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Procyanidins from *Acer komarovii* Bark[1]

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ABSTRACT

The bark of *Acer komarovii* was collected, ground, and extracted with 70% aqueous acetone to obtain concentrates. The concentrates were suspended in H_2O, and then successively partitioned with *n*-hexane, dichloromethane and ethylacetate to be freeze dried. A portion of ethylacetate fraction was chromatographed on a Sephadex LH-20 and a RP C-18 column with various aqueous MeOH-H_2O (1:0, 1:1, 1:2, 1:5, 1:7, 1:9, 1:10, 3:1, and 4:1, v/v) eluents. Four compounds were isolated; (-)-epicatechin (9.6 g), procyanidin A2 (epicatechin-(4β→8, 2β→*O*→7)-epicatechin) (1.3 g), procyanidin B2 (epicatechin-(4β→8)-epicatechin) (40.0 mg), and cinnamtannin B1 (epicatechin-(4β→8, 2β→*O*→7)-epicatechin-(4β→8)-epicatechin) (690 mg). The analysis of the bark procyanidins showed that the basic unit constituting condensed tannins was only (-)-epicatechin. This study, for the first time, report the procyanidins of *Acer komarovii* bark.

Keywords : *Acer komarovii* bark, ethylacetate fraction, column chromatography, (-)-epicatechin, procyanidins

1. INTRODUCTION

Acer komarovii is one of rare maple species growing in Korea and has a narrow distribution through Korean peninsula to northeast China and Russia. This tree grow in high mountain slope, dry bluffs or foothills. However, the tree is not useful for wood industry because of shrubby species (Lee 1985; Kim 1994).

The previous phytochemical reports on the genus *Acer* include diarylheptanoids (Morigawa *et al*. 2003; Akihisa *et al*. 2006), flavonoids (Tung *et al*. 2008; Kim *et al*. 1998; Kim *et al*. 2005), phenylethyl glycosides (Tung *et al*. 2008), coumarinolignans (Jin *et al*. 2007), neolignan glycosides (Dong *et al*. 2006), stilbene glycosides (Yang *et al*. 2005), and hydrolysable tannins (Bate-Smith 1977 and 1978; Hatano *et al*. 1990; Bedgood *et al*. 2005).

The World Health Organization (WHO) estimates that 80% of the people in developing countries rely on the traditional medicines for

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their primary health care needs and that 85% of the medicines are from the extracts of plants (Farnsworth *et al*. 1985). However, the phytochemical studies of the medicinal resources have not provided the sufficient evidences to confirm their biological activities. Therefore, it is clear that there are still many species for secondary metabolite investigation, and *Acer komarovii* is one of those species. However, there are a very little phytochemical studies on bark of *Acer komarovii* (Kwon and Bae 2009; Kwon and Bae 2013).

In this study, we report, for the first time, the isolation of several procyanidins which are consisted of the condensed tannins from the bark of *Acer komarovii* for future functional and/or biological uses.

2. MATERIALS and METHODS

2.1. General experimental

^{1}H and ^{13}C NMR spectra, including 2D-NMR such as HSQC (Heteronuclear Single Quantum Coherence) and HMBC (Heteronuclear Multiple Bond Correlation), were recorded on a Bruker (USA) Avance DPX 400 MHz and 600 MHz spectrometers using TMS Tetramethylsilane) as an internal standard and chemical shift was given in δ (ppm). EI-MS and MALDI-TOF-MS were performed with a Micromass Autospec M363 spectrometer. Column chromatography was done with Sephadex LH-20 and Medium pressure liquid chromatography was a Combiflash Retrieve (ISCO) apparatus with the column containing RP C-18 derivatized silica. TLC (Thin Layer Chromatography) was performed on DC-Plastikfolien Cellulose F (Merck) plates and developed with TBAW (t-BuOH:HOAc:H_2O (3:1:1, v/v/v)) and 6% HOAc. Spraying reagent was vanillin-EtOH-HCl (3:1:1, v/v/v) followed by heating.

2.2. Plant material

Acer komarovii bark was collected at Jeongseon, Gangwon province in September 2008 and identified by Prof. Wan-Geun Park, Department of Forestry, Kangwon National University. Then the bark was air dried and ground to be extracted.

2.3. Column chromatography

The bark (4 kg) was immersed in 70% aqueous acetone at room temperature for 5 days. After filtration, the residue was extracted two more times. The filtrates were combined together and evaporated on a rotary evaporator under reduced pressure at 40℃. The residue (0.5 kg) was suspended in water and successively fractionated with *n*-hexane (32 g), dichloromethane (57 g) and ethyl acetate (123 g) to get freeze dried powder.

The EtOAc soluble fraction (70 g) was chromatographed on a Sephadex LH-20 with MeOH-H_2O (3:1, v/v) to give 5 fractions: fr 1 (3.6 g), fr 2 (50 g), fr 3 (5.1 g), fr 4 (0.8 g), and fr 5 (1.8 g). Fr 2 was rewashed with MeOH-H_2O (1:1, v/v) to afford six subfractions:

fr 2-1, 2-2, 2-3, 2-4, 2-5, and 2-6. Fr 2-4 was eluted with MeOH-H_2O (1:5, 1:7, 1:10, v/v) to get compound **1** (9.6 g). Fr 2-5 and 2-6 were treated on RP C-18, and then on Sephadex LH-20 with MeOH-H_2O (1:0, 1:1, 1:2, 1:5, and 1:9, v/v) to isolate compound **3** (400 mg) and compound **4** (690 mg). Fr 3 was purified on RP C-18 with MeOH-H_2O (4:1, v/v) to afford compound **2** (1.3 g).

2.3.1. Compound 1

Brownish amorphous powder, R_f : 0.37 (TBAW) and 0.31 (6% HOAc).

EI-MS : Calculated for $C_{15}H_{14}O_6$ 290, Found *m/z* 290 $[M]^+$.

^{1}H-NMR (600 MHz) : 2.73 (1H, *dd*, *J* = 1.9 Hz and *J* = 16.8 Hz, H-4), 2.86 (1H, *dd*, *J* = 4.5 Hz and *J* = 16.8 Hz, H-4), 4.16 (1H, m, H-3), 4.80 (1H, *br* s, H-2), 5.92 (1H, *d*, *J* = 2.3 Hz, H-6), 5.94 (1H, *d*, *J* = 2.3 Hz, H-8), 6.75 (1H, *d*, *J* = 8.1 Hz, H-5′), 6.79 (1H, *dd*, *J* = 1.8 Hz and *J* = 8.1 Hz, H-6′), 6.97 (1H, *d*, *J* = 1.8 Hz, H-2′)

^{13}C-NMR (100 MHz) : 28.28 (C-4), 66.49 (C-3), 78.87 (C-2), 94.94 (C-8), 95.44 (C-6), 99.12 (C-10), 114.34 (C-2′), 114.94 (C-5′), 118.45 (C-6′), 131.30 (C-1′), 144.77 (C-3′), 144.94 (C-4′), 156.38 (C-9), 156.65 (C-5), 157.00 (C-7)

2.3.2. Compound 2

Yellowish amorphous powder, R_f : 0.33 (TBAW) and 0.20 (6% HOAc).

MALDI-TOF-MS : Calculated for $C_{30}H_{24}O_{12}$ 576, Found *m/z* 577 $[M + H]^+$, 599 $[M + Na]^+$.

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR : See Table 1.

2.3.3. Compound 3

Yellowish amorphous powder, R_f : 0.35 (TBAW) and 0.60 (6% HOAc).

MALDI-TOF-MS : Calculated for $C_{30}H_{26}O_{12}$ 578, Found *m/z* 579 $[M + H]^+$, 601 $[M + Na]^+$.

^{1}H (600 MHz) and ^{13}C (125 MHz) NMR : See Table 1.

2.3.4. Compound 4

Brownish amorphous powder, R_f : 0.34 (TBAW) and 0.31 (6% HOAc).

MALDI-TOF-MS : Calculated for $C_{45}H_{36}O_{18}$ 864, Found *m/z* 887 $[M + Na]^+$.

^{1}H (600 MHz) and ^{13}C (125 MHz) NMR : See Table 2.

3. RESULTS and DISCUSSION

3.1. Compound 1

Compound **1** was obtained as a brown amorphous powder from the bark. It showed a red color upon being sprayed with a vanillin-HCl-EtOH reagent on TLC. The R_f values were 0.37 (TBAW) and 0.31 (6% HOAc). A molecular formula of $C_{15}H_{14}O_6$ was supported by a molecular ion peak at *m/z* 290 $[M]^+$ on the EI-MS spectrum. ^{1}H-NMR and ^{13}C-NMR spectra showed signals characteristic for (-)-epicatechin From the previous data and by comparison with those of authentic samples, compound 1 was identified as ((+)-(2*R*,3*R*)-5,7,3′,4′-tetrahydroxy-

Table 1. ^{1}H and ^{13}C-NMR chemical shifts (δ, ppm) of compound **2** and **3**

Position	^{1}H [mult., J (Hz)]		^{13}C	
	2[a]	**3**[b]	**2**[a]	**3**[b]
Upper unit				
2		4.94 (*br s*)	100.23	75.21
3	4.05 (*d*, 3.4)	3.56 (*d*, 3.6)	68.13	71.30
4	4.41 (*d*, 3.4)	4.44 (*br s*)	29.31	35.47
5			157.05	155.70
6	6.01 (*d*, 2.2)	5.81 (*br s*)	98.35	94.39
7			158.18	156.42
8	6.07 (*d*, 2.2)	5.71 (*br s*)	96.67	93.56
9			154.30	156.42
10			104.30	101.78
1′			132.50	131.06
2′	7.14 (*d*, 2.2)	6.80 (*br s*)	115.67	114.55
3′			145.71	143.88
4′			146.82	144.16
5′	6.82 (*d*, 8.2)	6.64 (*d*, 8.3)	115.98	114.73
6′	7.02 (*dd*, 2.2, 8.2)	6.52 (*d*, 8.0)	119.83	117.59
Lower Unit				
2	4.92 (*br s*)	4.91 (*br s*)	81.82	77.31
3	4.24 (*m*)	3.42 (*br s*)	67.03	64.51
4	2.76 (*dd*, 2.2, 17.2) 2.95 (*dd*, 4.9, 17.2)	2.36 (*d*, 12.2) 2.70 (*d*, 12.2)	29.95	27.43
5			156.65	153.71
6	6.09 (*s*)	5.78 (*s*)	96.54	95.62
7			152.35	154.31
8			107.26	106.96
9			152.19	152.77
10			102.47	98.55
1′			131.25	130.13
2′	7.15 (*d*, 2.0)	7.00 (*br s*)	115.71	114.26
3′			146.05	144.08
4′			146.35	144.43
5′	6.80 (*d*, 8.2)	6.62 (*d*, 8.3)	116.08	114.73
6′	6.98 (*dd*, 2.0, 8.2)	6.82 (*br s*)	120.42	117.59

[a] Recorded in CD_3OD.
[b] Recorded in $(CD_3)_2SO$.

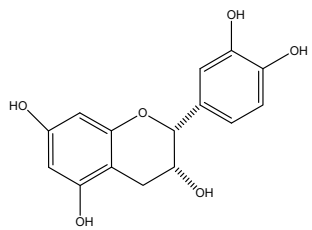
Table 2. ^{1}H and ^{13}C-NMR chemical shifts (δ, ppm) of compound **4** in CD_3OD

Position	^{1}H [mult., *J* (Hz)]			^{13}C		
	Upper unit	Middle unit	Lower unit	Upper unit	Middle unit	Lower unit
2		5.70 (*s*)	4.38 (*s*)	99.98	78.91	80.33
3	3.29 (*d*, 3.5)	4.12 (*br s*)	3.86 (*m*)	67.21	72.61	67.56
4	4.15 (*d*, 3.5)	4.56 (*s*)	2.83 (*br d*, 3.3)	28.90	38.31	29.88
5				156.80	155.81	156.06
6	5.96 (*d*, 2.3)	5.80 (*s*)	6.10 (*s*)	98.33	96.10	96.51
7				157.86	151.12	155.59
8	6.01 (*d*, 2.3)			96.59	106.46	108.87
9				154.19	151.82	155.81
10				104.98	106.76	100.09
1′				132.49	131.80	133.20
2′	7.09 (*d*, 2.0)	7.31 (*d*, 1.9)	6.82 (*m*)	115.78	116.75	115.51
3′				145.50	145.93	145.36
4′				146.63	146.31	145.79
5′	6.82 (*m*)	6.82 (*m*)	6.75 (*d*, 8.0)	116.16	115.78	116.04
6′	6.86 (*dd*, 2.0, 8.0)	7.19 (*dd*, 1.9, 8.3)	6.72 (*dd*, 1.7, 8.3)	119.91	121.39	119.14

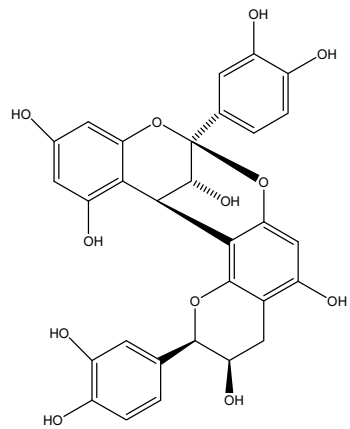
flavan-3-ol) (Hemingway *et al*. 1996, Nonaka and Nishioka 1982, Balde *et al*. 1995, Agrawal 1989).

3.2. Compound 2

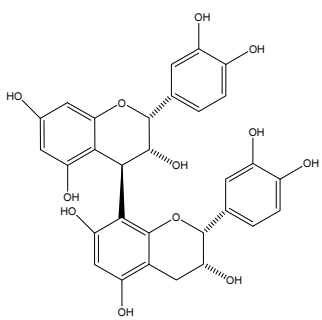
Compound **2** was obtained as a yellowish amorphous powder from the bar. It showed a red color upon being sprayed with the vanillin-HCl-EtOH reagent on TLC. The R_f values were 0.33 (TBAW) and 0.20 (6% HOAc). The MALDI-TOF-MS spectrum in the positive ion mode for **2** exhibited a molecular ion signal ($[M + Na]^+$) at *m/z* 599 that corresponds to the molecular ion of B-type procyanidin dimer (*m/z* 601 $[M+Na]^+$) without two protons, suggesting an A-type procyanidin dimer with a double linkage (C2-O-C7 and C-4-C-8 or C-4-C6) (Le Roux *et al*. 1998). The ^{1}H-NMR spectrum of compound **2** exhibited signals for the 3,4-*trans* A-type dimer of the AB coupling system at δ 4.05 and 4.41 (each 1H, *d*, *J* = 3.4 Hz, H-3C and 4C), two *meta*-coupled doublets at δ 6.01 and 6.07 (each 1H, *d*, *J* = 2.2 Hz, H-6A and H-8A), and one aromatic proton singlet at δ 6.09 (H-6D). Four aliphatic proton signals of the F-ring were observed at δ 4.92 (1H, *br s*, H-2), 4.24 (1H, *m*, H-3), 2.76 (1H, *dd*, *J* = 2.2, 17.2 Hz, H-4), and 2.95 (1H, *dd*, *J* = 4.9, 17.2 Hz, H-4). Two sets of ABX spin system signals of the B- and E-rings were observed at δ 6.80−7.15. These signals and the absence of H-2 in the upper flavan unit indicated that this compound was an epicatechin dimer of procyanidin



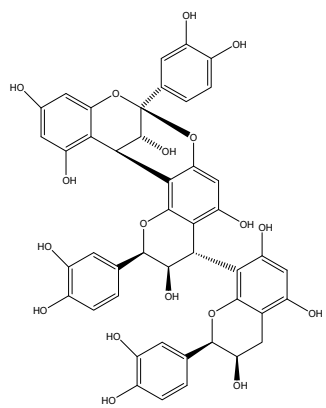
Compound **1**



Compound **2**



Compound **3**



Compound **4**

Fig. 1. Chemical structures of procyanidins isolated from *Acer komarovii* bark.

A-type. The 2,3-*cis* relative configuration of the lower epicatechin unit was determined on the basis of the broad singlet at δ 4.92 (H-2F) (Lou *et al*. 1999). In the ^{13}C-NMR spectrum of compound **2**, pyran ring carbon signals of two flavan units were evident at δ 100.23 and 81.82 (C-2C and C-2F), 68.13 and 67.03 (C-3C and C-3F), and 29.31 and 29.95 (C-4C and C-4F). A typical chemical shift for the ketal carbon was observed at δ 100.23 (C-2C) due to linkage of an oxygen to this carbon, which was thus shown to be involved in the ether C2-O-C7 linkage (Foo *et al*. 2000). The HSQC spectrum permits the assignment of each of the carbons directly to one proton. In the HMBC spectrum, the correlations were observed between δ 4.41 (H-4C) and δ 107.26 (C-8D), which confirmed the C4-C8 interflavan linkage. Therefore, the structure of compound **2** was identified as procyanidin A2 (epicatechin-(4$\beta\rightarrow$8, 2$\beta\rightarrow O\rightarrow$7)-epicatechin) by comparison with the previous data of authentic samples (Liu *et*

al. 2007; Hsieh *et al*. 2008).

3.3. Compound 3

Compound **3** was obtained as a brownish amorphous powder. It gave a red color upon being sprayed with the vanillin-HCl-EtOH reagent on TLC. The R_f values were 0.35 (TBAW) and 0.60 (6% HOAc). A molecular formula of $C_{30}H_{26}O_{12}$ was determined on the basis of the positive MALDI-TOF-MS peak at *m/z* 601 $[M+Na]^+$, which was two mass units higher than that of compound **2**. The ^{1}H-NMR spectrum of compound **3** exhibited the presence of the 2,3-*cis*-3,4-*trans* configuration of upper flavan unit signals at δ 4.94 (1H, *br s*, H-2C), 3.56 (1H, *d*, *J* = 3.6 Hz, H-3C), and 4.44 (1H, *br s*, H-4C); one aromatic singlet at δ 5.78 (H-6D); four pyran F-ring signals of the lower flavan unit at δ 4.91 (1H, *br s*, H-2F), 3.42 (1H, *br s*, H-3F), and 2.36 and 2.70 (each 1H, *d*, *J* = 12.2 Hz, H-4F). These results indicated the presence of an interflavan linkage at C4-C8 or C4-C6 (Hatano *et al*. 2002). In the ^{13}C-NMR spectrum of compound **3**, corresponding carbon signals were observed at δ 75.21 and 77.31 for C-2, 71.30 and 64.51 for C-3, and 35.47 and 27.43 for the substituted and unsubstituted flavanyl, respectively. The chemical shifts of the benzylic C-4s (δ 35.47 and 27.43) of the two epicatechin units indicated the presence of an epicatechin unit that does not link to the A-type procyanidin. The HMBC spectrum of showed that the proton signal (δ 4.44) for H-4 of the C-ring was correlated with the carbon signals (δ 107.26 and 152.19) of C-8 and C-9 of the D-ring. These results indicated that the epicatechin units were connected to C4 and C8. Based on the above results and previous literature data (Khan *et al*. 1997; Shoji *et al*. 2003), compound **3** was characterized as procyanidin B2 (epicatechin-(4$\beta\rightarrow$8)-epicatechin).

3.4. Compound 4

Compound **4** was obtained as a brownish amorphous powder. It was a red color upon being sprayed with the vanillin-HCl-EtOH reagent on TLC. The R_f values were 0.34 (TBAW) and 0.31 (6% HOAc). The MALDI-TOF-MS spectrum of compound **4** was recorded in positive ion mode and showed a molecular ion signal at *m/z* 887 $[M+Na]^+$, indicating a procyanidin trimer with an A-type interflavan linkage in the structure (Liu *et al*. 2007). In the ^{1}H-NMR spectrum, one signal in the upfield region at δ 2.83 (2H, *br d*, *J* = 3.3 Hz) was easily assigned to the H-4 of the lower unit. Signals of the A-type unit from the AB system appeared at δ 3.29 and 4.15 (each 1H, *d*, *J* = 3.5 Hz, H-3C and H-4C). This double-linked structure was also supported by a singlet ketal carbon signal at δ 99.98 in the ^{13}C-NMR spectrum. Two *meta*-coupled doublet signals were observed at δ 5.96 and 6.01 (each 1H, *d*, *J* = 2.3 Hz, H-6A and H-8A), along with two aromatic singlet signals at δ 5.80 (H-6D) and 6.10 (H-6G). In the ^{13}C-NMR spectrum of compound **4**, the signals at δ 29.88 and 28.90 were attributed to the C-4s of the upper and lower units,

respectively. Consequently, the signal at δ 38.31 was due to the C-4 of the middle unit. These signals provide a key insight into the 2D-NMR spectrum (Bruyne *et al*. 1996). The proton signals at δ 5.70 and 4.38 (each 1H, *s*) were assigned to the H-2s of the middle and lower units. Furthermore, the chemical shifts of the C-2s at δ 78.91 (F-ring) and 80.3 (I-ring) indicated that compound **4** consisted only of epicatechin units (Balde *et al*. 1995; Foo *et al*. 2000). In the HMBC spectrum, correlations were observed between H-4C (δ 4.15) and C-7D (δ 157.86), C-8D (δ 106.46) and C-9D (151.82), and H-4F (δ 4.56) and C-7G (δ 155.59) and C-8G (δ 108.87), which confirmed the C4-C8 interflavan linkage. Accordingly, the structure of compound **4** was identified as cinnamtannin B1 (epicatechin-(4β→8, 2β→*O*→7)-epicatechin-(4β→8)-epicatechin) (Kamiya *et al*. 2001; Hatano *et al*. 2002).

4. CONCLUSION

Procyanidins were isolated by Sephadex LH-20 and RP C-18 column chromatography from ethylacetate soluble fraction of *Acer komarovii* bark. The solvents for column analysis were various aqueous MeOH-H_2O (1:0, 1:1, 1:2, 1:5, 1:7, 1:9, 1:10, 3:1, and 4:1, v/v). Four compounds were isolated; (-)-epicatechin (9.6 g), procyanidin A2 (epicatechin-(4β→8, 2β→*O*→7)-epicatechin) (1.3 g), procyanidin B2 (epicatechin-(4β→8)-epicatechin) (40-0 mg), and cinnamtannin B1 (epicatechin-(4β→8, 2β→*O*→7)-epicatechin-(4β→8)-epicatechin) (690 mg). The characteristic of *Acer komarovii* bark procyanidins was that the only basic unit constituting condensed tannins is (-)-epicatechin. The procyanidins of *Acer komarovii* bark were reported for the first time in this study.

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REFERENCES

Agrawal, P.K. 1989. Carbon-13 NMR of Flavonoids. Elsevier, Amsterdam.

Akihisa, T., Taguchi, Y., Yasukawa, K., Tokuda, H., Akazawa, H., Suzuki, T., Kimura, Y. 2006. Acerogenin M, a cyclic diarylheptanoid, and other phenolic compounds from *Acer nikoense* and their anti-inflammatory and anti-tumor-promoting effects. Chemical & Pharmaceutical Bulletin 54(5): 735～739.

Balde, A.M., de Bruyne, T., Pieters, L., Kolodziej, H., Vanden Berghe, D., Claeys, M. Vlietinck, A. 1995. Oligomeric proanthocyanidins possessing a doubly linked structure from *Pavetta owariensis*. Phytochemistry 38(3): 719～723.

Bate-Smith, E.C. 1977. Astringent tannins of *Acer* species. Phytochemistry 16(9): 1421～1426.

Bate-Smith, E.C. 1978. Systematic aspects of the astringent tannins of *Acer* species. Phytochemistry 17(11): 1945～1948.

Bedgood, D.R. Jr., Bishop, A.G., Prenzler, P.D.,

Robards, K. 2005. Analytical approaches to the determination of simple biophenols in forest trees such as *Acer* (maple), *Betula* (birch), *Coniferus*, *Eucalyptus*, *Juniperus* (cedar), *Picea* (spruce) and *Quercus* (oak). Analyst 130(6): 809～823.

Bruyne, T., Pieters, L.A.C., Dommisse, R.A., Kolodziej, H., Wray, V., Domke, T., Vlietinck, A. J. 1996. Unambiguous assignments for free dimeric proanthocyanidin phenols from 2D NMR. Phytochemistry 43(1): 265～272.

Dong, L.P., Ni, W., Dong, J.Y., Li, J.Z., Chen, C.X., Liu, H.Y. 2006. A new neolignan glycoside from the leaves of *Acer truncatum*. Molecules 11(12): 1009～1014.

Farnsworth, N.R., Akerele, O., Bingel, A.S. 1985. Medicinal plants in therapy. Bulletin of the World Health Organization 63(6): 965～981.

Foo, L. Y., Lu, Y., Howell, A. B., Vorsa, N. 2000. A-type proanthocyanidin trimers from cranberry that inhibit adherence of uropathogenic P-fimbriated *Escherichia coli*. Journal of Natural Products 63(9): 1225～1228.

Hatano, T., Hattori, S., Ikeda, Y., Shingu, T., Okuda, T. 1990. Tannins of Aceraceous plants. Part II. Gallotannins having a 1,5-anhydro-D-glucitol core and some ellagitannins from *Acer* species. Chemical & Pharmaceutical Bulletin 38(7): 1902～1905.

Hatano, T., Miyatake, H., Natsume, M., Osakabe, N., Takizawa, T., Ito, H., Yoshida, T. 2002. Proanthocyanidin glycosides and related polyphenols from cacao liquor and their antioxidant effects. Phytochemistry 59(7): 749～758.

Hemingway, R.W., Tobiason, F.L., McGraw, G.W., Steynberg, J.P. 1996. Conformation and complexation of tannins: NMR spectra and molecular search modeling of flavan-3-ols. Magnetic Resonance in Chemistry 34(6): 424～433.

Hsieh, M.C., Shen, Y.J., Kuo, Y.H., Hwang, L.S. 2008. Antioxidative activity and active components of longan (*Dimocarpus longan* Lour.) flower extracts. Journal of Agricultural and Food Chemistry 56(16): 7010～7016.

Jin, W.Y., Thuong, P.T., Su, N.D., Min, B.S., Son, K.H., Chang, H.W., Kim, H.P., Kang, S.S., Sok, D.E., Bae, K.H. 2007. Antioxidant activity of cleomiscosins A and C isolated from *Acer okamotoanum*. Archives of Pharmacal Research 30(3): 275～281.

Kamiya, K., Watanabe, C., Endang, H., Umar, M., Satake, T. 2001. Studies on the constituents of bark of *Parameria laevigata* Moldenke. Chemical & Pharmaceutical Bulletin 49(5): 551～557.

Khan, M.L., Haslam, E., Williamson, M.P. 1997. Structure and conformation of the procyanidin B-2 dimer. Magnetic Resonance in Chemistry 35(12): 854～858.

Kim, H.J., Woo, E.R., Shin, C.G., Park, H.K. 1998b. A new flavonol glycoside gallate ester from *Acer okamotoanum* and its inhibitory activity against Human Immunodeficiency Virus-1 (HIV-1) integrase. Journal of Natural Products 61(1): 145～148.

Kim, J.H., Lee, B.C., Kim, J.H., Sim, G.S., Lee, D.H., Lee, K.E., Yun, Y.P., Pyo, H.B. 2005. The isolation and antioxidative effects of vitexin from Acer palmatum. Archives of Pharmacal Research 28(2): 195～202.

Kim, T.W. 1994. The woody plants of Korea in color. Kyohak Publishing co., Seoul, Korea.

Kwon, D.J., Bae, Y.S. 2009. Quercetin glycosides from bark of maple (Acer komarovii Pojark.). Journal of the Korean Wood Science and Technology 37(2): 171～176.

Kwon, D.J., Bae, Y.S. 2013. Flavonols from the bark of *Acer komarovii*. Chemistry of Natural

Compounds 49(1): 131～132.

Le Roux, E., Doco, T., Sarni-Manchado, P., Lozano, Y., Cheynier, V. 1998. A-type proanthocyanidins from pericarp of *Litchi chinensis*. Phytochemistry 48(7): 1251～1258.

Lee, C.B. 1985. Illustrated flora of Korea. Sung-Mun Publishing, Seoul, pp. 523.

Liu, L., Xie, B., Cao, S., Yang, E., Xu, X., Guo, S. 2007. A-type procyanidins from *Litchi chinensis* pericarp with antioxidant activity. Food Chemistry 105(4): 1446～1451.

Lou, H., Yamazaki, Y., Sasaki, T., Uchida, M., Tanaka, H., Oka, S. 1999. A-type proanthocyanidins from peanut skins. Phytochemistry 51(2): 297～308.

Morikawa, T., Tao, J., Toguchida, I., Matsuda, H., Yoshikawa, M. 2003. Structures of new cyclic diarylheptanoids and inhibitors of nitric oxide production from Japanese folk medicine *Acer nikoense*. Journal of Natural Products 66(1): 86～91.

Nonaka, G.I., Nishioka, I. 1982. Tannins and related compounds. VII. Phenylpropanoid- substituted epicatechins, cinchonains from *Cinchona succirubra*. Chemical & Pharmaceutical Bulletin 30(12): 4268～4276.

Shoji, T., Mutsuga, M., Nakamura, T., Kanda, T., Akiyama, H., Goda, Y. 2003. Isolation and structural elucidation of some procyanidins from apple by low-temperature nuclear magnetic resonance. Journal of Agricultural and Food Chemistry 51(13): 3806～3813.

Tung, N.H., Ding, Y., Kim, S.K., Bae, K.H., Kim, Y.H. 2008. Total peroxyl radical-scavenging capacity of the chemical components from the stems of *Acer tegmentosum* Maxim. Journal of Agricultural and Food Chemistry 56(22): 10510～10514.

Yang, H., Sung, S.H., Kim, Y.C. 2005b. Two new hepatoprotective stilbene glycosides from *Acer mono* leaves. Journal of Natural Products 68(1): 101～103.