Natural Product Sciences
15(1) : 12-16 (2009)

Phytochemical Constituents from *Metasequoia glyptostroboids* Leaves

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Abstract – Phytochemical investigation of *Metasequoia glyptostroboids* leaves resulted in the isolation of ten compounds. The structures were determined to be isoquercitrin (**1**), quercitrin (**2**), myricitrin (**3**), amentoflavone (**4**), sciadopitysin (**5**), isoginkgetin (**6**), 2,3-dihydrosciadopitysin (**7**), 2,3-dihydroisoginkgetin (**8**), 3β-acetoxy-8(17),13*E*-labdadien-15-oic acid (**9**) and β-sitosterol (**10**) by spectroscopic analyses. Isoquercitrin (**1**) was isolated from this plant for the first time.

Keywords – *Metasequoia glyptostroboids*, Isoquercitrin

Introduction

Metasequoia glyptostroboides Miki ex Hu is generally known as a typical living species in the genus *Metasequoia*. It is considered to be placed between Taxodiaceae and Cupressaceae in plant taxonomy. Previous phytochemical studies on *M. glyptostroboides* established the occurrence of flavonoids, diterpenes, steroids and fatty acids (Beckmann and Geiger, 1968; Beckmann *et al*., 1971; Braun and Breitenbach, 1977; Shuichi *et al*., 1969). Some of these compounds were reported to have pharmacological activities including anti-tyrosinase, anti-inflammatory and antioxidant activities (Cheng *et al*., 2007; Camuesco *et al*., 2006; Mario *et al*., 2008). To investigate bioactive compounds from *M. glyptostroboids*, eight flavonoids, one diterpene and one steroid were isolated from the EtOH (80%) extracts of *M. glyptostroboids* leaves. Structure identification of these compounds was based on spectroscopic analyses and comparing with published data. Isoquercitrin (**1**) was isolated from this plant for the first time.

Experimental

General – Melting points were determined using an Electrothermal apparatus uncorrected. Ultraviolet absorption spectra were obtained on a CARY 100 UV-Vis spectrophotometer. EI-MS and ESI-MS data were obtained on a Hewlett Packard 5989 and a Finnigan Navigator mass spectrometer respectively. ^{1}H- and ^{13}C-NMR spectra were recorded on a VARIAN VNMRS-400 spectrometer operating at 400 MHz for proton and 100 MHz for carbon respectively. The chemical shift values were reported in δ (ppm) relative to the internal standard TMS or residual solvent peak, the coupling constants (*J*) were reported in Hertz (Hz). Silica gel 60 (Merck, 70 - 230 mesh and 230-400 mesh) and Sephadex LH-20 (Pharmacia) were used for column chromatography. Silica gel F_{254} plates (Merck) were used for TLC.

Plant material – *M. glyptostroboids* leaves were collected in October, 2007 from Cheonan city, Chungcheongnam-Do, Korea. A voucher specimen (LDMG-2007-1) was deposited at the Coreana Cosmetics Co. Ltd. Songpa R&D Center, Korea.

Extraction and Isolation – The dried and ground *M. glyptostroboids* leaves (1.5 kg) were extracted with 80% EtOH at room temperature. The ethanol extract was evaporated under vacuum to yield a dark green residue (90 g). The residue was suspended in H_2O and partitioned with n-hexane, CH_2Cl_2 and EtOAc, successively. The n-hexane fraction (20 g) was chromatographed on a silica gel column eluting with n-hexane:EtOAc (5 : 1) to give compounds **9** (200 mg) and **10** (300 mg) as white amorphous powder, which were further purified by re-crystallization from EtOAc. The CH_2Cl_2 fraction (15 g) was subjected to silica gel CC eluting with gradient system of n-hexane:EtOAc (5 : 1 to 1 : 1), followed by Sephadex LH-20 CC eluting with CH_2Cl_2 : MeOH (1 : 1) to yield compounds **5** (100 mg), **6** (80 mg), **7** (70 mg) and **8** (50 mg) as yellow amorphous powder, which were further purified by re-crystallization from MeOH. The EtOAc fraction (21 g) was subjected to silica gel CC

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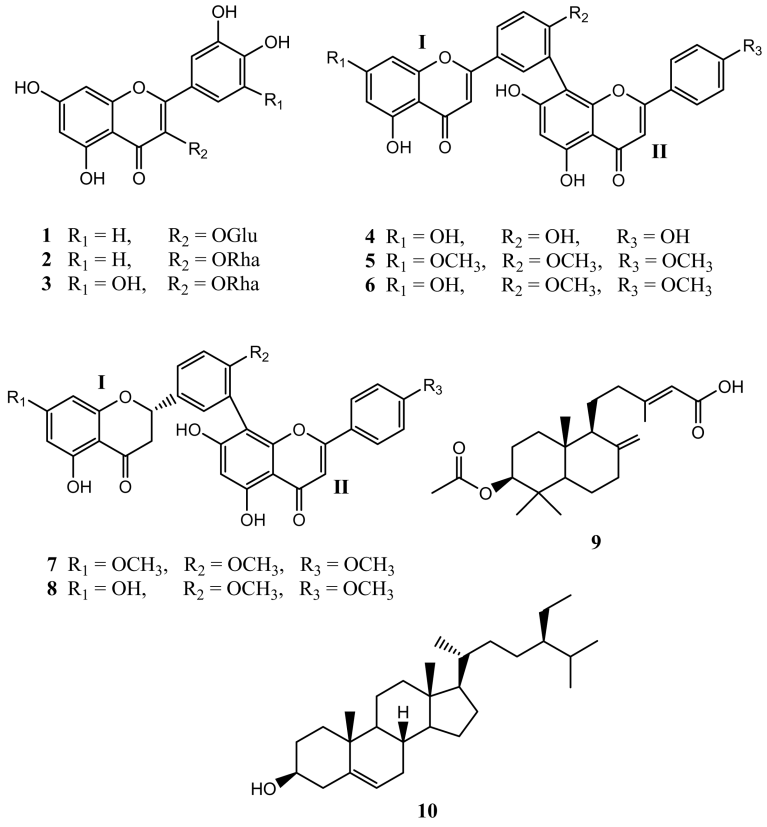

Fig. 1. Structures of compounds **1** - **10** from *M. glyptostroboids*.

eluting with gradient system of EtOAc : MeOH (30 : 1 to 10 : 1), followed by Sephadex LH-20 CC eluting with MeOH to yield compounds **1** (50 mg), **2** (160 mg), **3** (100 mg) and **4** (30 mg) as yellow amorphous powder, which were further purified by crystallization from MeOH.

Isoquercitrin (1) – yellow powder. mp, 238 - 242°C. UV (MeOH) λ_{max} nm: 258, 354. ESI-MS *m/z*: 465 $[M+H]^+$. ^{1}H-NMR (CD_3OD, 400 MHz): δ 7.74 (1H, d, *J* = 2.1 Hz, H-2'), 7.61 (1H, dd, *J* = 8.4, 2.1 Hz, H-6'), 6.89 (1H, d, *J* = 8.4 Hz, H-5'), 6.41 (1H, d, *J* = 2.1 Hz, H-8), 6.22 (1H, d, *J* = 2.1Hz, H-6), 5.29 (1H, d, *J* = 7.5 Hz, H-1"), 3.76 (1H, dd, *J* = 12.0, 2.4 Hz, H-6"a), 3.61 (1H, dd, *J* = 12.0, 5.1 Hz, H-6"b), 3.33~3.55 (3H, m, H-2", H-3", H-4"), 3.27 (1H, ddd, *J* = 7.5, 5.1, 2.4 Hz, H-5"); ^{13}C-NMR (CD_3OD, 100 MHz): δ 157.3 (C-2), 134.5 (C-3), 178.3 (C-4), 161.9 (C-5), 98.7 (C-6), 164.8 (C-7), 93.6 (C-8), 157.9 (C-9), 104.5 (C-10), 121.9 (C-1'), 114.8 (C-2'), 144.7 (C-3'), 148.7 (C-4'), 116.4 (C-5'), 122.0 (C-6'), 103.2 (C-1"), 74.6 (C-2"), 77.0 (C-3"), 70.0 (C-4"), 77.2 (C-5"), 61.4 (C-6").

Quercitrin (2) – yellow powder. mp, 182 - 185°C. UV (MeOH) λ_{max} nm: 258, 355. ESI-MS *m/z*: 449 $[M+H]^+$. ^{1}H-NMR (CD_3OD, 400 MHz): δ 7.33 (1H, d, *J* = 2.0 Hz, H-2'), 7.30 (1H, dd, *J* = 8.2, 2.0 Hz, H-6'), 6.90 (1H, d, *J* = 8.2 Hz, H-5'), 6.35 (1H, d, *J* = 2.0 Hz, H-8), 6.19 (1H, d, *J* = 2.0 Hz, H-6), 5.35 (1H, d, *J* = 1.6 Hz, H-1"), 4.23 (1H, dd, *J* = 3.6, 1.6 Hz, H-2"), 3.75 (1H, dd, *J* = 9.6, 3.6 Hz, H-3"), 3.41 (1H, m, H-5"), 3.35 (1H, dd, *J* = 9.6, 1.6 Hz, H-4"), 0.94 (3H, d, *J* = 6.4 Hz, H-6"); ^{13}C-NMR (CD_3OD, 100 MHz): δ 157.3 (C-2), 135.0 (C-3), 178.4 (C-4), 162.0 (C-5), 98.6 (C-6), 164.6 (C-7), 93.5 (C-8), 158.1 (C-9), 104.7 (C-10), 121.8 (C-1'), 115.2 (C-2'), 145.2 (C-3'), 148.6 (C-4'), 115.8 (C-5'), 121.7 (C-6'), 102.3 (C-1"), 70.8 (C-2"), 70.9 (C-3"), 72.1 (C-4"), 70.7 (C-5"), 16.5 (C-6").

Myricitrin (3) – yellow powder. mp, 194 - 197°C. UV (MeOH) λ_{max} nm: 257, 354. ESI-MS *m/z*: 465 $[M+H]^+$. ^{1}H-NMR (CD_3OD, 400 MHz): δ 6.95 (2H, s, H-2', 6'), 6.35 (1H, d, *J* = 2.0 Hz, H-8), 6.19 (1H, d, *J* = 2.0 Hz, H-6), 5.31 (1H, d, *J* = 1.6 Hz, H-1"), 4.22 (1H, dd, *J* = 3.6, 1.6 Hz, H-2"), 3.78 (1H, dd, *J* = 9.6, 3.6 Hz, H-3"), 3.50 (1H, m, H-5"), 3.35 (1H, dd, *J* = 9.6, 1.6 Hz, H-4"), 0.96 (3H, d, *J* = 6.4 Hz, H-6"); ^{13}C-NMR (CD_3OD, 100 MHz) : δ 157.3 (C-2), 135.1 (C-3), 178.5 (C-4), 162.0 (C-5), 98.6 (C-6), 164.6 (C-7), 93.5 (C-8), 158.2 (C-9), 104.7 (C-10), 120.7 (C-1'), 108.4 (C-2'), 145.6 (C-3'), 136.7 (C-4'),

145.6 (C-5'), 108.4 (C-6'), 102.4 (C-1''), 70.8 (C-2''), 70.9 (C-3''), 72.1 (C-4''), 70.7 (C-5''), 16.5 (C-6'').

Amentoflavone (4) – yellow powder. mp, 300°C. UV (MeOH) λ_{max} nm: 270, 338. EI-MS *m/z*: 538 $[M]^+$. ^{1}H-NMR (CD_3OD, 400 MHz): δ 7.92 (1H, d, *J* = 2.0 Hz, H-2'), 7.78 (1H, dd, *J* = 8.8, 2.0 Hz, H-6'), 7.45 (2H, d, *J* = 8.8 Hz, H-2''', 6'''), 7.04 (1H, d, *J* = 8.8 Hz, H-5'), 6.68 (2H, d, *J* = 8.8 Hz, H-3''', 5'''), 6.53 (1H, s, H-3''), 6.51 (1H, s, H-3), 6.41 (1H, d, *J* =2.0 Hz, H-8), 6.34 (1H, s, H-6''), 6.17 (1H, d, *J* =2.0 Hz, H-6); ^{13}C-NMR (CD_3OD, 100 MHz): δ 165.8 (C-2), 104.1 (C-3), 183.3 (C-4), 162.0 (C-5), 99.8 (C-6), 163.0 (C-7), 94.9 (C-8), 158.9 (C-9), 104.8 (C-10), 123.2 (C-1'), 132.5 (C-2'), 122.8 (C-3'), 160.4 (C-4'), 116.9 (C-5'), 129.0 (C-6'), 165.6 (C-2''), 103.1 (C-3''), 183.9 (C-4''), 162.1 (C-5''), 99.9 (C-6''), 162.7 (C-7''), 105.4 (C-8''), 155.9 (C-9''), 104.9 (C-10''), 121.2 (C-1'''), 128.9 (C-2'''), 116.5 (C-3'''), 161.9 (C-4'''), 116.5 (C-5'''), 128.9 (C-6''').

Sciadopitysin (5) – yellow powder. mp, 287 - 289°C. UV (MeOH) λ_{max} nm: 271, 330. EI-MS *m/z*: 580 $[M]^+$. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ 13.09 (1H, s, OH-5''), 12.94 (1H, s, OH-5), 10.89 (1H, s, OH-7''), 8.22 (1H, dd, *J* = 8.4, 1.6 Hz, H-6'), 8.10 (1H, d, *J* = 1.6 Hz, H-2'), 7.61 (2H, d, *J* = 8.8 Hz, H-2''', 6'''), 7.38 (1H, d, *J* = 8.4 Hz, H-5'), 7.00 (1H, s, H-3), 6.95 (2H, d, *J* = 8.8 Hz, H-3''', 5'''), 6.91 (1H, s, H-3''), 6.78 (1H, d, *J* =2.0 Hz, H-8), 6.46 (1H, s, H-6''), 6.37 (1H, d, *J* =2.0 Hz, H-6), 3.84 (3H, s, OCH_3-4'''), 3.83 (3H, s, OCH_3-7), 3.78 (3H, s, OCH_3-4'); ^{13}C-NMR (DMSO-d_6, 100 MHz): δ 163.6 (C-2), 103.8 (C-3), 181.9 (C-4), 160.5 (C-5), 98.1 (C-6), 165.2 (C-7), 92.7 (C-8), 157.3 (C-9), 103.6 (C-10), 122.4 (C-1'), 130.9 (C-2'), 121.6 (C-3'), 161.8 (C-4'), 111.7 (C-5'), 128.3 (C-6'), 163.0 (C-2''), 103.2 (C-3''), 182.1 (C-4''), 161.1 (C-5''), 98.6 (C-6''), 160.7 (C-7''), 104.8 (C-8''), 154.3 (C-9''), 103.6 (C-10''), 122.8 (C-1'''), 127.8 (C-2'''), 114.5 (C-3'''), 162.2 (C-4'''), 114.5 (C-5'''), 127.8 (C-6'''), 55.9 (OCH_3-4'), 56.0 (OCH_3-4'''), 55.5 (OCH_3-7).

Isoginkgetin (6) – yellow powder. mp, 210°C. UV (MeOH) λ_{max} nm: 213, 271, 330. EI-MS *m/z*: 566 $[M]^+$. ^{1}H-NMR (CD_3COCD_3, 400 MHz): δ 13.09 (1H, s, OH-5''), 12.95 (1H, s, OH-5), 8.13 (1H, dd, *J* = 8.4, 1.6 Hz, H-6'), 8.11 (1H, d, *J* = 1.6 Hz, H-2'), 7.61 (2H, d, *J* = 8.8 Hz, H-2''', 6'''), 7.34 (1H, d, *J* = 8.4 Hz, H-5'), 6.90 (2H, d, *J* = 8.8 Hz, H-3''', 5'''), 6.73 (1H, s, H-3''), 6.66 (1H, s, H-3), 6.51 (1H, d, *J* =2.0 Hz, H-8), 6.44 (1H, s, H-6''), 6.24 (1H, d, *J* =2.0 Hz, H-6), 3.85 (3H, s, OCH_3-4'''), 3.77 (3H, s, OCH_3-4'); ^{13}C-NMR (CD_3COCD_3, 100 MHz): δ 164.8 (C-2), 104.8 (C-3), 183.1 (C-4), 162.0 (C-5), 99.8 (C-6), 165.0 (C-7), 94.9 (C-8), 158.9 (C-9), 104.8 (C-10), 124.2 (C-1'), 132.2 (C-2'), 122.8 (C-3'), 163.4 (C-4'), 112.5 (C-5'), 129.1 (C-6'), 164.6 (C-2''), 104.1 (C-3''), 183.4 (C-4''), 162.6 (C-5''), 99.8 (C-6''), 162.4 (C-7''), 105.4 (C-8''), 155.8 (C-9''), 104.8 (C-10''), 124.2 (C-1'''), 128.8 (C-2'''), 115.3 (C-3'''), 163.6 (C-4'''), 115.3 (C-5'''), 128.8 (C-6'''), 55.9 (OCH_3-4'), 56.4 (OCH_3-4''').

2,3-Dihydrosciadopitysin (7) – yellow powder. mp, 150 - 152°C. UV (MeOH) λ_{max} nm: 278, 322. EI-MS *m/z*: 582 $[M]^+$. ^{1}H-NMR (CD_3COCD_3, 400 MHz): δ 13.08 (1H, s, OH-5''), 12.12 (1H, s, OH-5), 7.68 (2H, d, *J* = 8.8 Hz, H-2''', 6'''), 7.65 (1H, dd, *J* = 8.8, 2.0 Hz, H-6'), 7.63 (1H, d, *J* = 2.0 Hz, H-2'), 7.24 (1H, d, *J* = 8.8 Hz, H-5'), 6.99 (2H, d, *J* = 8.8 Hz, H-3''', 5'''), 6.69 (1H, s, H-3''), 6.42 (1H, s, H-6''), 6.04 (1H, d, *J* =2.0 Hz, H-8), 6.01 (1H, d, *J* =2.0 Hz, H-6), 5.60 (1H, dd, *J* = 13.2, 2.8 Hz, H-2), 3.85 (3H, s, OCH_3-4'''), 3.81 (3H, s, OCH_3-7), 3.79 (3H, s, OCH_3-4'), 3.31 (1H, m, H-3a), 2.85 (1H, m, H-3b); ^{13}C-NMR (CD_3COCD_3, 100 MHz): δ 80.1 (C-2), 43.9 (C-3), 197.5 (C-4), 164.2 (C-5), 95.6 (C-6), 168.9 (C-7), 94.7 (C-8), 163.6 (C-9), 103.8 (C-10), 132.1 (C-1'), 132.5 (C-2'), 121.9 (C-3'), 159.2 (C-4'), 112.1 (C-5'), 129.0 (C-6'), 165.0 (C-2''), 104.0 (C-3''), 183.5 (C-4''), 162.4 (C-5''), 99.7 (C-6''), 162.4 (C-7''), 105.4 (C-8''), 155.7 (C-9''), 105.6 (C-10''), 124.3 (C-1'''), 129.0 (C-2'''), 115.4 (C-3'''), 164.5 (C-4'''), 115.4 (C-5'''), 129.0 (C-6'''), 56.0 (OCH_3-4'), 56.1 (OCH_3-4'''), 55.5 (OCH_3-7).

2,3-Dihydroisoginkgetin (8) – pale yellow powder. UV (MeOH) λ_{max} nm: 280, 322. EI-MS *m/z*: 568 $[M]^+$. ^{1}H-NMR (CD_3COCD_3, 400 MHz): δ 13.09 (1H, s, OH-5''), 12.17 (1H, s, OH-5), 7.68 (2H, d, *J* = 8.8 Hz, H-2''', 6'''), 7.66 (1H, dd, *J* = 8.4, 1.6 Hz, H-6'), 7.63 (1H, d, *J* = 1.6 Hz, H-2'), 7.24 (1H, d, *J* = 8.4 Hz, H-5'), 6.99 (2H, d, *J* = 8.8 Hz, H-3''', 5'''), 6.68 (1H, s, H-3''), 6.42 (1H, s, H-6''), 5.98 (1H, d, *J* =2.0 Hz, H-8), 5.95 (1H, d, *J* =2.0 Hz, H-6), 5.60 (1H, dd, *J* = 13.2, 2.8 Hz, H-2), 3.84 (3H, s, OCH_3-4'''), 3.79 (3H, s, OCH_3-4'), 3.29 (1H, m, H-3a), 2.82 (1H, m, H-3b); ^{13}C-NMR (CD_3COCD_3, 100 MHz): δ 80.0 (C-2), 43.9 (C-3), 197.2 (C-4), 164.5 (C-5), 97.0 (C-6), 167.4 (C-7), 96.0 (C-8), 163.7 (C-9), 103.3 (C-10), 132.2 (C-1'), 132.5 (C-2'), 121.9 (C-3'), 159.2 (C-4'), 112.2 (C-5'), 129.0 (C-6'), 165.1 (C-2''), 104.0 (C-3''), 183.5 (C-4''), 162.4 (C-5''), 99.7 (C-6''), 162.1 (C-7''), 105.4 (C-8''), 155.8 (C-9''), 105.6 (C-10''), 124.3 (C-1'''), 129.0 (C-2'''), 115.4 (C-3'''), 164.5 (C-4'''), 115.4 (C-5'''), 129.0 (C-6'''), 56.0 (OCH_3-4'), 56.2 (OCH_3-4''').

3β-Acetoxy-8 (17),13*E*-labdadien-15-oic acid (9) – white needle. mp, 161 - 162°C. EI-MS *m/z*: 362 $[M]^+$. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 5.66 (1H, d, *J* = 1.2 Hz, H-14), 4.87 (1H, br. s, H-17a), 4.51 (1H, br. s, H-17b), 4.52 (1H, dd, *J* = 11.7, 4.8 Hz, H-3), 2.16 (3H, s, H-16), 2.05 (3H, s, $COCH_3$), 0.87 (3H, s, H-18), 0.84 (3H, s, H-19),

0.71 (3H, s, H-20); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 36.9 (C-1), 24.5 (C-2), 80.9 (C-3), 40.2 (C-4), 54.9 (C-5), 24.0 (C-6), 38.3 (C-7), 147.6 (C-8), 56.0 (C-9), 39.5 (C-10), 21.9 (C-11), 38.2 (C-12), 163.8 (C-13), 115.3 (C-14), 172.5 (C-15), 16.8 (C-16), 107.2 (C-17), 28.5 (C-18), 19.5 (C-19), 14.8 (C-20), 173.1 (CO), 21.6 (CH_3).

***β*-Sitosterol (10) –** white needle. mp, 142 - 143°C. EI-MS *m/z*: 414 $[M]^+$. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 5.36 (1H, d, *J* = 5.4 Hz, H-6), 3.53 (1H, m, H-3), 1.02 (3H, s, H-19), 0.93 (6H, d, *J* = 6.6 Hz, H-21, H-26), 0.83 (3H, t, *J* = 6.6 Hz, H-29), 0.84 (3H, d, *J* = 6.6 Hz, H-27), 0.69 (3H, s, H-18); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 37.5 (C-1), 32.2 (C-2), 72.0 (C-3), 46.1 (C-4), 141.0 (C-5), 122.0 (C-6), 31.9 (C-7), 32.2 (C-8), 50.4 (C-9), 36.8 (C-10), 20.1 (C-11), 40.0 (C-12), 42.6 (C-13), 57.0 (C-14), 24.6 (C-15), 28.5 (C-16), 56.3 (C-17), 12.2 (C-18), 19.0 (C-19), 36.4 (C-20), 19.3 (C-21), 34.2 (C-22), 26.3 (C-23), 46.1 (C-24), 29.4 (C-25), 19.7 (C-26), 20.1 (C-27), 23.3 (C-28), 12.1 (C-29).

Results and Discussion

Column chromatographic separation of the hexane-, CH_2Cl_2- and EtOAc- soluble fractions of the ethanol extract of *M. glyptostroboids* leaves with silica gel and Sephadex LH-20 led to the isolation of eight flavonoids (**1 - 8**), one diterpene (**9**) and one sterol (**10**).

The structures of **2**, **4**, **5**, **8, 9** and **10** were identified to be quercitrin (**2**) (Jang *et al*., 2006), amentoflavone **(4)** (Ohmoto and Yoshida, 1983), sciadopitysin (**5**) (Fonseca *et al*., 2000; Tang *et al*., 2001), 2,3-dihydroisoginkgetin (**8**) (Cheng *et al*., 2007), 3*β*-acetoxy-8 (17),13*E*-labdadien-15-oic acid (**9**) (Zdero *et al*., 1992) and *β*-sitosterol (**10**) (Lee *et al*., 2008) by comparing of ^{1}H-, ^{13}C-NMR and MS data with the literatures.

Analysis of the ^{1}H- and ^{13}C-NMR spectra of compound **1** showed the presence of one aromatic system and one sugar moiety. The ^{1}H-NMR resonances of two *meta* coupled doublets at δ 6.22 and 6.41 ppm (1H, d, *J* = 2.1 Hz) characterized the 6- and 8-protons of a 5,7 dihydroxyflavonoid A-ring. The signals at δ 7.74 (1H, d, *J* = 2.1 Hz), 7.61 (1H, dd, *J* = 8.4, 2.1 Hz) and 6.89 (1H, d, *J* = 8.4 Hz) were attributed to the 2'-, 6'- and 5'-protons of a 3',4' di-*O*-substituted flavonoid B-ring. Thus the aglycone of **1** was identified as 3,5,7,3',4'-pentahydroxyflavonol (quercetin). The sugar was identified as *β*–D-glucopyranosyl moiety based on the ^{1}H-NMR doublet at δ 5.29 (d, *J* = 7.5 Hz) for anomeric proton and the signals at 3.76 (1H, dd, *J* = 12.0, 2.4 Hz), 3.61 (1H, dd, *J* = 12.0, 5.1 Hz), 3.27 (1H, ddd, *J* = 7.5, 5.1, 2.4Hz) for H-6'' and H-5''. Its position was determined by the carbon (C-3) shift at δ 134.5 (Agrawal, 1989). Thus, compound **1** was identified as isoquercitrin by comparing the spectral data with those reported in the literature (Jang *et al*., 2006). This identification was corroborated by ESI-MS data which exhibited a quasimolecular ion peak at *m/z* 465 $[M+H]^+$ and fragment ion peak at *m/z* 303 $[M+H-162]^+$ indicating the elimination of one glucosyl moiety. Isoquercitrin (**1**) was isolated from this plant for the first time.

Compound **3** was obtained as yellow powder, the ^{1}H- and ^{13}C-NMR spectra showed the presence of one aromatic system and one sugar moiety similar to compound **2**. The ^{1}H-NMR resonances of singlet at δ 6.95 ppm (2H, s) was attributed to the 2'- and 6'-protons of a 3',4',5'-tri-*O*-substituted flavonoid B-ring. Thus, compound **3** was identified as myricitrin by comparing the spectral data with those reported in the literature (Fiasson *et al*., 2001).

In the ^{1}H-NMR spectra of compound **6**, two chelated hydroxyl groups had resonances at δ 13.09 and 12.95 (1H, s) and two *O*-methyl groups had resonances at δ 3.85 and 3.77 (3H, s). The signals at δ 6.24 and 6.51 (1H, d, *J* = 2.0 Hz) were ascribable to H-6 and H-8 on I-A ring respectively. Those at δ 8.11 (1H, d, *J* = 1.6 Hz), 8.13 (1H, dd, *J* = 8.4, 1.6 Hz) and 7.34 (1H, d, *J* = 8.4 Hz, H-5') were attributed to the 2'-, 6'- and 5' protons of I-B ring. The signals at δ 7.61 and 6.90 (2H, d, *J* = 8.8 Hz) characterized the 2'''-, 6'''- and 3'''-, 5'''-protons of II-B ring respectively. The ^{1}H- and ^{13}C-NMR spectra of compound **6** showed the presence of two flavonol units similar to compound **5.** Thus, compound **6** was identified as isoginkgetin by comparing the spectral data with those reported in the literature (Tang *et al*., 2001).

Compound **7** was obtained as yellow powder. The ^{1}H-NMR resonances of singlet at δ 13.08 and 12.12 (1H, s) showed two chelated hydroxyl groups. The signals at ä 3.85, 3.81 and 3.79 (3H, s) showed three *O*-methyl groups. The signals at 5.60 (1H, dd, *J* = 13.2, 2.8 Hz, H-2), 3.31 (1H, m, H-3a) and 2.85 (1H, m, H-3b) arose from I-C ring and the ^{13}C-NMR signals at δ 80.0 (C-2) and 43.9 (C-3) indicated the presence of a flavanone unit. Furthermore, the flavone unit in compound **7** was similar to compound **8**. Thus, compound **7** was identified as 2,3-dihydrosciadopitysin by comparing the spectral data with those reported in the literature (Cheng *et al*., 2007; Fonseca *et al*., 2000).

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(Accepted March 17, 2009)