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Phenolic Compounds from the Branches of *Malus sieboldii* (Regel) Rehder and Their Antioxidative Activities

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Malus is a genus of about 35-50 species of deciduous woody plants in the family Roseaceae that includes apple (*M. pumila*), a common orchard fruit. The species *M. sieboldii* (Regel) Rehder is a shrub 2-6 m tall native to Japan and Korea.¹ This plant has been used as an ornamental tree for its showy flowers in the spring. The extracts from the leaves of *M. sieboldii* have been reported to exhibit scavenging activities on 2,2-diphenyl-1-picrylhydrazyl (DPPH) radicals² and inhibition activities on nitric oxide production.³ However, as far as we know, no phytochemical study on *M. sieboldii* has yet been published.

Antioxidants exert protective effects in human health against oxidative damage associated with reactive oxygen species (ROS). ROS are chemically reactive substances that can attack lipids, proteins and nucleic acids within living organisms. ROS include free radicals (O2.-, HO., RO. and ROO^{\cdot}) and neutral molecules (¹O₂ and H₂O₂). Even though ROS generation is a normal metabolic process,⁴ its excessive formation can cause peroxidation in human tissues, ultimately leading to various diseases related with aging.⁵ When the skin is exposed to ultraviolet (UV) rays, ROS are generated in excess to induce aged-skin symptom such as wrinkles. In order to reduce the cumulative effects of ROS-related damage, the addition of antioxidants to food or cosmetic formulations has been considered.⁶ The development of novel antioxidative agents, especially from natural sources, has attracted attention in terms of their ecologically friendly properties.⁷

We are continuously conducting studies to find biologically active natural products, especially for use in cosmetic formulations from plants in Jeju Island, a place of great biodiversity in Korea.⁸ Preliminary study indicated that the ethanol extract prepared from the branches of *Malus sieboldii* exhibited significant DPPH radical scavenging activities. Therefore, we decided to carry out a full phytochemical investigation of the *M. sieboldii* extract to determine the bioactive metabolites. Described herein are the isolation and structural determination of the chemical constituents in the plant extract. In addition, the antioxidative properties of the isolates were examined using the DPPH and ABTS⁺ radical scavenging activity tests.

The ethanol extract (147.4 g) was prepared from the branches of *M. sieboldii* (1.0 kg) with a 14.7% yield. The extract suspended in water was partitioned successively to provide *n*-hexane, ethyl acetate (EtOAc), and *n*-butanol fractions. The extract and fractions were then tested for their anti-oxidative capacities using DPPH radical scavenging assay first reported by Blois.⁹ Ascorbic acid showing an SC₅₀ (50% radical scavenging concentration) value of 7.1 µg/mL was used as a positive control in this experiment.

As shown in *Table* 1, the ethanol extract exhibited considerable anti-oxidative activity with an SC₅₀ value of 40.3 µg/mL. Among the solvent fractions, the EtOAc soluble layer displayed the highest potency with SC₅₀ of 18.3 µg/mL. The *n*-butanol fraction also exhibited considerable activity, whereas the *n*-hexane and water portions showed very poor antioxidative activities. As another method to determine the *in vitro* anti-oxidation capacities for the extracts, an assay using ABTS [2,2'-azino-bis(3-ethylbenzothiazo-line-6-sulfonic acid)] was used.¹⁰ ABTS is a chemical that can be oxidized by persulfate to yield an ABTS radical

Table 1. DPPH and $ABTS^+$ radical scavenging activities (SC₅₀) of the solvent fractions

Fractions	DPPH SC50 (µg/mL)	$ABTS^+ SC_{50}(\mu g/mL)$
Extract	40.3	4.8
<i>n</i> -Hexane	> 100	37.2
Ethyl acetate	18.3	2.4
n-Butanol	19.6	4.3
Water	> 100	23.8
Ascorbic acid	7.1	2.1

cation (ABTS⁺) featuring a characteristic blue green color in solution. In the presence of antioxidants such as phenolic compounds, this radical cation is converted back to its colorless non-radical form, which can be monitored by a spectrophotometer. After assaying the ethanol extract and solvent fractions from *M. sieboldii*, the ethanol extract, as well as EtOAc and *n*-butanol fractions, exhibited very strong radical scavenging activities (*Table* 1). The activity of the EtOAc fraction was comparable to that of the positive control, ascorbic acid.

Polyphenol compounds such as tannins and flavonoids are found in virtually all plant families. Polyphenols function as natural antioxidants via the scavenging of reactive oxygen species. As the solvent fractions from M. sieboldii exhibited DPPH radical inhibition activities, the total polyphenolic contents were measured for their extract and fractions (Fig. 1). The amount of total phenols was quantified by colorimetric measurement using the Folin-Ciocalteu (FC) assay,¹¹ which measures the change in color from yellow of the FC reagent to dark blue in the presence of antioxidant samples. The gallic acid equivalent (GAE) per 100 mg sample was calculated based on the calibration curve. As shown in Fig. 1, the ethanol extract was found to have 19.1 mg GAE polyphenols. Comparing the solvent fractions, the EtOAc fraction exhibited the highest polyphenol concentration with 45.3 mg GAE.

As the EtOAc-soluble layer showed the highest radical scavenging activities and polyphenol contents, it was chosen for further fractionation to identify the active constituents. The EtOAc fraction was subjected to vacuum liquid chromatography with gradients of *n*-hexane/EtOAc followed by EtOAc/methanol to provide 37 fractions. Each fraction was purified by repeated column chromatography with silica gel or Sephadex LH-20, leading to the isolation of seven compounds (1-7) (*Fig.* 2). The chemical structures of the isolates were characterized by spectro-



Figure **1.** Total polyphenol contents for the fractions from *M. sieboldii.*



Figure 2. Structures of compounds isolated from M. sieboldii.

scopic data including 1D and 2D NMR spectra.

Compound 1 showed 15 signals in its ¹³C NMR spectrum, where twelve olefinic carbons and two oxygen-bearing sp^3 carbons were easily identified. The presence of aromatic rings was also suggested by analysis of ¹H and DEPT NMR signals. Diastereotopic methylene proton (H₂-4) signals appeared at δ 2.73 and 2.86 with a large coupling constant (J=16.7). Based on other spectroscopic data, compound **1** was verified as epi-catechin, a phenolic compound commonly found in plant species.¹² Compound 2 was estimated to possess 20 carbons according to ¹³C and DEPT NMR spectra. The data indicated that it contains $15 sp^2$ carbons, including one carbonyl (& 179.9 ppm) and five oxygenbearing sp³ carbons. In the ¹H NMR spectrum, the *meta*coupled protons (H-5 and H-7) appeared at δ 6.16 and 6.35 with J = 2.1. In addition, ABX spin system was observed for H-2', H-5' and H-6'. The signal of H-5' (δ 6.89) showed an ortho-coupling to H-6' (δ 7.48) with ³J = 8.3 Hz. The signal of H-6' exhibited meta- as well as ortho-coupling to H-2' (δ 7.52) with ⁴J = 2.1 Hz. The 15 sp² carbons and the corresponding proton signals in 2 suggested a skeleton comprised of a flavonol, quercetin. A pentose attached to the quercetin was surmised as arabinose with α -configuration, as determined by its coupling constant (J=3.0 Hz) of the anomeric proton (H-1", δ 5.45). Compound 2 was, therefore, identified as quercetin 3-O- α -arabinofuranoside.¹³ Compound 3 showed 18 signals, including $15 sp^2$ carbons and six oxygen-bearing sp^3 carbons, in the ¹³C and DEPT spectra. The NMR study revealed that the B ring of quercetin was appeared in the structure of 3. In addition, the arabinose unit shown in 2 was also detected in 3. Comparative analysis of the spectra of 2 and 3 suggested that 3 has one additional methoxy group ($\delta_c 62.0$) attached in the A ring of compound 2. The methoxy group was assigned by the observation of the heteronuclear multiple bond correlation (HMBC) cross peak between 8-OCH₃ ($\delta_{\rm H}$ 3.88) and C-8 ($\delta_{\rm C}$ 129.5). Therefore, compound **3** was identified as 8-methoxyquercetin 3-O- α -arabinofuranoside. Although, the structure of flavonol glycoside 3 has been identified from a plant Dryas octopetala,¹⁴ as far as we know, its carbon NMR data has not been published. In this study, we completely assigned the proton and carbon peaks for 3 using 1D and 2D NMR spectra. Compound 4 showed 19 peaks in the ¹³C NMR spectrum, corresponding to one carbonyl (δ 206.6, C-9), three methylene (δ 62.6, 48.7, 30.9) and five oxygenated methine carbons. Inspection of ¹H NMR determined the para-substituted symmetric benzene ring with signals at δ 6.52 (2H, d, J = 8.5 Hz) and 6.90 (2H, d, J= 8.5 Hz). In addition, meta-coupled protons at d 6.02 (H-3') and 5.79 (H-5') with J = 2.3 Hz were also assigned in another benzene ring. The presence of a sugar glucose was revealed by the ¹H and ¹³C NMR spectra. Combination of the observation data enabled compound 4 to be identified as phlorizin (phloretin 2'-O-β-D-glucopyranose).¹⁵ Compound 5 showed very similar ¹H and ¹³C signals in the NMR spectra to those of compound 4. The only difference observed was that the symmetry of a benzene ring in 4 disappeared in compound 5. It was suggested that compound 5 has an additional hydroxyl group in the aromatic ring at C-3. Compound 5 was identified as 3-hydroxyphlorizin.¹⁶ Examination of the NMR spectra revealed compound 6 to be comprised of a skeleton of quercetin, as observed in 2. The presence of an additional sugar unit, glucose, was suggested in 6 by the observation of peaks for anomeric proton ($\delta_{\rm H}$ 4.91) and carbon ($\delta_{\rm C}$ 104.0), along with oxygenated methylene and methynes. The β -configuration of the glucose was established by the coupling constant (J = 7.3 Hz) of the anomeric proton. The position of the sugar was determined at C-4' by comparison of the NMR data to the literature values. Thus, compound 6 was identified as quercetin 4'-O- β -Dglucopyranoside.¹⁷ Inspection of the NMR data indicated that compound 7 is also a glycoside bearing a glucose unit. In the ¹³C NMR spectrum, the aglycone has 13 peaks, all of which are sp^2 carbons. A carbonyl peak appeared at d 183.1 (C-4). A phenyl group was identified by proton peaks at d 7.89 (2H, H-2', H-6'), 7.44 (2H, H-3', H-5') and 7.51 (1H, H-4'). Meta-coupled aromatic protons were observed at δ 7.01 (1H, H-6) and 6.87 (1H, H-8) with J = 1.2 Hz. A

singlet proton was observed at δ 7.13 (1H, H-3). Based on these data, along with the ¹³C NMR data, the compound was determined as chrysin glycoside, chrysin 7-*O*- β -D-gluco-pyranoside.¹⁸

The antioxidative activities were examined for the isolated compounds 1-7 utilizing DPPH and ABTS radical scavenge methods. DPPH is a relatively stable radical species bearing a characteristic deep violet color in solution, and radical scavenging activity can be determined by a loss of DPPH absorbance at 515 nm. The inhibition activities for the isolated compounds were measured at their concentrations of 3.0-100 µg/mL, and the results are summarized in Table 2. These activities were expressed as SC₅₀, i.e., the concentration needed to reduce 50% of DPPH, and compared to ascorbic acid as a positive control (SC₅₀ 54.2 µM). Among the isolates, quercetin 3-Oarabinoside (2) was determined to possess the highest free radical scavenging activity with SC_{50} of 39.7 μ M, showing more potency than the positive control. The epi-catechin (1) and 8-methoxyquercetin glycoside (3) also exhibited strong inhibition activities with SC₅₀ values of 54.2 and 54.7 µM, respectively. ABTS assay was used as an alternative method to measure the antioxidative capacities for the isolated compounds and the results are summarized in Table 2. In this test, except compound 7, the remaining six compounds (1-6) were very strong scavengers against ABTS radicals. Compared to ascorbic acid (SC₅₀ 13.4 µM), isolates 1-6 had more potent activities with SC₅₀ values below 11.2 M. Phlorizin (4) showed the most potent inhibition activity against ABTS radical, despite its relatively low activity on DPPH radical (see Table 2).

In conclusion, seven phenolic compounds were identified from the ethanol extracts of *M. sieboldii* branches: *epi*-cathechin (1), quercetin 3-O- α -arabinofuranoside (2), 8-methoxyquercetin 3-O- α -arabinofuranoside (3), phlorizin (4), 3-hydroxyphlorizin (5), quercetin 4'-O- β -D-glucopyranoside (6) and chrysin 7-O- β -D-glucopyranoside

Table 2. SC_{50} values of DPPH and $ABTS^+$ radical scavenging activities of compounds 1-7 isolated from *M. sieboldii*

Compounds	DPPH SC50 (µM/mL)	$ABTS^+SC_{50}(\mu M/mL)$
1	54.2	5.1
2	39.7	6.8
3	54.7	7.0
4	173.7	3.9
5	72.4	9.5
6	126.9	11.2
7	>240	129.9
Ascorbic acid	54.2	13.4

(7). All seven compounds were isolated for the first time from this woody plant. Among the isolates, quercetin glycoside **2** showed the most potent DPPH free radical scavenging activity with an SC₅₀ value of 39.7 μ M, where ascorbic acid (SC₅₀ 54.2 μ M) was used as a positive control. In the study of ABTS⁺ radical scavenging assay, compounds **1-6** possessed more potency than ascorbic acid (SC₅₀ 13.4 μ M). Based on these results, *M. sieboldii* extracts are expected to be useful antioxidative agents with potential applications in food and cosmetic industries.

EXPERIMENTAL

Reagents and instruments

The chemical reagents 2,2-diphenyl-1-picrylhydrazyl (DPPH) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) were purchased from Aldrich. All solvents used were of analytical grade. A Biochrom Libra S22 UV-visible spectrophotometer was used to screen the radical inhibition activities. ¹H (400 MHz) and ¹³C (100.6 MHz) nuclear magnetic resonance (NMR) spectra were recorded on a JNM-LA 400 instrument (JEOL) with chemical shift (d) data in ppm relative to the solvent used. Merck silica gel (0.063-0.2 mm) was used for normal phased column chromatography. Silica gel 60 F₂₅₄ coated on aluminum plates by Merck was used for thin layer chromatography (TLC). Gel filtration chromatography (GFC) was performed using Sephadex LH-20 (25-100 mm) from Fluka.

Plant material

The branches of *M. sieboldii* were collected in November 2010 from Halla Botanical Garden in Jeju Island, Korea. A voucher specimen (sample number 317) was deposited at the herbarium of the Department of Chemistry, Jeju National University.

Extraction and isolation

The shade dried *M. sieboldii* branches (1.0 kg) were cut into small pieces, and extracted with 70% ethanol (20 L) two times at room temperature for 24 h. The gummy extract (147.4 g) was obtained after concentration of the filtered solution. Part of the ethanol extract (30.0 g) was suspended in water (1.0 L), and fractionated into *n*-hexane (1.0 g), ethyl acetate (9.4 g), *n*-butanol (7.0 g) and water (10.6 g) portions. A portion (4.5 g) of the ethyl acetate (EtOAc) layer was subjected to vacuum liquid chromatography (VLC) on silica gel, using step-gradients (*n*-hexane/EtOAc to EtOAc/MeOH, 300 mL each) to provide 37 fractions (V1-V37). Fraction V15 was purified by silica gel column chromatography (CC) using CHCl₃-MeOH (3:1) eluent to afford compound 1 (18.8 mg). Fraction V23 (1.0 g) was column chromatographed over Sephadex LH-20 using CHCl₃-EtOAc-MeOH (2:2:1) to give 12 subfractions (V-23-1 to V23-12), and V-23-4 was identified to be compound 3 (24.0 mg). Fraction V-23-7 was purified over Sephadex LH-20 using CHCl3-EtOAc-MeOH-H₂O (2:2:1:0.2) to give compounds 2(1.2 mg)and 4 (8.9 mg). Compound 7 (77.1 mg) was obtained by recrystallization over MeOH from fraction V24. The MeOHsoluble V24 fraction (V24-M, 1.3 g) was subjected to VLC on silica gel using CHCl3-MeOH (100:0 to 50:50, step-gradients, 300 mL each) to provide five fractions (V24-M1 to V24-M5). Fraction V24-M4 was purified over Sephadex LH-20 using CHCl₃-EtOAc-MeOH-H₂O (2:2:1:0.2) to give compound 5 (42.0 mg). Fraction V24-M5 was recrystallized over MeOH to afford compound 6 (104.2 mg).

Compound 1: ¹H NMR (400 MHz, CD₃OD) δ 6.97 (1H, d, *J* = 1.8 Hz, H-2'), 6.80 (1H, dd, *J* = 8.2, 1.8 Hz, H-5'), 6.75 (1H, d, *J* = 8.2 Hz, H-6'), 5.94 (1H, d, *J* = 2.3 Hz, H-6), 5.91 (1H, d, *J* = 2.3 Hz), 8.81 (1H, brs, H-2), 4.17 (1H, m, H-3), 2.86 (1H, dd, *J* = 16.7, 4.6 Hz, H-4), 2.73 (1H, dd, *J* = 16.7, 2.8 Hz, H-4); ¹³C NMR (100 MHz, CD₃OD) δ 158.1 (C-5), 157.7 (C-7), 157.7 (C-9), 146.0 (C-3'), 145.8 (C-4'), 132.4 (C-1'), 119.5 (C-6'), 116.0 (C-5'), 115.4 (C-2'), 100.1 (C-10), 96.4 (C-8), 96.0 (C-6), 79.9 (C-2), 67.6 (C-3), 29.4 (C-4).

Compound **2**: ¹H NMR (400 MHz, CD₃OD) δ 7.52 (1H, d, *J* = 2.1 Hz, H-2'), 7.48 (1H, dd, *J* = 8.3, 2.1 Hz, H-6'), 6.89 (1H, d, *J* = 8.3 Hz, H-5'), 6.35 (1H, d, *J* = 2.1 Hz, H-8), 6.17 (1H, d, *J* = 2.1 Hz, H-6), 5.45 (1H, d, *J* = 3.0, H-1"), 4.32 (1H, dd, *J* = 3.0, 0.9 Hz, H-2"), 3.89–3.91 (2H, m, H-3", H-4"), 3.50 (2H, m, H-5"). ¹³C NMR (100 MHz, CD₃OD) δ 179.9 (C-4), 167.8 (C-7), 163.1 (C-5), 159.2 (C-9), 158.8 (C-2), 150.1 (C-4'), 146.5 (C-3'), 134.8 (C-3), 123.2 (C-6'), 123.0 (C-1'), 116.8 (C-2'), 116.5 (C-5'), 109.5 (C-1"), 105.2 (C-10), 100.5 (C-6), 95.2 (C-8), 88.1 (C-4"), 83.4 (C-2"), 78.8 (C-3"), 62.6 (C-5").

Compound **3**: ¹H NMR (400 MHz, CD₃OD) δ 7.59 (1H, d, *J* = 2.1 Hz, H-2'), 7.56 (1H, dd, *J* = 8.3, 2.1 Hz, H-6'), 6.94 (1H, d, *J* = 8.3 Hz, H-5'), 6.23 (1H, s, H-6), 5.48 (1H, d, *J* = 3.0 Hz, H-1"), 4.34 (1H, dd, *J* = 3.0, 0.9 Hz, H-2"), 3.89–3.92 (2H, m, H-3", H-4"), 3.88 (3H, s, 8-OCH₃), 3.52 (2H, m, H-5"). ¹³C NMR (100 MHz, CD₃OD) δ 180.0 (C-4), 160.3 (C-5), 159.0 (C-2), 158.1 (C-7), 150.6 (C-9), 150.1 (C-4'), 146.5 (C-3'), 134.9 (C-3), 129.5 (C-8), 123.3 (C-1'), 123.1 (C-6'), 116.8 (C-2'), 116.6 (C-5'), 109.6 (C-1"), 105.1 (C-10), 100.7 (C-6), 88.3 (C-2"), 88.2 (C-4"), 78.8 (C-3"), 62.6 (C-5"), 62.0 (8-OCH₃).

Compound 4: ¹H NMR (400 MHz, CD₃OD) δ 6.90 (2H,

d, J = 8.5 Hz, H-2 & H-6), 6.52 (2H, d, J = 8.5 Hz, H-3 & H-5), 6.02 (1H, d, J = 2.3 Hz, H-3'), 5.79 (1H, d, J = 2.3 Hz, H-5'), 5.03 (1H, d, J = 7.3 Hz, H-1"), 3.73 (1H, m, H-8), 3.56 (1H, dd, J = 12.0, 5.8 Hz, H-8), 3.23–3.31 (6H, m, H-2", H-3", H-4", H-5", H-6"). ¹³C NMR (100 MHz, CD₃OD) & 206.6 (C-9), 167.7 (C-6'), 166.3 (C-4'), 162.4 (C-2'), 156.4 (C-4), 134.0 (C-1), 130.5 (C-2 & C-6), 116.2 (C-3 & C-5), 106.8 (C-1'), 102.1 (C-1"), 98.5 (C-5"), 95.7 (C-3'), 78.6 (C-3"), 78.5 (C-5"), 74.8 (C-2"), 71.2 (C-4"), 62.5 (C-6"), 48.7 (C-8), 30.9 (C-7).

Compound **5**: ¹H NMR (400 MHz, CD₃OD) δ 6.69 (1H, d, *J* = 2.0 Hz, H-2), 6.62 (2H, d, *J* = 8.0 Hz, H-5), 6.56 (1H, d, *J* = 8.0, 2.0 Hz, H-6), 6.17 (1H, d, *J* = 2.1 Hz, H-3'), 5.95 (1H, d, *J* = 2.1 Hz, H-5'), 5.05 (1H, d, *J* = 7.3 Hz, H-1"), 3.91 (1H, dd, *J* = 9.5, 2.0 Hz, H-6"), 3.57 (1H, dd, *J* = 9.5, 5.3 Hz, H-6"), 3.44 (2H, m, H-8), 3.24–3.33 (4H, m, H-2", H-3", H-4", H-5"). ¹³C NMR (100 MHz, CD₃OD) δ 206.6 (C-9), 167.7 (C-6'), 166.2 (C-6'), 162.4 (C-2'), 146.1 (C-4), 144.3 (C-3), 134.8 (C-1), 120.8 (C-6), 116.7 (C-5), 116.4 (C-2), 106.8 (C-1'), 102.1 (C-1"), 98.5 (C-5'), 95.5 (C-3'), 78.6 (C-5"), 78.5 (C-3"), 74.8 (C-2"), 71.9 (C-4"), 62.5 (C-6"), 48.5 (C-8), 31.2 (C-7).

Compound **6**: ¹H NMR (400 MHz, pyridine- d_5) δ 7.70 (1H, d, J = 2.0 Hz, H-2'), 7.62 (1H, dd, J = 8.7, 2.0 Hz, H-6'), 7.23 (1H, d, J = 8.7 Hz, H-5'), 6.31 (1H, d, J = 1.8 Hz, H-8), 6.14 (1H, d, J = 1.8 Hz, H-6), 4.91 (1H, d, J = 7.3 Hz, H-1''), 3.94 (1H, dd, J = 12.0, 1.8 Hz, H-6''), 3.76 (1H, J = 12.0, 5.1 Hz, H-6''), 3.45–3.57 (4H, m, H-2'', H-3'', H-4'', H-5''). ¹³C NMR (100 MHz, pyridine- d_5) δ 178.0 (C-4), 166.2 (C-7), 162.9 (C-5), 158.0 (C-9), 149.4 (C-2), 148.6 (C-3'), 147.2 (C-4'), 139.1 (C-3), 128.0 (C-1'), 120.8 (C-6'), 118.3 (C-5'), 117.7 (C-2'), 105.0 (C-10), 104.0 (C-1''), 99.8 (C-6), 94.9 (C-8), 79.7 (C-5''), 79.0 (C-3''), 75.4 (C-2''), 71.6 (C-4''), 62.8 (C-6'').

Compound 7: ¹H NMR (400 MHz, pyridine- d_5) δ 7.89 (2H, d, J = 7.6 Hz, H-2', H-6'), 7.51 (1H, t, J = 7.3 Hz, H-4'), 7.44 (2H, dd, J = 7.6, 7.3 Hz, H-3', H-5'), 7.13 (1H, s, H-3), 7.01 (1H, brs, H-6), 6.87 (1H, brs, H-8), 5.88 (1H, d, J = 7.3 Hz, H-1"), 4.60 (1H, dd, J = 12.0, 1.8 Hz, H-6"), 4.43 (1H, dd, J = 12.0, 6.3 Hz, H-6"), 4.38 (1H, t, J = 8.5 Hz, H-3"), 4.38 (1H, t, J = 8.5 Hz, H-4"), 4.37 (1H, m, H-5"), 4.25 (1H, m, H-2"). ¹³C NMR (100 MHz, pyridine- d_5) δ 183.1 (C-4), 164.5 (C-2), 164.4 (C-7), 162.7 (C-5), 158.2 (C-9), 132.4 (C-4'), 131.7 (C-1'), 129.6 (C-3' & C-5'),

127.0 (C-2' & C-6'), 106.9 (C-10), 106.5 (C-3), 101.9 (C-1"), 101.1 (C-6), 95.6 (C-8), 79.4 (C-5"), 78.6 (C-3"), 75.0 (C-2"), 71.3 (C-4"), 62.5 (C-6").

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