 doi:10.20944/preprints201911.0354.v1

*Communication*

# Phenolic Constituents with Antioxidant and α-glucosidase Inhibitory Activities from Sugar Maple (*Acer saccharum* Marsh.) Fall Leaves

**Liangliang Yao[1], Suyou Zhu[1], Chuying Chen[2,3], Youxin Yang[2,3], Wenwen Peng[2], Chunpeng Wan[2,3]***

[1] Affiliated Hospital of Jiangxi University of Traditional Chinese Medicine, Nanchang, Jiangxi 330006, People's Republic of China. llyao86@163.com (L.Y.); lanina_1@sina.com (S.Z.)
[2] College of Agronomy, Jiangxi Agriculture University, Nanchang, 330045, People's Republic of China. cy.chen@jxau.edu.cn (C.C.); yangyouxin@jxau.edu.cn (Y.Y.); pengwenwen123@sina.com (W.P.)
[3] Jiangxi Key Laboratory for Postharvest Technology and Nondestructive Testing of Fruits & Vegetables, Jiangxi Agriculture University, Nanchang, 330045, People's Republic of China.
* Correspondence: chunpengwan@jxau.edu.cn (C.W.), Tel.: +86-791-83813185 (C.W.).

**Abstract:** To elucidate the chemical compositions of the sugar fall maple leaves, the methanol extracts were firstly fractionated by ethyl acetate and n-butanol respectively. The phenolic acids-rich fractions (ethyl acetate extracts) were further purified by various chromatographic columns including XAD macroporous resin, Sephadex LH-20, ODS and semi-preparative HPLC to yield the compounds. The isolated compounds were characterized by $^{1}$H-Nuclear Magnetic Resonance ($^{1}$H-NMR), $^{13}$C-NMR, and high resolution electrospray ionisation mass spectral (HR-ESI-MS) spectroscopy. Twenty eight phenolics including fourteen flavonoids (**1-14**), five quinic acid derivatives (**15-19**), five galloyl tannins (**20-24**) and four other phenolic acids (**25-28**) were isolated and their structures were identified. The isolated compounds were evaluated for their antioxidant and α-glucosidase inhibitory activities. All of the phenolics constituents showed DPPH scavenging antioxidant activities. While, glycosides of quercetin and myricetin, galloyl tannins were showed promising α-glucosidase inhibitory activity. All of the compounds except **4, 11, 12** and **28** were isolated from sugar maple for the first time. Moreover, Compounds **9, 10, 14, 20, 21, 23, 25** and **26** were isolated from the Acer species for the first time.

**Keywords:** *Acer saccharum*; sugar maple; phenolics; chebulate derivatives; antioxidant; α-glucosidase inhibitory

## 1. Introduction

The genus Acer (Aceraceae) contains nearly 200 species of which thirteen, including the sugar maple (*A. saccharum*), red maple (*A. rubrum L.*), norway maple (*A. platanoides*), and silver Maple (*A. saccharinum*) are indigenous to North America [1]. The phytochemistry studies of the genus Acer revealed phenolics constituents including flavonoids [2], tannins, phenylpropanoids were the major constituents of Acer species. Except phenolics constituents, several other types of compounds such as benzoic acid derivatives, terpenoids, diarylheptanoids, phenylethanoid glycosides and alkaloids were also existed in Acer species [3]. Diarylheptanoids compounds were abundant existed in *A. nikoense* [4], phenylethanoid glycosides were mainly existed in *A. tegmentosum* [5] and *A. nikoense* [6]. Phenolics including acertannin, lignans, flavonoids, phenolic glycosides, were also the predominant compounds reported from *A. saccharum* [7-9].

Preliminary biological activities studies of Acer species have proved theirs human health benefits. The extracts of Acer species and main compounds have shown antioxidant, antidiabetic, anti-inflammatory, antitumor, hepatoprotective, and antiobesity activities, as well as promoting osteoblast differentiation [3]. *A. saccharum* hot water extracts have shown safe dietary antioxidants potential [10]. Sugar maple extracts and its main constituent acertannin have shown

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 28 November 2019 doi:10.20944/preprints201911.0354.v1



anti-hyperglycemic effects [11]. In order to continue our research on isolation and identification antioxidant and α-glucosidase inhibitory constituents from Acer species. The antioxidant and α-glucosidase inhibitory activities of sugar maple summer and fall leaves were compared. Herein we worked on the chemical constituents of the sugar maple fall leaves and led to the identification of twenty eight phenolics.

## 2. Results

The structures of the compounds were elucidated by a combination of spectroscopic methods (ESI-MS, $^{1}H$ and $^{13}C$ NMR data), and comparison with literature data. Twenty eight phenolics including fourteen flavonoids (**1-14**), five quinic acid derivatives (**15-19**), five galloyl tannins (**20-24**) and four other phenolic acids (**25-28**) were isolated and their structures were identified as quercetin-3-O-β-D-glucoside (**1**) [12], quercetin-3-O-β-D-galactoside (**2**) [12], quercetin-3-O-α-L-arabinoside (**3**) [12], quercetin-3-O-α-L-rhamnoside (**4**) [13], kaempferol-3-O-α-L-rhamnoside (**5**) [14], myricetin-3-O-α-L-rhamnoside (**6**) [14], quercetin-3-O-(2''-O-galloyl)-α-L-rhamnoside (**7**) [15], quercetin-3-O-(3''-O-galloyl)-α-L-rhamnoside (**8**) [16], quercetin-3-O-(6''-O-galloyl)-β-D-glucoside (**9**) [17], quercetin-3-O-(6''-O-galloyl)-β-D-galactoside (**10**) [18], epi-catechin (**11**) [19], catechin (**12**) [19], epicatechin-3-O-gallate (**13**) [20], dihydroquercetin-3-O-β-D-glucopyranoside (**14**) [21], 5-O-caffeoylquinic acid (**15**) [22], 3-O-caffeoylquinic acid (**16**) [22], 5-O-caffeoylquinic acid methyl ester (**17**) [12], 3-O-caffeoylquinic acid methyl ester (**18**) [23], 5-O-coumaroylquinic acid methyl ester (**19**) [12], 1,2,4-trigalloyl-β-D-glucose (**20**) [24,25], 1,3,4-trigalloyl-α-D-glucose (**21**) [24], 1,2,3,4,6-Pentagalloylglucose (**22**) [26], 1,2,4-trigalloyl-3,6-HHDP-α-D-glucose (**23**) [27], 2,3,4-trigalloyl-1,6-HHDP-α-D-glucose (**24**) [28], 11,12-dimethyl-chebulate (**25**) [29], 12,13-dimethyl-chebulate (**26**) [29] (**Figure 1**), protocatechuic acid (**27**) [30], and methyl gallate (**28**) [31]. An HPLC-DAD profile of the ethyl acetate extract of sugar maple leaves and the isolates compounds were shown in supporting information (S1). All of the compounds except **4, 11, 12** and **28** were isolated from sugar maple for the first time. Moreover, Compounds **9, 10, 14, 20, 21, 23, 25** and **26** were isolated from the Acer species for the first time.

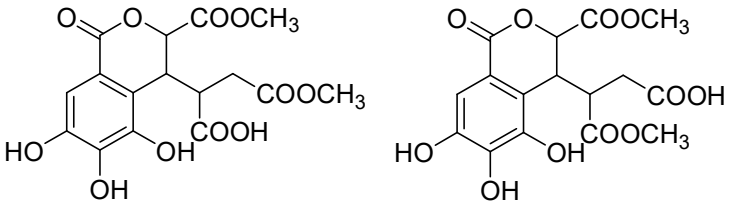


**Figure 1.** The structures of compounds **25-26**.

The extracts of sugar maple fall and summer leaves were firstly evaluated for their antioxidant and α-glucosidase inhibitory activities. The results (Table 1) showed that sugar maple fall leaves extracts possessed better activities than summer leaves extracts. Moreover, the EtOAc fraction of sugar maple fall leaves showed the best activities. So the final isolation were conducted on this fraction. 28 phenolics were identified and evaluated for their antioxidant and α-glucosidase inhibitory activities. The isolated compounds were evaluated for their antioxidant and α-glucosidase inhibitory activities. Overall, all of the phenolics constituents showed DPPH scavenging antioxidant activities, the flavonol glycosides, quinic acid derivatives, galloyl tannins and other phenolic acids all showed comparable or superior antioxidant activities compared to the positive controls, BHT ($IC_{50}$ = 51.53 μg/mL). However, glycosides of quercetin and myricetin, galloyl tannins were showed promising α-glucosidase inhibitors compared with the clinical drug, acarbose ($IC_{50}$ = 370.15 μg/mL).

**Table 1**. Antioxidant and α-glucosidase inhibitory activities of compounds **1–28** from sugar maple

| No | DPPH | α-glucosidase | No | DPPH | α-glucosidase |
|---|---|---|---|---|---|
| | $EC_{50}$ (μg/mL) | | | $EC_{50}$ (μg/mL) | |
| 1 | 17.74 ± 0.64 | 283.99 ± 2.61 | 20 | 11.50 ± 0.67 | 370.90 ± 18.16 |
| 2 | 18.21 ± 0.84 | 275.68 ± 2.93 | 21 | 10.43 ± 0.41 | 584.03 ± 26.87 |
| 3 | 76.38 ± 7.28 | 298.21 ± 5.68 | 22 | 7.99 ± 0.52 | 6.32 ± 0.96 |
| 4 | 35.04 ± 1.91 | 190.03 ± 9.30 | 23 | 7.59 ± 0.39 | 14.69 ± 0.64 |
| 5 | 59.42 ± 10.68 | 514.25 ± 16.06 | 24 | 12.49 ± 0.54 | 27.90 ± 1.76 |
| 6 | 22.16 ± 4.42 | 156.27 ± 8.98 | 25 | 9.94 ± 0.81 | — |
| 7 | 4.96 ± 2.00 | 57.62 ± 4.10 | 26 | 9.51 ± 2.25 | — |
| 8 | 8.47 ± 2.45 | 102.88 ± 11.93 | 27 | 1.46 ± 0.62 | 1749.37 ± 131.44 |
| 9 | 1.90 ± 0.68 | 373.39 ± 9.18 | 28 | not detect | not detect |
| 10 | 2.01 ± 0.32 | 379.26 ± 10.14 | FLME | 16.78 ± 4.17 | 152.38 ± 13.46 |
| 11 | 5.74 ± 0.17 | 1943.43 ± 63.62 | FLEF | 0.96 ± 0.28 | 118.11 ± 2.25 |
| 12 | 14.05 ± 0.43 | 1642.57± 185.74 | FLBF | 10.79 ± 3.20 | 92.00 ± 4.12 |
| 13 | 22.49 ± 0.77 | 137.59 ± 5.43 | FLWF | 22.31 ± 5.26 | 96.11 ± 10.80 |
| 14 | 110.97 ± 1.69 | — | SLME | 11.15 ± 2.21 | 57.86 ± 13.92 |
| 15 | 31.34 ± 2.03 | — | SLEF | 1.94 ± 0.63 | 46.73 ± 2.71 |
| 16 | 18.86 ± 4.09 | — | SLBF | 7.82 ± 3.60 | 99.38 ± 3.23 |
| 17 | 35.33 ± 1.03 | — | SLWF | 81.85 ± 5.44 | 453.46 ± 6.83 |
| 18 | 21.60 ± 3.68 | — | Acarbose | — | 370.15 ± 11.99 |
| 19 | 33.13 ± 1.34 | — | BHT | 51.53 ± 3.31 | — |

Fall leaves methanol extract (FLME), Fall leaves EtOAc fraction (FLEF), Fall leaves n-butanol fraction (FLBF), Fall leaves water layer fraction (FLWF); Summer leaves methanol extract (SLME), Summer leaves EtOAc fraction (SLEF), Summer leaves n-butanol fraction (SLBF), Summer leaves water layer fraction (SLWF). butylated hydroxytoluene (BHT)

## 3. Discussion

Phenolics including tannins and flavonoids are the characteristic metabolites reported from the genus Acer [2-3]. Furthermore, flavonoids (chalcone, and anthocyanins), Cyclopropylamino acids have been proposed as chemotaxonomic markers to differentiate various Acer taxa [1, 32, 33]. Here, twenty eight phenolics including fourteen flavonoids (**1–14**), five quinic acid derivatives (**15–19**), five galloyl tannins (**20–24**) and four other phenolic acids (**25–28**) were isolated from *A. saccharum* leaves. All of the compounds except **4, 11, 12** and **28** were isolated from sugar maple for the first time. Moreover, Compounds **9, 10, 14, 20, 21, 23, 25** and **26** were isolated from the Acer species for the first time. The widespread presence of flavan-3-ol derivatives and quercetin glycosides in sugar maple is in agreement with the previous report from *A. rubrum*, *A. ginnala*, *A. truncatum Bunge*, and *A. glabrum* [2-3]. The presence of quinic acid derivatives in sugar maple is in agreement with the previous report from *A. truncatum Bunge*, *A.saccharum* and *A. pseudoplatanus* [3, 34] This is the first report of chebulate derivatives (**25-26**) from an *Acer* species, both compounds were isolated from the leaves of *Dipteronia dyeriana*, belongs to the family Aceraceae. Two chebulate derivatives (**25-26**) found in *A.saccharum* revealed the relationship of the genus of *Acer* and *Dipteronia*, which is a significant chemotaxonomic finding. However, whether these compounds may be regarded as chemotaxonomic markers for *A. saccharum* would require further studies.

The isolated compounds were evaluated for their antioxidant and α-glucosidase inhibitory activities. Overall, all of the phenolics constituents showed DPPH scavenging antioxidant activities, the flavonol glycosides, quinic acid derivatives, galloyl tannins and other phenolic acids all showed comparable or superior antioxidant activities compared to the positive controls. The structure-activity relationship (SAR Figure 2) reveals the antioxidant activities were highly related to the number of phenolic hydroxyl group [35]. And the antioxidant activities were also highly related to the number of galloyl [36]. As for the α-glucosidase inhibitory activity, only flavonoids and galloyl tannins were showed promising inhibitory activity. The SAR reveals the α-glucosidase inhibitory activity were highly related to the number of phenolic hydroxyl group and galloyl [36].

 doi:10.20944/preprints201911.0354.v1



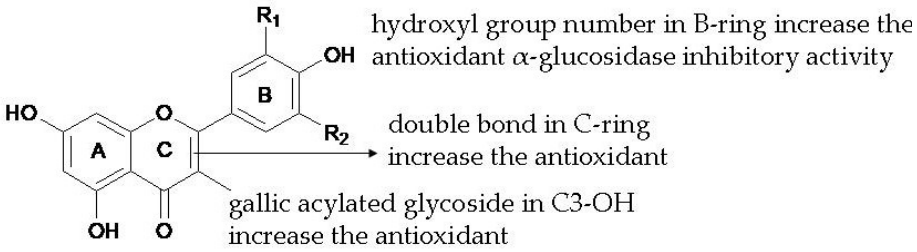


**Figure 2.** The structure-activity relationship of flavonoids with antioxidant and α-glucosidase inhibitory activity

## 4. Materials and Methods

### *4.1. Plant Material*

The leaves of sugar maple were collected in autumn of November 2010 and in summer of June 2014 respectively from the campus of University of Rhode Island and identified by Mr. J. Peter Morgan (Senior Gardener, College of Pharmacy, University of Rhode Island, Kingston, Rhode Island, USA). A voucher specimen (16JPM17-ASA-101410FL for sugar maple fall leaves, 16JPM19-ASA-6182014 for sugar maple summer leaves) has been deposited in the Heber Youngken Medicinal Garden and Greenhouse (College of Pharmacy, University of Rhode Island).

### *4.2. Equipment and Reagents*

$^{1}H$ and $^{13}C$ Nuclear Magnetic Resonance (NMR) data were recorded on a Varian 500 MHz instrument with TMS as internal standard. Electrospray Ionization Mass Spectral (ESI-MS) data were acquired on a Q-Star Elite (Applied Biosystems MDS) mass spectrometer equipped with a Turbo Ionspray source and were obtained by direct infusion of pure compounds. Medium pressure liquid chromatography (MPLC) separations were carried out on pre-packed C18 columns connected to a DLC-10/11 isocratic liquid chromatography pump (D-Star Instruments, Manassas, VA) with a fixed-wavelength detector. High performance liquid chromatography (HPLC) were performed on a Hitachi Elite LaChrom system consisting of a L2130 pump, L-2200 autosampler, and a L-2455 Diode Array Detector all operated by EZChrom Elite software. All solvents were of either ACS or HPLC grade and were purchased from Wilkem Scientific (Pawtucket, RI).

### *4.3. Extraction and Chromatography*

The sugar maple fall leaves (0.8 Kg, dry weight) were extracted exhaustively with MeOH (3 × 4 L) at room temperature to yield a dried MeOH extract (200 g). A portion of the extract (210 g) was re-suspended in H2O (2.0 L) and successively partitioned with EtOAc (3 × 2.0 L) and n-butanol to yield a dried EtOAc (55 g) and n-butanol (44 g) extracts, respectively. 100 g sugar maple summer leaves were extracted by the same method as mentioned ahead.

The EtOAc extract (50 g) was chromatographed on a XAD column (3 × 10 inch) eluting with a gradient system of MeOH/H2O (1:1 to 9:1, v/v) to afford 3 sub-fractions (A1-A3) which were combined based on analytical HPLC analyses.

Fraction A1 was separated by Sephadex LH-20 (1.5 × 23 inch) eluted with MeOH to give 5 sub-fractions (B1-B5). Sub-fractions B1 was separated by semi-preparative HPLC eluted with a gradient system MeOH/H2O (2.8 mL/min) to yield compounds **25** and **26**.

Sub-fractions B2 was chromatographed on a C18 MPLC column (2 × 15 cm) eluting with a gradient system of MeOH/H2O (1:9 to 4:6, v/v) to afford 4 sub-fractions (C1- C4).

Sub-fractions C1 was separated by semi-preparative HPLC eluted with MeOH/H2O (33/67, *v/v*; 2.8 mL/min) to yield compounds **16**, **27** and **28**.

Sub-fractions C2 was separated by Sephadex LH-20 (1.5 × 23 inch) eluted with MeOH to give 2 main sub-fractions(C2A and C2B). C2A were separated by semi-preparative HPLC eluted with MeOH/H2O (32/68, *v*/*v*; 2.8 mL/min) to yield compounds **15**, **16**, **18**. C2B were separated by semi-preparative HPLC eluted with MeOH/H2O (32/68, *v*/*v*; 2.8 mL/min) to yield compounds **11** and **12**

Sub-fractions C4 was separated by Sephadex LH-20 (1.0 × 21 inch) eluted with MeOH to give 3 main sub-fractions(C4A and C4C). C4A was separated by semi-preparative HPLC eluted with MeOH/H2O (35/65, *v*/*v*; 2.8 mL/min) to yield compounds **17** and **19**. C4B was separated by semi-preparative HPLC eluted with MeOH/H2O (36/64, *v*/*v*; 2.8 mL/min) to yield 5 sub-fractions (C4B1-C4B5). C4B4 was separated by semi-preparative HPLC to yield compounds **14**.

Sub-fractions B3 was chromatographed on a C18 MPLC column (2 × 15 cm) eluting with a gradient system of MeOH/H2O (1:9 to 4:6, *v*/*v*) to afford 4 sub-fractions (D1- D4). D2 was separated by semi-preparative HPLC eluted with MeOH/H2O (28/72, v/v; 2.8 mL/min) to yield compounds **20** and **21**. D4 was separated by semi-preparative HPLC eluted with MeOH/H2O (46/54, *v*/*v*; 2.8 mL/min) to yield compounds **6**, **9**, **10** and **13**.

Sub-fractions B5 was separated by semi-preparative HPLC eluted with MeOH/H2O (40/60, *v*/*v*; 2.8 mL/min) to yield compounds **22**, **23** and **24**.

Fraction A3 was separated by Sephadex LH-20 (1.5 × 23 inch) eluted with MeOH to give 3 sub-fractions (E1-E3). Sub-fractions E2 was chromatographed on a C18 MPLC column (2 × 15 cm) eluting with a gradient system of MeOH/H2O (2:8 to 7:3, *v*/*v*) to afford 3 sub-fractions (E2A- E2C). Sub-fractions E2A was separated by semi-preparative HPLC eluted with MeOH/H2O (50/50, *v*/*v*; 2.8 mL/min) to yield compounds **1—4** and **7**. Sub-fractions E2C was separated by semi-preparative HPLC eluted with MeOH/H2O (51/49, *v*/*v*; 2.8 mL/min) to yield **5** and **8**. Detailed flow chart of the isolation procedure was shown in supporting information (S2).

### *4.4. Antioxidant and α-glucosidase inhibitory activities*

The antioxidant and α-glucosidase inhibitory activities of isolates were evaluated as described previously [12].

### *4.5. NMR and MS Data of Compounds **1**–**28***

The $^{1}$H- and $^{13}$C-NMR data of these compounds (**1**–**28**) were listed as follows.

Quercetin-3-*O*-*β*-D-glucoside (**1**), $^{1}$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz): 7.61 (1H, d, *J* = 2.1 Hz, H-2'), 7.48 (1H, dd, *J* =8.5, 2.1 Hz, H-6'), 6.76 (1H, d, *J* =8.5 Hz, H-5'), 6.30 (1H, d, *J* = 2.1 Hz, H-8), 6.10 (1H, d, *J* = 2.1 Hz, H-6), 5.15 (1H, dd, *J* = 7.8 Hz, H-1''), 3.63 (1H, dd, *J* = 2.4, 11.9 Hz, H-6a''), 3.53 (1H, dd, *J* = 2.4, 11.9 Hz, H-6b''), 3.45 –3.30 (3H, m, H-2'', 3'', 4''), 3.23 (1H, m, 5'').

Quercetin-3-*O*-*β*-D-galactoside (**2**), $^{1}$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz): 7.74 (1H, d, *J* = 2.1 Hz, H-2'), 7.49 (1H, dd, *J* =8.5, 2.1 Hz, H-6'), 6.77 (1H, d, *J* =8.5Hz, H-5'), 6.30 (1H, d, *J* = 2.1 Hz, H-8), 6.10 (1H, d, *J* = 2.1 Hz, H-6), 5.06 (1H, dd, *J* = 7.8 Hz, H-1''), 3.76 (1H, d, *J* = 3.4 Hz, H-3''), 3.71 (1H, dd, *J* = 7.9, 9.7 Hz, H-2''), 3.54 (1H, dd, *J* = 6.1, 8.3 Hz, H-5''), 3.47 (2H, m, H-6''), 3.33 (1H, t, *J* = 8.9 Hz, H-4'').

Quercetin-3-*O*-*α*-L-arabinopyranoside (**3**), $^{1}$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz), 7.65 (1H, d, *J* = 2.1 Hz, H-2'), 7.47 (1H, dd, *J* = 8.5, 2.1 Hz, H-6'), 6.78 (1H, d, *J* = 8.5 Hz, H-5'), 6.29 (1H, d, *J* = 2.0 Hz, H-8), 6.10 (1H, brs, H-6), 5.07 (1H, d, *J* = 6.5 Hz, H-1''), 3.81 (1H, dd, *J* = 8.4, 6.6 Hz, H-2''), 3.72 (2H, m, H-4'', 5''), 3.55 (1H, m, H-3''), 3.35 (1H, dd, J = 13.5, 3.1 Hz, H-5'').

Quercetin-3-O-*α*-L-rhamnoside (**4**), (+) ESIMS, m/z 449.1290 $[M + H]^+$, $^{1}$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz): 7.25 (1H, d, J = 2.0 Hz, H-2'), 7.20 (1H, dd, J = 8.3, 1.9 Hz, H-6'), 6.82 (1H, d, J = 8.3 Hz, H-5'), 6.26 (1H, d, J = 1.9 Hz, H-8), 6.09 (1H, d, J = 1.9 Hz, H-6), 5.27 (1H, d, J = 1.1 Hz, H-1''), 4.15 (1H, m), 3.69 (1H, m), 3.34 (1H, brs), 3.23 (1H, m), 0.87 (3H, d, J = 6.1 Hz, $CH_3$).

Kaempferol-3-O-*α*-L-rhamnoside (**5**), (+) ESIMS, m/z 431.1873 $[M + H]^+$, $^{1}$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz): 7.67 (2H, d, J = 8.8 Hz, H-2', 6'), 6.84 (2H, d, J = 8.8 Hz, H-3', 5'), 6.27 (1H, d, J = 2.0 Hz,

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 28 November 2019 doi:10.20944/preprints201911.0354.v1



H-8), 6.10 (1H, d, J = 2.0 Hz, H-6), 5.28 (1H, d, J = 1.6 Hz, H-1''), 4.13 (1H, m), 3.61 (1H, m), 3.25 (1H, brs), 3.21 (1H, m), 0.87 (3H, d, J = 5.7 Hz, $CH_3$).

Myricetin-3-O-α-L-rhamnoside (**6**), (-) ESIMS, m/z 463.2451 [M - H]$^-$, $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz): 6.85 (2H, s, H-2', 6'), 6.27 (1H, d, *J* = 2.1 Hz, H-8), 6.10 (1H, d, *J* = 2.1 Hz, H-6), 5.21 (1H, d, *J* =1.5 Hz, H-1''), 4.11 (1H, m), 3.69 (1H, m), 3.34 (1H, brs), 3.25 (1H, m), 0.86 (3H, d, J = 6.3 Hz, $CH_3$).

Quercetin-3-O-(2''-O-galloyl)-α-L-rhamnoside (**7**), $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz): 7.27 (1H, d, J = 2.0 Hz, H-2'), 7.24 (1H, dd, J = 8.3, 2.1 Hz, H-6'), 6.98 (2H, s, H-2''', 6'''), 6.84 (1H, d, J = 8.3 Hz, H-5'), 6.27 (1H, d, J = 1.9 Hz, H-8), 6.10 (1H, d, J = 1.9 Hz, H-6), 5.53 (1H, dd, J = 3.0, 1.4 Hz, H-2''), 5.41 (1H, d, J = 1.1 Hz, H-1''), 3.92 (1H, m), 3.38 (2H, m), 0.94 (3H, d, J = 5.6 Hz, $CH_3$).

Quercetin-3-O-(3''-O-galloyl)-α-L-rhamnoside (**8**), $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz): 7.28 (1H, d, J = 2.1 Hz, H-2'), 7.30 (1H, dd, J = 8.3, 2.1 Hz, H-6'), 7.07 (2H, s, H-2''', 6'''), 6.84 (1H, d, J = 8.3 Hz, H-5'), 6.29 (1H, d, J = 2.1 Hz, H-8), 6.11 (1H, d, J = 2.1 Hz, H-6), 5.12 (1H, dd, J = 9.7, 3.3 Hz, H-3''), 5.29 (1H, d, J = 1.8 Hz, H-1''), 4.38 (1H, m), 3.57 (1H, m), 3.48 (1H, m), 0.90 (3H, d, J = 6.2 Hz, $CH_3$).

Quercetin-3-O-(6''-O-galloyl)-β-D-glucoside (**9**), (-) ESIMS, m/z 615.3062 [M - H]$^-$, $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz): 7.47 (1H, d, *J* = 2.1 Hz, H-2'), 7.43 (1H, dd, *J* =8.5, 2.1 Hz, H-6'), 6.84 (2H, s, H-2''', 6'''), 6.62 (1H, d, *J* =8.5 Hz, H-5'), 6.23 (1H, d, *J* = 2.1 Hz, H-8), 6.07 (1H, d, *J* = 2.1 Hz, H-6), 5.11 (1H, dd, *J* = 7.8 Hz, H-1''), 4.26 (1H, d, *J* = 11.8 Hz, H-6a''), 4.18 (1H, dd, *J* = 1.6, 11.8 Hz, H-6b''), 3.42 –3.33 (3H, m, H-2'', 3'', 5''), 3.23 (1H, m, 4'').

**Table 2**. $^{13}$C NMR Data for Compounds **1–5, 11-14** (125 MHz, $CD_3OD$)

| | $\delta_C$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| no. | **1** | **2** | **3** | **4** | **5** | **11** | **12** | **12** | **14** |
| 2 | 157.4 | 157.5 | 157.3 | 157.2 | 157.8 | 78.4 | 81.4 | 77.2 | 83.5 |
| 3 | 134.2 | 134.3 | 134.2 | 134.8 | 134.8 | 66.1 | 67.4 | 68.6 | 72.1 |
| 4 | 178.1 | 178.0 | 178.1 | 178.2 | 178.2 | 27. 9 | 27.1 | 25.5 | 197.0 |
| 5 | 161.5 | 161.5 | 161.7 | 161.8 | 161.8 | 156.1 | 156.1 | 155.9 | 167.3 |
| 6 | 98.4 | 98.4 | 98.4 | 98.5 | 98.4 | 95.1 | 94.9 | 94.5 | 95.9 |
| 7 | 164.5 | 164.6 | 164.6 | 164.4 | 164.4 | 156.5 | 156.3 | 156.4 | 163.9 |
| 8 | 93.4 | 93.3 | 93.3 | 93.4 | 93.3 | 94.6 | 94.1 | 95.1 | 94.9 |
| 8a | 157.0 | 157.0 | 157.0 | 157.9 | 157.1 | 155.9 | 155.4 | 155.9 | 163.0 |
| 4a | 104.0 | 104.1 | 103.2 | 104.5 | 104.5 | 98. 7 | 99.4 | 98.0 | 100.5 |
| 1' | 121.6 | 121.8 | 121.6 | 121.5 | 121.2 | 130.9 | 130.8 | 130.0 | 128.6 |
| 2' | 116.1 | 116.3 | 116.0 | 114.9 | 130.4 | 113.9 | 113.8 | 113.7 | 116.8 |
| 3' | 144.4 | 144.5 | 144.6 | 145.0 | 115.1 | 144.3 | 144.8 | 144.5 | 145.1 |
| 4' | 148.4 | 148.5 | 148.5 | 148.4 | 160.1 | 144.5 | 144.8 | 144.5 | 147.6 |
| 5' | 114.6 | 114.6 | 114.7 | 115.5 | 115.1 | 114.6 | 114.7 | 114.6 | 115.5 |
| 6' | 121.4 | 121.5 | 121.4 | 121.4 | 130.4 | 118.1 | 118.6 | 118.0 | 123.2 |
| 1'' | 102.8 | 103.9 | 102.3 | 102.1 | 102.1 | | | 120.0 | 102.6 |
| 2'' | 74.4 | 71.7 | 71.4 | 70.6 | 70.6 | | | 108.8 | 73.5 |
| 3'' | 76.7 | 73.7 | 72.7 | 70.7 | 70.7 | | | 144.9 | 76.2 |
| 4'' | 69.8 | 68.6 | 67.7 | 71.8 | 71.7 | | | 138.4 | 70.1 |
| 5'' | 77.1 | 75.6 | 65.5 | 70.5 | 70.5 | | | 144.9 | 77.0 |
| 6'' | 61.1 | 60.5 | | 16.2 | 16.2 | | | 108.8 | 61.1 |
| 7'' | | | | | | | | 166.2 | |

Quercetin-3-O-(6''-O-galloyl)-β-D-galactoside (**10**), (-) ESIMS, m/z 615.3697 [M - H]$^-$, $^1$H NMR (500 MHz, $CD_3OD$): δ 7.68 (1H, d, *J* = 2.1 Hz, H-2'), 7.42 (1H, dd, *J* =8.5, 2.1 Hz, H-6'), 6.79 (2H, s, H-2''', 6'''), 6.71 (1H, d, *J* =8.5Hz, H-5'), 6.26 (1H, d, *J* = 2.1 Hz, H-8), 6.07 (1H, d, *J* = 2.1 Hz, H-6), 5.01 (1H, dd, *J* = 7.8 Hz, H-1''), 4.26 (1H, d, *J* = 11.8 Hz, H-6a''), 4.10 (1H, dd, *J* = 5.6, 11.8 Hz, H-6b''), 3.76- 3.42 (4H, m).

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 28 November 2019 doi:10.20944/preprints201911.0354.v1



Epi-catechin (**11**), $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, *J*/Hz), 6.76 (1H, d, J = 8.2 Hz, H-5'), 6.80 (1H, dd, J = 8.2, 1.7 Hz, H-6'), 6.98 (1H, brs, H-2'), 5.94 (1H, s, H-6), 5.96 (1H, s, H-8), 2.74 (1H, dd, J = 16.7, 2.4 Hz, H-4b), 2.86 (1H, dd, J = 16.8, 4.7 Hz, H-4a), 4.17 (1H, m, H-3), 4.81 (1H, s, H-2)

Catechin (**12**), $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, *J*/Hz), 6.61 (1H, dd, J = 8.1, 1.9 Hz, H-6'), 6.66 (1H, d, J = 8.1 Hz, H-5'), 6.74 (1H, d, J = 1.9 Hz, H-2'), 5.76 (1H, brs, H-6), 5.83 (1H, brs, H-8), 2.42 (1H, dd, J = 16.2, 8.2 Hz, H-4b), 2.75 (1H, dd, J = 16.1, 5.4 Hz, H-4a), 3.87 (1H, m, H-3), 4.46 (1H, d, J = 7.6 Hz, H-2).

Epicatechin-3-O-gallate (**13**), $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, *J*/Hz), 6.94 (2H, s, H-2''', 6'''), 6.93 (1H, brs, H-2'), 6.80 (1H, dd, *J* = 1.8, 8.3 Hz, H-6'), 6.69 (1H, d, *J* = 8.3 Hz, H-5'), 5.96 (2H, s, H-6,8), 5.52 (1H, brs, H-3), 5.03 (1H, s, H-2), 3.01 (1H, dd, *J* = 4.6, 17.4 Hz, H-4a), 2.86 (1H, dd, *J* = 2.0, 17.4 Hz, H-4b).

Dihydroquercetin-3-O-β-D-glucopyranoside (**14**), (-) ESIMS, m/z 465.2664 $[M - H]^-$, $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, *J*/Hz), 7.38 (1H, d, J=1.8 Hz, H-2'), 7.10(1H, dd, J=8.3, 1.9 Hz, H-6'), 6.89(1H, d, J=8.2 Hz, H-5'), 5.93(1H, d, J=2.1 Hz, H-8), 5.88(1H, d, J=2.1 Hz, H-6), 4.98(1H, d, J=7.2 Hz, H-1''), 4.57(1H, d, J=11.7 Hz, H-2), 3.90(1H, dd，J=9.6, 2.0 Hz, H-3), 3.68–3.35 (6H, m, H-2'', 3'', 4'', 5'', 6'').

**Table 3.** $^1$H-NMR ($^1$H-Nuclear Magnetic Resonance, 500 MHz, $CD_3OD$) characteristics of the quinic acid derivatives **15–19** isolated from fall sugar maple leaves.

| No. | 15 | 16 | 17 | 18 | 19 |
|---|---|---|---|---|---|
| | δH (J Hz) | δH (J Hz) | δH (J Hz) | δH (J Hz) | δH (J Hz) |
| 2 | 1.96–2.17 (2H, m) | 1.94–2.14 (2H, m) | 1.90–2.13 (2H, m) | 1.90–2.12 (2H, m) | 1.90–2.12(2H, m) |
| 3 | 4.08 (1H, ddd, 1.8,4.9,4.9) | 5.23 (1H, brd, 4.1) | 4.05 (1H, brs) | 4.07 (1H, brs) | 4.07 (1H, brs) |
| 4 | 3.65 (1H, dd, 3.1, 8.8) | 3.63 (1H, dd, 3.1, 8.5) | 3.63 (1H, dd, 3.1, 7.5) | 4.96 (1H, dd, 3.1, 9.4) | 3.76 (1H, dd, 3.0, 8.1) |
| 5 | 5.25 (1H, ddd, 4.5, 9.4, 9.4) | 4.07 (1H, ddd, 3.6, 8.5, 8.5) | 5.18 (1H, ddd, 9.0, 9.0, 4.5) | 5.24 (1H, ddd, 4.5, 9.4, 9.4) | 5.25 (1H, ddd, 4.5, 9.4, 9.4) |
| 6 | 1.96–2.17 (2H, m) | 1.94–2.14 (2H, m) | 1.90–2.13 (2H, m) | 1.90–2.12 (2H, m) | 1.90–2.12(2H, m) |
| 2′ | 6.96 (1H, d, 2.1) | 6.95 (1H, d, 2.1) | 6.94 (1H, d, 2.0) | 7.09 (1H, d, 1.9) | 7.37 (1H, d, 8.7) |
| 3′ | | | | | 6.70 (1H, d, 7.9) |
| 5′ | 6.68 (1H, d, 8.2) | 6.68 (1H, d, 8.2) | 6.68 (1H, d, 8.2) | 6.70 (1H, d, 7.9) | 6.70 (1H, d, 7.9) |
| 6′ | 6.86 (1H, dd, 2.1, 8.2) | 6.86 (1H, dd, 2.1, 8.2) | 6.85 (1H, dd, 2.0, 8.2) | 6.96 (1H, dd, 1.9, 7.9) | 7.37(1H, d, 8.7) |
| 7′ | 7.48 (1H, d, 15.9) | 7.47 (1H, d, 15.9) | 7.42 (1H, d, 15.9) | 7.52(1H, d, 15.9) | 7.52(1H, d, 15.9) |
| 8′ | 6.19 (1H, d, 15.9) | 6.18 (1H, d, 15.9) | 6.13 (1H, d, 15.9) | 6.25(1H, d, 15.9) | 6.22(1H, d, 15.9) |
| $OCH_3$ | | | 3.60 (3H, s) | 3.88 (3H, s) | 3.80 (3H, s) |

5-*O*-Caffeoylquinic acid (**15**), $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, *J*/Hz) see table 3. $^{13}$C-NMR (125 MHz, $CD_3OD$) 74.8(C-1), 36.8(C-2), 70.0(C-3), 72.1(C-4), 70.5(C-5), 37.4(C-6), 175.6(C-7), 126.4(C-1′), 113.8(C-2′), 145.3(C-3′), 148.1(C-4′), 115.1(C-5′), 121.6(C-6′), 145.7(C-7′), 113.8(C-8′), 167.3(C-9′).

3-*O*-Caffeoylquinic acid (**16**), $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, *J*/Hz) see table 3. $^{13}$C-NMR (125 MHz, $CD_3OD$) 72.0(C-1), 36.8(C-2), 70.1(C-3), 70.6(C-4), 69.9(C-5), 37.4(C-6), 175.6(C-7), 126.4(C-1′), 113.8(C-2′), 145.4(C-3′), 148.1(C-4′), 115.0(C-5′), 121.5(C-6′), 145.7(C-7′), 113.8(C-8′), 167.2(C-9′).

3-*O*-Caffeoylquinic acid methyl ester (**17**), (-)ESIMS, *m*/*z* 367.2286$[M-H]^-$. $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, *J*/Hz) see table 3.

5-*O*-Caffeoylquinic acid methyl ester (**18**), $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, *J*/Hz) see table 3.

5-*O*-Coumaroylquinic acid methyl ester (**19**), (-)ESIMS, *m*/*z* 337.2081$[M-H]^-$. $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, *J*/Hz) see table 3.

1,2,4-trigalloyl-β-D-glucose (**20**), $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz) see table 4.

1,3,4-trigalloyl-α-D-glucose (**21**), $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz) see table 4.

1,2,3,4,6-Pentagalloylglucose(**22**), (-)ESIMS, *m*/*z* 939.4211 $[M-H]^-$. $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, *J*/Hz) see table 4. $^{13}$C-NMR (125 MHz, $CD_3OD$), 109.2, 109.0, 109.0, 109.0, 108.9 (galloyl-C-2, 6),

 doi:10.20944/preprints201911.0354.v1



119.6, 118.9, 118.8, 118.8, 118.3 (galloyl-C-1), 139.3, 138.9, 138.9, 138.7, 138.6 (galloyl-C-4), 145.1, 145.0, 145.0, 144.9, 144.9 (galloyl-C-3, 5), 166.5, 165.9, 165.6, 165.5, 164.8 (galloyl-C-7), 92.4 (glu-C-1), 73.0 (glu-C-5), 72.7 (glu-C-3), 70.8 (glu-C-2), 68.4 (glu-C-4), 61.7 (glu-C-6).

1,2,4-trigalloyl-3,6-HHDP-*α*-D-glucose (**23**), $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz) see table 4.

2,3,4-trigalloyl-1,6-HHDP-*α*-D-glucose (**24**), (-)ESIMS, m/z 937.4019 [M-H]$^-$. $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz) see table 4.

**Table 4.** $^1$H-NMR ($^1$H-Nuclear Magnetic Resonance, 500 MHz, $CD_3OD$) characteristics of the galloyl tannins **20–24** isolated from fall sugar maple leaves.

| No. | 20 | 21 | 22 | 23 | 24 |
|---|---|---|---|---|---|
| | δH (J Hz) | δH (J Hz) | δH (J Hz) | δH (J Hz) | δH (J Hz) |
| **1** | 6.02(1H, d, 8.4) | 6.42(1H, d, 3.8) | 6.14(1H, d, 8.3) | 6.41(1H, d, 4.5) | 5.98(1H, d, 2.8) |
| 2 | 5.33(1H, dd, 8.4,9.6) | 4.10(1H, dd, 3.7,10.0) | 5.48(1H, dd, 8.4, 9.8) | 5.30(1H, d, 4.5) | 5.35(1H, dd, 2.8, 6.9) |
| 3 | 4.13(1H, t, 9.5) | 5.80(1H, t, 9.8) | 5.80(1H, t, 9.7) | 5.68(1H, d, 3.3) | 5.66(1H, t, 6.6) |
| 4 | 5.19(1H, t, 9.8) | 5.39(1H, t, 9.8) | 5.52(1H, t, 9.8) | 4.98(1H, d, 3.3) | 5.00(1H, dd, 2.4, 6.3) |
| 5 | 3.88(1H, m) | 3.90(1H, m) | 4.30(1H, m) | 4.61(1H, m) | 4.45(1H, m) |
| 6 | 3.70(1H, dd, 2.2,12.6)<br>3.61(1H, dd, 5.4,12.6) | 3.67(1H, dd, 2.2,12.5)<br>3.59(1H, dd, 4.7,12.5) | 4.41(1H, d, 10.6)<br>4.28(1H, m) | 4.32(2H, m) | 4.77(1H, d, 12.1)<br>4.28(1H, dd, 5.1,11.8) |
| 2′6′ | 7.12 (2H, s) | 7.23 (2H, s) | 7.02(2H, s) | 7.04(2H, s) | 6.98(2H, s) |
| 2″6″ | 7.05 (2H, s) | 7.03 (2H, s) | 6.96 (2H, s) | 7.00 (2H, s) | 6.97 (2H, s) |
| 2‴6‴ | 7.03 (2H, s) | 6.97 (2H, s) | 6.88(2H, s) | 6.97(2H, s) | 6.93(2H, s) |
| 2⁗/6⁗ | | | 6.85 (2H, s) | 6.82 (1H, s) | 6.69 (1H, s) |
| 2⁗′/6⁗′ | | | 6.80 (2H, s) | 6.67 (1H, s) | 6.63 (1H, s) |

11,12-dimethyl-chebulate (**25**), (-)ESIMS, m/z 383.1908 [M-H]$^-$. $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz): 6.94 (1H, s, H-8), 5.24(1H, d, J =1.2 Hz, H-3), 3.79(1H, dd, J =9.3, 1.2 Hz, H-4), 3.08 (1H, m, H-9), 2.72 (1H, dd, J =17.0, 8.8 Hz, H-10), 2.37 (1H, d, J = 17.0, 5.7 Hz, H-10), 3.53, 3.42(6H, s, 11,12 OCH3). 175.0(C-13), 172.3(C-11), 169.8(C-12), 164.8(C-1), 145.4(C-7), 142.6(C-5), 139.3(C-6), 116.0(C-4a), 114.7(C-8a), 107.8(C-8), 77.4(C-3), 51.9, 50.7(11,12 OCH3), 43.5(C-9), 35.6(C-4), 33.6(C-10).

12,13-dimethyl-chebulate (**26**), (-)ESIMS, m/z 383.1938 [M-H]$^-$. $^1$H-NMR (500 MHz, $CD_3OD$, δ, ppm, J/Hz): 6.94 (1H, s, H-8), 5.17(1H, d, J =1.1 Hz, H-3), 3.74(1H, dd, J =7.1, 1.1 Hz, H-4), 3.09 (1H, m, H-9), 2.77 (1H, dd, J =17.2, 10.7 Hz, H-10), 2.35 (1H, d, J = 17.2, 4.4 Hz, H-10), 3.57, 3.53(6H, s, 12,13 OCH3). 173.7(C-13), 173.7(C-11), 169.9(C-12), 164.7(C-1), 145.5(C-7), 142.4(C-5), 139.4(C-6), 116.1(C-4a), 114.6(C-8a), 107.6(C-8), 77.0(C-3), 51.9, 51.3(12,13 OCH3), 43.8(C-9), 35.9(C-4), 33.5(C-10).

protocatechuic acid (**27**), (-)ESIMS, *m/z* 153.0874 [M-H]$^-$. $^1$H-NMR (500 MHz, $CD_3OD$) δ 7.34(1H, s, H-2), 7.32(1H, dd, *J*=2.1, H-6), 6.69(1H, d, *J*=7.9, H-5). $^{13}$C-NMR (125 MHz, $CD_3OD$) δ 116.3 (C-5), 114.3 (C-2), 121.7 (C-1), 122.5 (C-6), 144.6 (C-3), 150.1 (C-4) 168.7 (C-7).

methyl gallate (**28**), (-)ESIMS, *m/z* 183.0099 [M-H]$^-$. $^1$H-NMR (500 MHz, $CD_3OD$), 6.94(2H, s, H-2,6), 3.72(3H, s, $OCH_3$). $^{13}$C-NMR (125 MHz, $CD_3OD$) δ 108.6(C-2, 6), 120.0(C-1), 138.3(C-4), 145.1(C-3, 5), 167.6(C-7), 50.8 (CO**OCH**$_3$)

**Supplementary Materials:** The following are available online at www.mdpi.com/xxx/s1, Figure S1: An HPLC-DAD profile of the ethyl acetate extract of sugar maple leaves and the isolates compounds. Figure S2: Extraction and isolation flow chart of compounds **1–28** from sugar maple leaves.

**Author Contributions:** conceptualization, C.W.; methodology, C.W.; validation, L.Y.; S.Z.; formal analysis, C.W.; investigation, C.W.; data curation, W.P.; C.C.; Y.Y.; and C.W.; writing—original draft preparation, L.Y.; S.Z.; writing—review and editing, C.W.; supervision, project administration, and funding acquisition, C.W.

**Funding:** This research was funded by China Scholarship Council funding for Chunpeng Wan, grant number 201408360027 and The APC was funded by Natural Science Foundation in Jiangxi Province (20181BCB24005).

**Acknowledgments:** The authors would like to thank Mr. J. Peter Morgan (Senior Gardener, College of Pharmacy, University of Rhode Island, Kingston, Rhode Island, USA) for assistance with plant authentication.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Wan, C.; Yuan, T.; Xie, M.; Seeram, N.P. Acer rubrum phenolics include A-type procyanidins and a chalcone. *Biochem. System. Ecol.*, **2012**, 44, 1-3.
2. Liu, W.; Ouyang, Y.; Wan, C.P. Flavonoids of the Genus of Acer. *Asian J. Chem.*, **2013**, *25*, 7075-7078.
3. Bi, W.; Gao, Y.; Shen, J.; He, C.; Liu, H.; Peng, Y.; Zhang, C.; Xiao, P. Traditional uses, phytochemistry, and pharmacology of the genus Acer (maple): a review. *J. Ethnopharmacol*., **2016**, *189*, 31-60.
4. Yonezawa, T.; Lee, J. W.; Akazawa, H.; Inagaki, M.; Cha, B. Y.; Nagai, K.; Woo, J. T. Osteogenic activity of diphenyl ether-type cyclic diarylheptanoids derived from Acer nikoense. *Bioorg. Med. Chem. Lett.*, **2011**, *21*, 3248-3251.
5. Tung, N.H.; Ding, Y.; Kim, S.K.; Bae, K.; Kim, Y.H. Total peroxyl radical-scavenging capacity of the chemical components from the stems of *Acer tegmentosum* maxim. *J. Agri. Food Chem*., **2008**, *56*, 10510-10514.
6. Morikawa, T.; Tao, J.; Ueda, K.; Matsuda, H.; Yoshikawa, M.. Medicinal foodstuffs. XXXI. Structures of new aromatic constituents and inhibitors of degranulation in RBL-2H3 cells from a Japanese folk medicine, the stem bark of Acer nikoense. *Chem. Pharm. Bull*., **2003**, *51*, 62-67.
7. Yuan, T.; Wan, C.; González-Sarrías, A.; Kandhi, V.; Cech, N. B.; Seeram, N. P. Phenolic glycosides from sugar maple (Acer saccharum) bark. *J. Nat. Prod*., **2011**, *74*, 2472-2476.
8. Yoshikawa, K.; Kawahara, Y.; Arihara, S.; Hashimoto, T. Aromatic compounds and their antioxidant activity of Acer saccharum. *J. Nat. Med*., **2011**, *65*, 191-193.
9. St-Pierre, F.; Achim, A.; Stevanovic, T. Composition of ethanolic extracts of wood and bark from Acer saccharum and Betula alleghaniensis trees of different vigor classes. *Ind. Crop. Prod.*, **2013**, *41*, 179-187.
10. Bhatta, S.; Ratti, C.; Poubelle, P. E.; Stevanovic, T. Nutrients, antioxidant capacity and safety of hot water extract from sugar maple (Acer saccharum M.) and red maple (Acer rubrum L.) bark. *Plant Foods Hum. Nutr*., **2018**, *73*, 25-33.
11. Honma, A.; Koyama, T.; Yazawa, K. Anti-hyperglycemic effects of sugar maple Acer saccharum and its constituent acertannin. *Food Chem*., **2010**, *123*, 390-394.
12. Wan, C.; Yuan, T.; Cirello, A. L.; Seeram, N. P. Antioxidant and α-glucosidase inhibitory phenolics isolated from highbush blueberry flowers. *Food Chem*., **2012**, *135*, 1929-1937.
13. Kumaran, A.; Karunakaran, R.J. Activity-guided isolation and identification of free radical-scavenging components from an aqueous extract of Coleus aromaticus. *Food Chem*., **2007**, *100*, 356-361.
14. Carvalho, A.A.; Santos, L.R.D.; Farias, R.R.S.D.; Chaves, M.H.; Feitosa, C.M.; Vieira Júnior, G.M.; Pessoa, C.D.Ó. Phenolic derivatives and antioxidant activity of polar extracts from Bauhinia pulchella. Quí*mica Nova*, **2018**, *41*, 405-411.
15. Isobe, T.; Kanazawa, K.; Fujimura, M.; Noda, Y. Flavonoids of Polygonum sieboldi and P. filiforme. B. Chem. Soc. JPN., **1981,** *54*, 3239-3239.
16. Lin, W.H.; Deng, Z.W.; Lei, H.M.; Fu, H.Z.; Li, J. Polyphenolic compounds from the leaves of Koelreuteria paniculata Laxm. *J. Asian. Nat. Prod. Res*., **2002,** *4*, 287-295.
17. Collins, F.W.; Bohm, B.A.; Wilkins, C.K. Flavonol glycoside gallates from Tellima grandiflora. *Phytochemistry*, **1975**, *14*, 1099-1102.
18. Liu, Y.Z.; Wang, C.F.; Zhang, Z.Z. Studies on chemical constituents of Chamaenerion angustifolium I. Flavonoids from Chamaenerion angustifolium. *Chinese Traditional and Herbal Drugs*, **2002**, *33*, 289-290.
19. Mendez, J.; Bilia, A.R.; Morelli, I. Phytochemical investigations of Licania genus. Flavonoids and triterpenoids from Licania pittieri. *Pharm. Acta. Helv*., **1995**, *70*, 223-226.
20. Kwon, D.J.; Bae, Y.S. Chemical constituents from the stem bark of Acer barbinerve. *Chem. Nat. Compd*, **2011**, *47*, 636–638.
21. Li, Q.; Shen, Y.; Li, P. Study on Five Flavanoids in Barks of Quercus pannosa Hand.-Mazz. *Chinese Pharmaceutical Journal*, **2008**, *43*, 336-338.
22. Wan, C.; Li, S.; Liu, L.; Chen, C.; Fan, S. Caffeoylquinic Acids from the Aerial Parts of Chrysanthemum coronarium L. *Plants*, 2017, *6*, 10.

23. Chan, E.W.C.; Lim, Y.Y.; Ling, S.K.; Tan, S.P.; Lim, K.K.; Khoo, M.G. Caffeoylquinic acids from leaves of Etlingera species (Zingiberaceae). LWT-*Food Sci. Tech*., **2009**, *42*, 1026-1030.
24. Hussein, S.A.; Barakat, H.H.; Merfort, I.; Nawwar, M.A. Tannins from the leaves of Punica granatum. *Phytochemistry*, **1997**, *45*, 819-823.
25. Sugimoto, K.; Nakagawa, K.; Hayashi, S.; Amakura, Y.; Yoshimura, M.; Yoshida, T.; Yamaji, R.; NakaNo, Y.; Inui, H. Hydrolyzable tannins as antioxidants in the leaf extract of Eucalyptus globulus possessing tyrosinase and hyaluronidase inhibitory activities. *Food Sci. Tech. Res*., **2009**, *15*, 331-336.
26. Zhu, K.; Wang, Z., Li, C., Li, J., Xiao, W. Chemical constituents of Guizhi Fuling Capsula (II). *Chinese Traditional and Herbal Drugs*, **2011**, *42*, 1087-1089.
27. Tanaka, T.; Nonaka, G. I.; Nishioka, I. Punicafolin, an ellagitannin from the leaves of Punica granatum. *Phytochemistry*, **1985**, *24*, 2075-2078.
28. Hatano, T.; Hattori, S.; Ikeda, Y.; Shingu, T.; Okuda, T. Gallotannins having a 1, 5-anhydro-D-glucitol core and some ellagitannins from Acer species. *Chem. Pharm. Bull*., **1990**, 38, 1902-1905.
29. Li, X.; Wang, Y.; Wang, H.; Shi, Y.; Long, C. Phenolic derivatives from the leaves of Dipteronia dyeriana. *Tianran Chanwu Yanjiu Yu Kaifa*, **2010**, *22*, 5-10.
30. Wang, XS; Che, QM; Li, YM; He, Y. A StudyonChemical Constituents in Seeds of Crataegus pinnatifida Bge.var.major N.E.Br. *China Journal of Chinese Material Medicine*, **1999**, *24*, 739-740.
31. Cai, B.; Wang, B.; Liang, H.; Zhao, Y. Chemical constituents from roots of Distylium myricoides. *Zhongguo Zhong Yao Za Zhi* **2009**, *34*, 2331.
32. Fowden L, Pratt H M. Cyclopropylamino acids of the genus Acer: distribution and biosynthesis. Phytochemistry, **1973**, *12*, 1677-1681.
33. Ji, S.B.; Yokoi, M.; Saito, N, Mao, L.S. Distribution of anthocyanins in Aceraceae leaves. *Biochem. System. Ecol*., **1992**, *20*, 771-781.
34. Zhang, L.; Tu, Z.C.; Yuan, T.; Ma, H.; Niesen, D.B.; Wang, H.; Seeram, N.P. New gallotannin and other phytochemicals from sycamore maple (Acer pseudoplatanus) leaves. *Nat. Prod. Com*., **2015**, *10*, 1977-1980.
35. Lien, E.J.; Ren, S.; Bui, H.H.; Wang, R. Quantitative structure-activity relationship analysis of phenolic antioxidants. *Free Rad. Bio. Med*., **1999**, *26*, 285-294.
36. Wan, C.; Yuan, T.; Li, L.; Kandhi, V.; Cech, N.B.; Xie, M.; Seeram, N.P. Maplexins, new $\alpha$-glucosidase inhibitors from red maple (Acer rubrum) stems. *Bioorg. Med. Chem. Lett*., **2012**, *22*, 597-600.