (log ε) 283 (3.12), 232 (4.12), 204 (4.07); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.75~6.91 (m, Ar-H), 5.93 (2H, s, -OCH_2O-), 4.85 (1H, d, J = 5.6 Hz, H-6), 4.40 (1H, d, J = 7.2 Hz, H-2), 4.10 (1H, d, J = 10.0 Hz, H-8), 3.89 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 3.81 (2H, m, H-4, H-8), 3.30 (2H, m, H-4, H-5), 2.86 (1H, m, H-1); ^{13}C-NMR ($CDCl_3$,100 MHz) δ: 149.0 (C-3'), 148.2 (C-4'), 148.2 (C-3"), 147.4 (C-4"), 135.3 (C-1"), 131.1 (C-1'), 119.8 (C-6"), 117.9 (C-6'), 111.2 (C-5'), 109.1 (C-2"), 108.4 (C-2'), 106.8 (C-5"), 101.3 (-OCH_2O-), 87.9 (C-2), 82.2 (C-6), 71.2 (C-8), 70.0 (C-4), 56.1 (OCH_3×2), 54.8 (C-1), 50.4 (C-5); EI-MS m/z: 370 $[M]^+$

Eudesmin (2) – $C_{22}H_{26}O_6$;mp: 98 - 100 °C; IR V_{max} (KBr) 1605, 1590, 1518, 1449, 1263, 1235, 1143, 1027 cm^{-1};UV λ_{max}MeOH nm (log ε) 278 (2.89), 231 (4.04), 203 (4.05); ^{1}H-NMR ($CDCl_3$,400 MHz) δ: 6.84-6.91 (6H, m, Ar-H), 4.77 (2H, d, J = 4.0 Hz, H-2 and H-6), 4.26 (2H, dd, J = 6.6 and 8.6 Hz, H-4 and H-8), 3.88-3.90 (2H, m, H-4 and H-8), 3.90, 3.88 (each 3H, s, OCH_3), 3.12 (2H, m, H-1 and H-5); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 146.8 (C-3', C-3"), 146.2 (C-4', C-4"), 131.1 (C-1', C-1"), 115.9 (C-6', C-6"), 108.6 (C-5', C-5"), 106.8 (C-2', C-2"), 83.4 (C-2, C-6), 69.3 (C-4, C-8). 53.6, 53.5 (each, 2×OCH_3), 51.8 (C-1, C-5); EI-MS m/z: 386 $[M]^+$

Aschantin (3) – $C_{22}H_{24}O_7$; UV λ_{max}MeOH nm (log ε) 282 (3.10), 203 (4.10); ^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 6.79-6.89 (3H, m, Ar-H), 5.96 (2H, s, -OCH_2O-), 4.62 (2H, d, J = 5.2 Hz, H-2, H-6), 4.08-4.15 (2H, m, H-4eq, H-8eq), 3.78-3.73 (2H, m, H-4ax, H-8ax), 3.74 (6H, s, 2×OCH_3), 3.59 (3H, s, OCH_3), 2.93-3.06 (2H, m, H-1 and H-5); ^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 152.9 (C-3', C-5'), 147.4 (C-3"), 146.5 (C-4"), 137.2 (C-4'), 136.6 (C-1'), 135.5 (C-1"), 119.4 (C-6"), 108.0 (C-5"), 106.6 (C-2"), 103.1 (C-6', C-2'), 100.9 (-OCH_2O-), 85.1 (C-6), 84.9 (C-2), 71.2 (C-4), 71.1 (C-8), 60.0 (OCH_3), 55.9 (2×OCH_3), 53.8 (C-5), 53.7 (C-1); EI-MS m/z: 400 $[M]^+$

Kobusin (4) – $C_{21}H_{22}O_6$; colorless oil; UV λ_{max}MeOH nm (log ε) 283 (2.98), 232 (4.02); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.88~6.75 (6H, m, Ar-H), 5.93 (2H, s, -OCH_2O-), 4.73~4.71 (2H, m, H-2, H-6), 4.25~4.20 (2H, m, H-4eq, H-8eq), 3.88 (3H, s, OCH_3), 3.87 (3H, s, OCH_3), 3.88~3.84 (2H, m, H-4ax, H-8ax), 3.10~3.05 (2H, m, H-1, H-5); ^{13}C-NMR ($CDCl_3$,100 MHz) δ: 149.4 (C-3'), 148.8 (C-4'), 148.2 (C-3"), 147.3 (C-4"), 135.3 (C-1"), 133.7 (C-1'), 119.6 (C-6"), 118.5 (C-6'), 111.2 (C-5'), 109.4 (C-2'), 108.4 (C-5"), 106.7 (C-2"), 101.3 (-OCH_2O-), 86.0 (C-6), 86.0 (C-2), 72.0 (C-8), 71.9 (C-4), 56.1, 56.1 (2×OCH_3), 54.5 (C-1), 54.5 (C-5); EI-MS m/z: 370 $[M]^+$, 339 $[M-OCH_3]^+$

Magnolin (5) – $C_{23}H_{28}O_7$; mp: 90~91 °C; IR V_{max} (KBr) 1588, 1521, 1465, 1268, 1237, 1130, 1026 cm^{-1}; UV λ_{max}MeOH nm (log ε) 277 (3.16), 229 (4.35), 203 (4.09); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.84-6.92 (3H, m, Ar-H), 6.58 (2H, s, Ar-H), 4.75-4.78 (2H, m, H-2, H-6), 4.27-4.32 (2H, m, H-4eq, H-8eq), 3.91-3.96 (2H, m, H-4ax, H-8ax), 3.91 (3H, s, OCH_3), 3.88 (9H, s, OCH_3), 3.84 (3H, s, OCH_3), 3.08-3.16 (2H, m, H-1, H-5); ^{13}C-

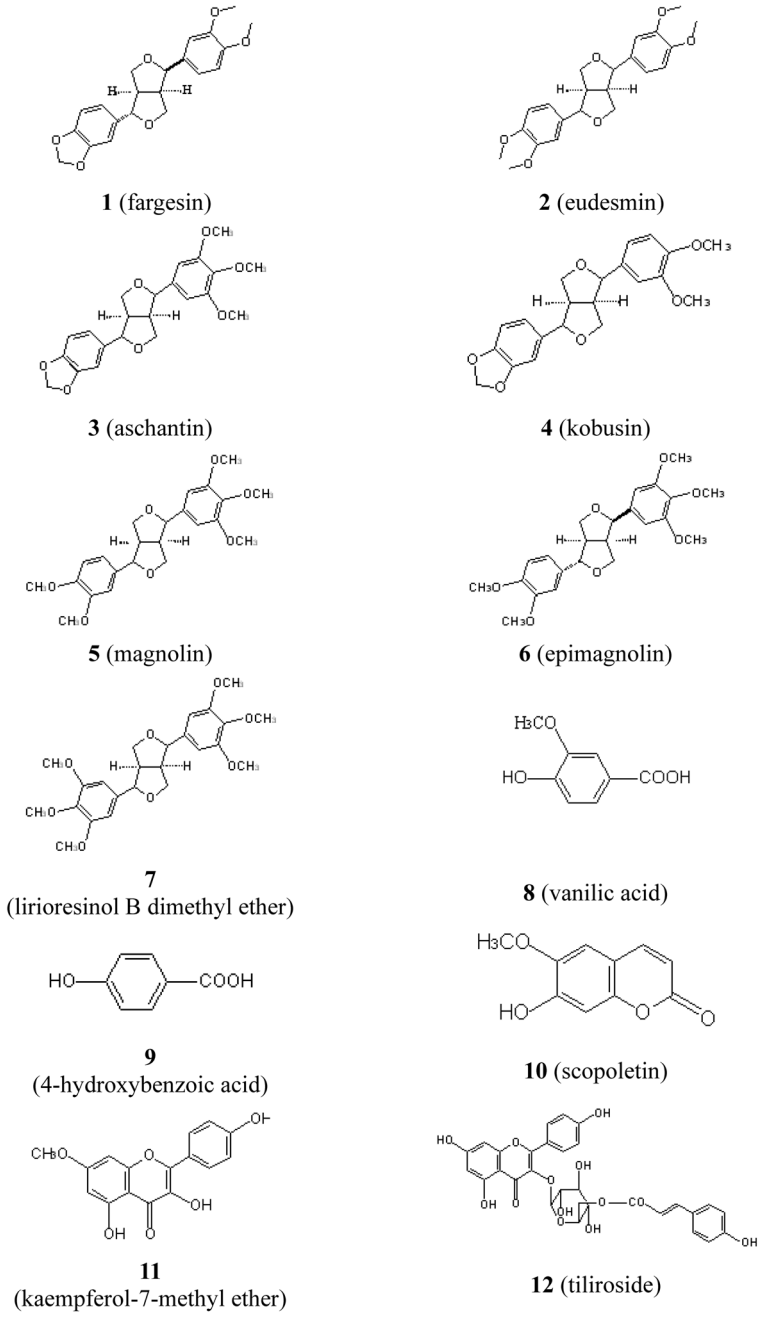

Fig. 1. The chemical structures of compounds isolated from *M. biondii.*

NMR ($CDCl_3$,100 MHz) δ: 153.6 (C-3', 5'), 149.4 (C-4"), 148.8 (C-3"), 137.6 (C-4'), 137.0 (C-1'), 133.6 (C-1"), 118.5 (C-6"), 111.2 (C-5"), 109.4 (C-2"), 103.0 (C-2', 6'), 86.2 (C-2), 85.9 (C-6), 72.2 (C-8), 72.0 (C-4), 61.1, 56.4, 56.4, 56.4, 56.2 (5×OCH_3), 54.6 (C-1), 54.3 (C-5); EI-MS m/z: 416 $[M]^+$

Epimagnolin (6) – $C_{23}H_{28}O_7$; mp: 77~78 °C; IR V_{max} (KBr) 1592, 1519, 1459, 1259, 1237, 1131, 1024 cm^{-1}; UV λ_{max}MeOH nm (log ε) 278 (3.61), 230 (4.27); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.60~6.94 (5H, m, Ar-H), 4.88 (1H, d, J = 5.6 Hz, H-2), 4.44 (1H, d, J = 6.8 Hz, H-6), 4.16 (1H, d, J = 9.6 Hz, H-4eq), 3.91 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 3.88 (6H, s, OCH_3), 3.84 (3H, s, OCH_3), 3.85~3.89 (2H, m, H-4ax, 8eq), 3.31~3.38 (2H, m, H-1, 8ax), 2.90~2.95 (1H, m, H-5); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 153.6 (C-3", 5"), 149.1 (C-4'), 148.2 (C-3'), 137.3 (C-4"), 137.1 (C-1"), 131.1 (C-1'), 117.9 (C-6'), 111.3 (C-5'), 109.2 (C-2'), 103.2 (C-2"), 103.1 (C-6"),

88.0 (C-6), 82.2 (C-2), 71.3 (C-4), 70.1 (C-8), 61.0, 56.4, 56.3, 56.3, 56.1 (5 × OCH_3), 54.8(C-5), 50.1(C-1); EI-MS m/z: 416 $[M]^+$

Lirioresinol B dimethyl ether (7) – $C_{24}H_{30}O_8$; mp: 132~133 ºC; IR V_{max} (KBr) 1588, 1512, 1464, 1238, 1135, 1057 cm^{-1}; UV λ_{max}MeOH nm (log ε) 270 (3.14), 203 (4.17); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.58 (4H, s, Ar-H), 4.75 (2H, d, *J* = 4.0 Hz, H-2, H-6), 4.31 (2H, dd, *J* = 6.8 and 9.2 Hz, H-4, H-8), 3.92-3.96 (2H, m, H-4, H-8), 3.88 (12H, s, OCH_3), 3.84 (6H, s, OCH_3), 3.11 (2H, m, H-1, H-5); ^{13}C-NMR ($CDCl_3$,100 MHz) δ: 153.4 (C-3", C-5", C-3', C-5'), 137.4 (C-4", C-4'), 136.7 (C-1", C-1'), 102.8 (C-6", C-2", C-6', C-2'), 86.0 (C-2, C-6), 72.0 (C-4, C-8), 60.9 (2×OCH_3), 56.2 (4×OCH_3), 54.4 (C-1, C-5); EI-MS m/z: 446 $[M]^+$

Vanilic acid (8) – $C_8H_8O_4$;mp: 203.9 ºC; IR V_{max} (KBr) 3485 (OH), 1682 (C = O), 1599, 1524 (aromatic C = C), 1301 cm^{-1}; UV λ_{max}MeOH nm (log ε) 290 (3.79), 259 (3.58), 217 (4.37), 204 (3.91); ^{1}H-NMR (CD_3OD, 400 MHz) δ: 7.55 (1H, dd, *J* = 8.8 and 2.0 Hz, H-6), 7.55 (1H, d, *J* = 2.0 Hz, H-2), 6.83 (1H, d, *J* = 8.8 Hz, H-5), 3.89 (3H, s, OCH_3); ^{13}C-NMR (CD_3OD, 100 MHz) δ: 169.0 (C-7), 151.4 (C-4), 147.4 (C-3), 124.0 (C-6), 122.0 (C-1), 114.6 (C-5), 112.5 (C-2), 55.1 (OCH_3); EI-MS m/z: 168 $[M]^+$

4-Hydroxybenzoic acid (9) – $C_7H_6O_3$;mp: 198 ºC; IR V_{max} (KBr) 3393 (OH), 1678 (C = O), 1608, 1596, 1511 (aromatic C = C), 1246 cm^{-1};UV λ_{max}MeOH nm (log ε) 254 (3.38), 203 (3.79); ^{1}H-NMR (CD_3OD, 400 MHz) δ: 7.87 (2H, d, *J* = 8.8 Hz, H-2, 6), 6.81 (2H, d, *J* = 8.8 Hz, H-3, 5); ^{13}C-NMR (CD_3OD, 100 MHz) δ: 168.1 (C-7), 161.3 (C-4), 131.0 (C-2, 6), 120.8 (C-1), 114.0 (C-3, 5); EI-MS m/z: 138 $[M]^+$

Scopoletin (10) – $C_{10}H_8O_4$; mp: 210~211 ºC; IR V_{max} (KBr) 3295 (OH), 1705 (C = O), 1608, 1563, 1512 (C = C) cm^{-1}; UV λ_{max}MeOH nm (log ε) 344 (3.77), 297 (3.39), 252 (3.76), 228 (4.12), 203 (3.98); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.60 (1H, d, *J* = 9.6 Hz, H-4), 6.92 (1H, s, H-5), 6.85 (1H, s, H-8), 6.27 (1H, d, *J* = 9.6 Hz, H-3), 3.96 (3H, s, OCH_3); ^{13}C-NMR ($CDCl_3$,100 MHz) δ: 161.7 (C-2), 150.5 (C-9), 149.9 (C-7), 144.2 (C-6), 143.6 (C-4), 113.6 (C-3), 117.7 (C-5), 107.7 (C-10), 103.4 (C-8), 56.6 (OCH_3); EI-MS m/z: 192 $[M]^+$

Kaempferol-7-methyl ether (11) – $C_{16}H_{12}O_6$;mp: 225 ºC; IR V_{max} (KBr) 3421 (OH), 1658 (C = O), 1615, 1570, 1509 (aromatic C = C) cm^{-1};UV λ_{max}MeOH nm (log ε) 366 (4.01), 266 (4.22), 203 (4.28); ^{1}H-NMR (CD_3OD, 400 MHz) δ: 8.09 (2H, d, *J* = 8.8 Hz, H-2', H-6'), 6.90 (2H, d, *J* = 8.8 Hz, H-3', H-5'), 6.40 (1H, d, *J* = 2.4 Hz, H-6), 6.18 (1H, d, *J* = 2.0 Hz, H-8), 3.31 (3H, s, OCH_3); ^{13}C-NMR (CD_3OD, 100 MHz) δ: 176.2 (C-4), 164.5 (C-7), 161.3 (C-5), 159.4 (C-4'), 157.1 (C-9), 146.8 (C-2), 135.9 (C-3), 129.5 (C-2', C-6'), 122.5 (C-1'), 115.1 (C-3',C-5'), 103.3 (C-10), 98.1 (C-6), 93.3 (C-8), 48.7 (OCH_3); EI-MS m/z: 300 $[M]^+$, 286 $[M\text{-}CH_2]^+$

Tiliroside (12) – $C_{30}H_{26}O_{13}$;mp: 206 ºC; IR V_{max} (KBr) 3460 (OH), 1684 (C = O), 1608, 1590, 1503 (aromatic C = C), 1182 (esrer C-O) cm^{-1}; UV λ_{max}MeOH nm (log ε) 315 (4.44), 267 (4.34), 203 (4.55); ^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 12.58 (1H, br. s, 5-OH), 7.99 (2H, d, *J* = 8.8 Hz, H-2', H-6'), 7.38 (2H, d, *J* = 8.6 Hz, H-2"', H-6"'), 7.35 (1H, d, *J* = 15.8 Hz, H-7"'), 6.86 (2H, d, *J* = 8.8 Hz, H-3', H-5'), 6.79 (2H, d, *J* = 8.6 Hz, H-3"', H-5"'), 6.38 (1H, d, *J* = 2.2 Hz, H-8), 6.15 (1H, d, *J* = 2.2 Hz, H-6). 6.12 (1H, d, *J* = 15.8 Hz, H-8"'), 5.48 (1H, d, *J* = 4.4 Hz, H-1"), 4.26 (1H, d, *J* = 1.8 and 12.0 Hz, H-6"), 4.03 (1H, d, *J* = 6.4 and 12.0 Hz, H-6"), 3.17-3.36 (m, sugar proton); ^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 178.8 (C-4), 167.6 (C-9"'), 165.8 (C-7), 162.6 (C-9), 161.5 (C-4'), 161.3 (C-4"'), 157.9 (C-5), 157.8 (C-2), 146.1 (C-7"'), 134.5 (C-3), 132.3 (C-2', C-6'), 131.6 (C-2"', C-6"'), 126.4 (C-1'), 122.2 (C-1"'), 117.2 (C-3"', C-5"'), 116.5 (C-3', C-5'), 115.1 (C-8"'), 105.3 (C-10), 102.4 (C-6), 100.3 (C-1"), 95.2 (C-8), 77.7 (C-3"), 75.7 (C-2"), 75.6 (C-5"), 71.4 (C-4"), 64.4 (C-6"); FAB-MS m/z: 595 $[M + H]^+$

Results and Discussion

In the ^{1}H-NMR spectrum of compound **1**, aryl group proton signals at δ 6.75 - 6.91, a methylenedioxy singlet at δ 5.93, two methoxy singlets at δ 3.86 and 3.89 were observed. And the presence of two benzylic hydrogen signals at δ 4.85 and 4.40 coupled with two methine proton signals at δ 3.30~3.35 and 2.06 suggested the axial-equatorial configuration of phenyl group (Xu, *et al*., 2004). ^{13}C-NMR spectrum of **1** revealed a methylenedioxy carbon signal at δ 101.0, an axial aryl signal at δ 131.0, and an equatorial aryl group at δ 135.0 ppm, respectively. Therefore, the structure of **1** was determined as fargesin.

The ^{1}H-NMR spectrum of compound **2** is similar to those of **1**, but a methylenedioxy signal at δ 5.93 was disappeared, instead four methoxy singlets were observed at δ 3.90 and δ 3.88. And benzylic methylene proton double was also appeared at δ 4.77. Due to presence of total 11 carbon peaks in ^{13}C-NMR, compound **2** was guessed to have symmetrical structure, and it was identified as eudesmin from the comparison with those of previous data (Iida, *et al*., 1982).

Compound **3**, isolated as a viscous oil. In the ^{1}H-NMR spectrum of **3**, three methoxy signals at δ 3.74 and 3.59, a

methylenedioxy singlet at δ 5.92, a multiplet signals due to three aromatic protons at δ 6.75~6.85 were observed. And a benzylic hydrogen doublet at δ 4.58 (2H) and a multiplet at δ 3.75~4.15 (4H) strongly suggested the presence of diequatorial phenyl group. Accordingly, with a methylenedioxy carbon signals at δ 100.9 and two equatorial aryl carbon signals at δ 135.5 and 136.6 in ^{13}C-NMR, **3** was identified as aschantin (Xu, *et al*., 2004).

Compared to those of compound **3**, the spectral data of compound **4** showed similar pattern but two methoxy proton singlets were observed at δ 3.87 and 3.88 in the ^{1}H-NMR spectrum and the structure of **4** was determined as kobusin with the comparison of previous report (Xu, *et al*., 2004).

Compound **5** was obtained as colorless needles. In the ^{1}H-NMR spectrum of 5, a multiplet due to aromatic protons at δ 6.84~6.92 (3H), an aromatic proton singlet at δ 6.58 (2H) and five methoxy singlets at δ 3.84, 3.88 and 3.91 were observed. In the ^{13}C-NMR spectrum, methylenedioxy carbon signal was not shown compared to **3**, instead five methoxy carbon signals were observed. Accordingly, was identified as magnolin (Okuno, *et al*., 1988).

The ^{1}H and ^{13}C-NMR spectrum of compound **6** was very similar to those of **5**, but benzylic hydrogen doublets at ä 4.44 and 4.88 were observed with methane proton signals at δ 2.90~2.95 and δ 3.28~3.31. And the presence of an axial aryl carbon signal at δ 131.1 and an equatorial aryl signal at δ 137.1 shown in the ^{13}C-NMR spectrum suggested the axial-equatorial configuration of two phenyl groups and **6** was identified as epimagnolin and the comparison of previous report supported it (Miyazawa, *et al*., 1992).

In the ^{1}H-NMR spectrum of compound **7**, aromatic proton singlet at δ 6.58 (4H) and six methoxy singlets at δ 3.84 and 3.88 were observed. And the patterns of remaining signals were very similar to those of compound **2**. Because of nine carbon signals shown in the ^{13}C-NMR spectrum, a symmetrical structure in **2** was assumed and it was identified as lirioresinol B dimethyl ether (Ma, *et al*., 1995).

The structure of remaining compounds, **8**~**12**, were determined as vanilic acid, 4-hydroxybenzoic acid, scopoletin, kaempferol-7-methyl ether, and tiliroside, respectively (Yaguchi, *et al*., 1988; Yazaki, *et al*., 1986; Do, *et al*., 1992; Kuroyanggi, *et al*., 1978).

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