Constituents of *Geranium thunbergii* Sieb. et Zucc. XV.[1] Modified Dehydroellagitannins, Geraniinic Acids B and C, and Phyllanthusiin F

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Three new hydrolyzable tannins, geraniinic acids B and C, and phyllanthusiin F, were isolated from the water-soluble portion of 70% aqueous acetone homogenate of the *Geranium thunbergii* leaves and their structures were determined by spectroscopic and chemical methods. These tannins are regarded as modified metabolites of geraniin, a major component of this plant. Phyllanthusiins, which are tannins characteristic of the *Phyllanthus* species of Euphorbiaceae, were also isolated from this plant.

Key words *Geranium thunbergii*; Geraniaceae; geraniinic acid B; geraniinic acid C; phyllanthusiin F; modified dehydroellagitannin

Geranium thunbergii Sieb et Zucc. (Geraniaceae), which is rich in tannins has long been used as a remedy for intestinal disorders in Japan. In the early investigation of the leaves of this plant, we isolated crystalline geraniin (**1**) as a major tannin constituent, and elucidated its unique structure from spectroscopic and chemical evidence,[2] which was very recently confirmed by X-ray crystallography.[3] Subsequent investigations of the leaves revealed the presence of three other dehydroellagitannins, furosinin, furosin and didehydrogeraniin.[1] These tannins are all regarded as the metabolites of geraniin. In addition, a notable ellagitannin, elaeocarpusin, which is a condensate of geraniin and ascorbic acid, was also obtained along with geraniinic acid A from the water-soluble portion of the extract.[4] Further investigation of the polar fraction of the leaves has resulted in the isolation of additional new modified dehydroellagitannins named geraniinic acid B (**2**), geraniinic acid C (**3**) and phyllanthusiin F (**6**), along with some known tannins. We report here the structural elucidation of those constituents.

A concentrated 70% aqueous acetone homogenate of the dried leaves of *G. thunbergii* was extracted with ether, ethyl acetate and *n*-BuOH. The water-soluble extract obtained after *n*-BuOH extraction was repeatedly chromatographed over Diaion HP-20 and MCI-gel CHP-20P with aqueous MeOH to afford geraniinic acid B (**2**) and geraniinic acid C (**3**), and phyllanthusiin F (**6**), along with known tannins, geraniin **(1)**, corilagin (**4**), phyllanthusiins B, C (**7**) and E.

Geraniinic acid B (**2**) had a pseudo-molecular ion peak at *m/z* 970 $(M+NH_4)^+$ in the electrospray ionization mass spectrum (ESI-MS), corresponding to the molecular formula $C_{41}H_{28}O_{27}$. The ^{1}H-NMR spectrum of **2** showed a 2H singlet (δ 7.19) and three 1H singlets (δ 7.06, 6.64, 7.01) ascribable to a galloyl, a hexahydroxydiphenoyl (HHDP) and an A-ring proton of the dehydrohexahydroxydiphenoyl (DHHDP) group as seen in **1**. Aliphatic proton signals also closely resembled those of **1** including signals characteristic of a $^1C_4$ glucopyranose core. The principal difference in the spectra of **2** and **1** was the presence of an extra broad singlet at δ 5.14, which is coupled with a doublet (br d, J=1 Hz) at δ 5.33, in the former. The DHHDP group in **1** is characterized by formation of an equilibrium mixture between six- and five-membered hemiacetal structures (**1a**, **1b**) in the presence of water to give duplication of signals in the NMR spectrum. However, no duplicated signal in the ^{1}H-NMR spectrum of **2** was observed upon addition of D_2O to the NMR solvent (acetone-d_6), suggesting a lack of the potential triketonic function in **2**. The presence of the corilagin moiety as a partial structure of **2** was indicated by partial hydrolysis in hot water yielding **4**. From these data, geraniinic acid B was assumed to be an analog of **1**, which differs from **1** only in the structure of the B-ring of an acyl unit attached to O-2/O-4. This assumption was consistent with the ^{13}C-NMR spectrum of **2**, which was very similar to that of crystalline geraniin (**1a**) except for signals due to the cyclohexenetrione moiety. Instead of signals due to the ketonic carbon (δ 191.7, C-4″), *gem*-diol (δ 92.4, C-6″) and hemiacetal (δ 96.1, C-5″) carbons in the B-ring of **1a**, signals attributable to two ester carbonyl (or carboxyl) carbons (δ 161—171) and a methine carbon (δ 80.1) were observed in **2**. From these NMR spectral features, along with the MS data and the findings described below, a lactone-carboxylic acid structure was assigned to the B-ring of **2**. If **2** has an alternative dihydrocoumarin-type δ-lactone moiety as seen in chebulagic acid (**5**), **2** should have an IR absorption band at around 1775 cm^{-1} and exhibit a significant upfield shift (*ca*. 6 ppm) of the C-6′ signal relative to C-4′ in the ^{13}C-NMR, both of which are observed with chebulagic acid.[5] However, such characteristics were not observed with **2**, indicating that the hydroxyl group at C-6′ in geraniinic acid B does not participate in lactone formation. An α,β-unsaturated δ-lactone structure of the B-ring was indicated by the ^{1}H–^{13}C long-range shift correlation spectrum (COLOC) in which the methine signal at δ 5.14 (H-2″) correlated with two carboxyl carbon resonances at δ 161.2 and 171.1 through three- and two-bond couplings. The carboxyl signal at δ 171.1 also showed a three-bond correlation with a broad doublet at δ 5.33 (H-3″) which similarly correlated with an ester carbonyl carbon at δ 164.5 assignable to C-7″ (see Fig. 1). The assignment of the C-7″ signal was based on a cross peak with H-4 of the glucose residue. Thus the B-ring was located at O-4 of the glucose. The binding modes of the other acyl groups in **2** were also consistent with long-range correlations in COLOC. The nuclear Overhauser enhance-

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ment and exchange spectroscopy (NOESY) spectrum of **2** showed a clear nuclear Overhauser effect (NOE) between H-3″ (B-ring) and the anomeric proton of the glucose core, which is similar to that observed in **1**, thus establishing an *R*-configuration at C-3″. An allylic coupling constant ($J_{3'',5''}$=1 Hz) of H-3′ which should arise from maximum overlapping of the π–σ bond indicates the conformation of the B-ring as shown in Fig. 1. The *trans*-arrangement of H-2″ and H-3″ in this conformation was consistent with their small coupling constants (<1 Hz) in the ^{1}H-NMR spectrum. The circular dichroism (CD) spectrum of **2** showed a strong negative Cotton effect at 220 nm analogous to that of **1**,[2] indicating the *R*-configuration of the HHDP group. Furthermore, atropisomerism of the HHDP moiety in **2** was confirmed by formation of dimethyl (*R*)-hexamethoxydiphenate,[2] $[\alpha]_D$ +21°, upon methanolysis of the tridecamethyl derivative of **2**. Consequently, the structure of geraniinic acid B was determined to be **2**.

Geraniinic acid C (**3**) has the molecular formula, $C_{41}H_{28}O_{27}$ [*m/z* 970 $(M+NH_4)^+$], identical with that of geraniinic acid B (**2**). The NMR, IR and CD spectral data were very similar to those of **2**. The only significant difference in the ^{1}H-NMR spectra of these two compounds was a large coupling constant (J=6 Hz) between H-2″ (δ 5.63) and H-3″ (δ 5.17) in **3**, instead of a small one ($<J$=1 Hz) for the corresponding signals in **2** (see Experimental). An α-orientation of H-3″ in **3** was established by NOE with the anomeric proton in NOESY. This fact and the analogy of the allylic coupling constant ($J_{3'',5''}$=1 Hz) of the H-3″/H-5″ signals between **3** and **2** indicated that the conformation of the B-ring at O-4 should be the same in these two compounds. The coupling constant ($J_{2'',3''}$=6 Hz) of H-2″ and H-3″ in **3** was thus rationalized by their *cis*-geometry. A remarkable difference ($\Delta\delta$ 0.49 ppm) in the H-2″ signal between **2** and **3** was attributed to the anisotropic effect of the A-ring. The proposed structure **3** for geraniinic acid C was substantiated by methylation with dimethyl sulfate which afforded the expected tridecamethyl derivative, along with a by-product, nona-*O*-methylcorilagin (**4a**).

Thus, geraniinic acids B (**2**) and C (**3**) were concluded to

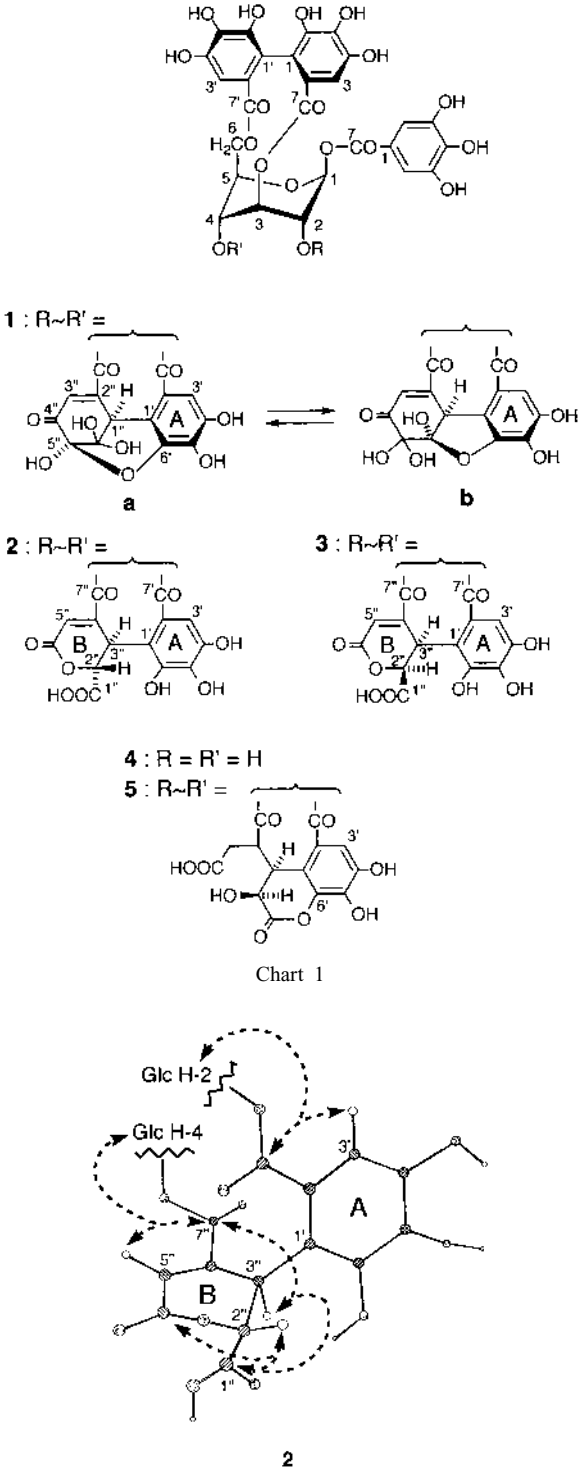

Chart 1

Fig. 1. Stereostructure and ^{1}H–^{13}C Long-Range Correlations of the O-2/O-4 Acyl Moiety in **2**

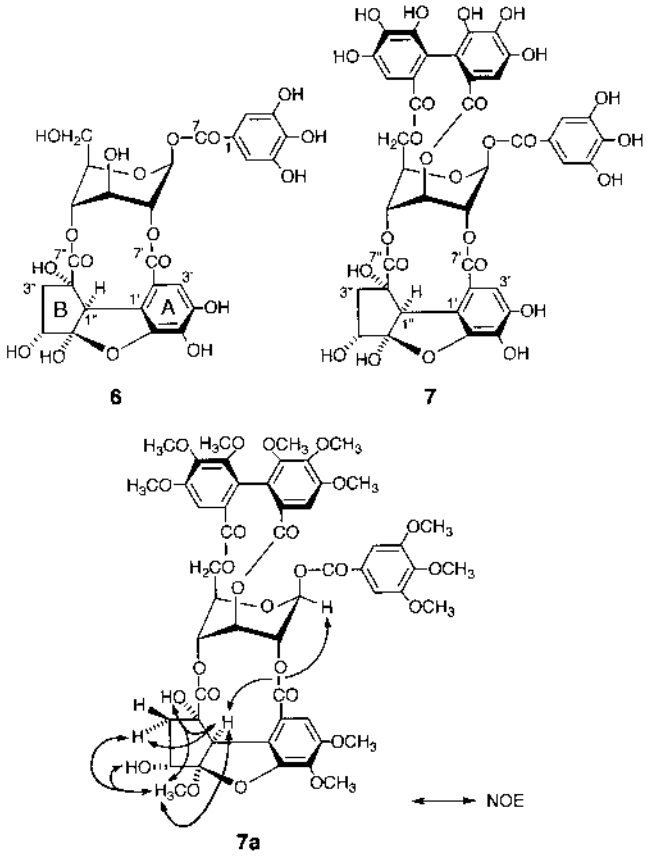

Chart 2

be isomers associated with the stereochemistry at C-2″ and C-3″ of the B-ring.

The third new compound (**6**) was named phyllanthusiin F, as it was regarded as an analog of phyllanthusiin C (**7**) based on the following data. It showed an $(M+NH_4)^+$ ion peak at *m/z* 642, and the molecular formula $C_{26}H_{24}O_{18}$ was determined by high-resolution (HR) ESI-MS [*m/z* 642.1344 $(M+NH_4)^+$ (Calcd for $C_{26}H_{24}O_{18}+NH_4$, 642.1306)]. The ^{1}H-NMR spectrum of **6** exhibited a 2H singlet (δ 7.15) due to a galloyl group and a 1H singlet (δ 7.01) in the aromatic proton region. The sugar proton signals were characteristic of $^1C_4$ glucopyranose, among which the H-3 and H-6 signals appeared at high fields (δ 4.52 and 4.21/3.96, respectively) relative to the corresponding signals of **1**—**3**, suggesting the presence of free hydroxyl groups at C-3 and C-6. The spectrum also showed an isolated methine proton signal (δ 4.61), and another methine signal (δ 4.57, br dd, *J*=7, 12 Hz) which is coupled with methylene protons [δ 2.34 (dd, *J*=7, 12 Hz) and 2.17 (br t, *J*=12 Hz)]. The chemical shifts and coupling patterns of these signals, along with the aromatic 1H singlet (δ 7.01), were in agreement with those of the acyl group at O-2/O-4 in phyllanthusiin C (**7**).[6] Thus, the structure of this compound was presumed to be **6** and confirmed by partial hydrolysis of **7** with tannase yielding **6** and ellagic acid.

The stereochemistry of the O-2/O-4 acyl group in phyllanthusiin C (**7**), which was left unassigned, has been determined by NOESY measurement of dodecamethylphyllanthusiin C (**7a**)[6] as follows. The absolute configuration at C-1″ of the B-ring was found to be the same as that of **1**—**3** and **5** by an NOE correlation between H-1″ and the anomeric proton. The H-1″ signal also showed NOEs with a methoxyl signal at δ 3.41 (C-5″-OMe) and a hydroxyl proton signal at δ 4.43 (s, C-2″-OH). The methoxy signal was correlated with another hydroxyl proton signal at δ 4.16 (d, *J*=3.5 Hz) assignable to C-4″-OH, establishing the α-configurations for all of the functional groups (OH, OMe) on the B-ring (Chart 2). Thus the stereostructure **6** was assigned to phyllanthusiin F.

Hydrolyzable tannins, which are regarded as the metabolites at the highly reactive DHHDP group of geraniin (**1**), include chebulagic acid (**5**), phyllanthusiins, acalyphidins,[7] repandusinic acid A[8] and many others which have been found especially in the Euphorbiaceous plants.[9] Geraniinic acids B and C are the new members of the oxidative metabolites of **1**. It is also noteworthy that phyllanthusiins, which have been hitherto found only in the *Phyllanthus* species of Euphorbiaceae, were first isolated from the other family Geraniaceae.

Experimental

Optical rotations were recorded on a JASCO DIP-1000 polarimeter. ^{1}H- and ^{13}C-NMR spectra were measured in acetone-d_6+D_2O and methanol-d_4 on Varian VXR-500 (500 MHz for ^{1}H-NMR and 125.7 MHz for ^{13}C-NMR) instruments. Chemical shifts are given in δ (ppm) values relative to that of the solvent [acetone-d_6 (δ_H 2.04; δ_C 29.8), methanol-d_4 (δ_H 3.35; δ_C 49.8)] on a tetramethylsilane scale. ESI-MS spectra were recorded on a Micromass Auto Spec OA-Tof mass spectrometer (solvent: 50%MeOH+0.1%AcONH$_4$, flow rate: 20 μl/min). CD spectra were recorded on a JASCO J-720W spectrometer. Normal-phase HPLC was conducted on a YMC-Pack SIL A-003 (YMC Co., Ltd.) column (4.6 mm i.d.×250 mm) developed with *n*-hexane–MeOH–tetrahydrofuran (THF)–formic acid (55 : 33 : 11 : 1) containing oxalic acid (450 mg/1.2 l) (flow rate, 1.5 ml/min; detection 280 nm) at room temperature. Reversed-phase HPLC was performed on a YMC-Pack ODS-A A-302 (YMC Co., Ltd.) column (4.6×150 mm) developed with 10 mM H_3PO_4–10 mM KH_2PO_4–CH_3CN (45 : 45 : 15) (flow rate, 1.0 ml/min; detection 280 nm) at 40 °C. Detection was effected with a Simadzu SPD-6A spectrophotometric detector at 280 nm. Solvents were evaporated under reduced pressure below 40 °C.

Plant Materials The leaves of *G. thunbergii* cultivated in the herbal garden of our Faculty were collected in August. A voucher specimen is deposited in the Herbarium, Faculty of Pharmaceutical Sciences, Okayama University.

Extraction and Isolation The dried leaves (997 g) of *G. thunbergii* were homogenized in acetone–H_2O (7 : 3) (4 l×3). The filtered homogenate was concentrated and extracted with Et_2O, EtOAc and *n*-BuOH, successively. The remaining aqueous solution was concentrated to give a brownish residue (124 g), and the aqueous extract was subjected to column chromatography over Dia-ion HP-20 with H_2O and increasing amounts of MeOH in H_2O (10%→20%→40%→60%) and MeOH. Fractionation was achieved by monitoring the HPLC (normal and reversed-phase) eluate. The 40% MeOH eluate (12 g) was further purified by repeated column chromatography on MCI-gel CHP-20P with aqueous MeOH to give corilagin (**4**) (1.4 g), phyllanthusiins B (60 mg), C (**7**) (103 mg), E (142 mg), geraniin (**1**) (380 mg), geraniinic acids B (**2**) (36 mg), C (**3**) (46 mg), and phyllanthusiin F (**6**) (17 mg).

Geraniinic Acid B (**2**): A pale yellow amorphous powder. $[\alpha]_D$ −77° (*c*=1.7, acetone). ESI-MS *m/z*: 970 $(M+NH_4)^+$. HR ESI-MS *m/z*: 970.1190 $(M+NH_4)^+$, Calcd for $C_{41}H_{28}O_{27}+NH_4$, 970.1162. UV λ_{max} (MeOH) nm (log ε): 219 (4.83), 275 (4.40). CD (MeOH) [θ] (nm): -12×10^4 (225), $+0.2\times10^4$ (260), -3.4×10^4 (283). IR (KBr) cm^{-1}: 3380 (OH), 1704 (ester CO), 1599 (C=C). ^{1}H-NMR (acetone-d_6+D_2O) δ 7.19 (2H, s, galloyl-H), 7.06 (1H, s, HHDP H-3), 7.01 (1H, s, A-ring H-3′), 6.64 (1H, s, HHDP H-3′), 6.57 [1H, br s, Glucose (Glc) H-1], 6.36 (1H, d, *J*=1 Hz, B-ring H-5″), 5.44 (1H, m, Glc H-4), 5.36 (1H, m, Glc H-3), 5.33 (1H, br d, *J*=1 Hz, B-ring H-3″), 5.32 (1H, br s, Glc H-2), 5.14 (1H, br s, B-ring H-2″), 4.82 (1H, br t, *J*=11 Hz, Glc H-6), 4.61 (1H, br dd, *J*=8, 10 Hz, Glc H-5), 4.27 (1H, br dd, *J*=8, 11 Hz, Glc H-6). ^{13}C-NMR (acetone-d_6+D_2O) δ 37.9 (B-ring C-3″), 63.9 (Glc C-6), 64.4 (Glc C-3), 65.9 (Glc C-4), 71.5 (Glc C-2), 73.1 (Glc C-5), 80.1 (B-ring C-2″), 91.7 (Glc C-1), 148.6, (B-ring C-4″), 122.9 (B-ring C-5″), 107.9 (HHDP C-3′), 110.0, 111.9 (HHDP C-3, A-ring C-3′), 110.9 (2C) (galloyl C-2, 6), 115.0 (HHDP C-1′), 117.1 (HHDP C-1), 120.4 (galloyl C-1), 122.9 (B-ring C-5″), 123.3 (A-ring C-2′), 124.9 (HHDP C-2), 125.8 (HHDP C-2′), 136.4 (A-ring C-5′), 137.6, 138.3 (HHDP C-5, 5′), 139.5 (galloyl C-4), 144.2 (2C), 144.4, 145.0 (2C), 145.3 (HHDP C-4, 4′, 6, 6′, A-ring C-4′, 6′), 145.9 (2C) (galloyl C-3, 5), 161.2 (B-ring C-6″), 164.5 (B-ring C-7″), 164.9 (galloyl C-7), 166.1 (HHDP C-7), 166.2 (A-ring C-7′), 168.3 (HHDP C-7′), 171.1 (B-ring C-1″).

Geraniinic Acid C (**3**): A pale yellow amorphous powder. $[\alpha]_D$ −85° (*c*=1.2, acetone). ESI-MS *m/z*: 970 $(M+NH_4)^+$. HR ESI-MS *m/z*: 970.1179 $(M+NH_4)^+$, Calcd for $C_{41}H_{28}O_{27}+NH_4$, 970.1162. UV λ_{max} (MeOH) nm (log ε): 219 (4.80), 275 (4.38). CD (MeOH) [θ]: -12.4×10^4 (225), $+0.4\times10^4$ (260), -4.5×10^4 (283). IR (KBr) cm^{-1}: 3380 (OH), 1718 (ester CO), 1607 (C=C). ^{1}H-NMR (acetone-d_6+D_2O) δ 7.20 (2H, s, galloyl-H), 7.10 (1H, s, HHDP H-3), 6.93 (1H, s, A-ring H-3′), 6.67 (1H, br s, Glc H-1), 6.65 (1H, s, HHDP H-3′), 6.41 (1H, d, *J*=1 Hz, B-ring H-5″), 5.63 (1H, d, *J*=6 Hz, B-ring H-2″), 5.50 (1H, m, Glc H-4), 5.35 (1H, m, Glc H-3), 5.27 (1H, br s, Glc H-2), 5.17 (1H, dd, *J*=1, 6 Hz, B-ring H-3″), 4.91 (1H, br t, *J*=11 Hz, Glc H-6), 4.73 (1H, br dd, *J*=8, 10 Hz, Glc H-5), 4.25 (1H, br dd, *J*=8, 11 Hz, Glc H-6). ^{13}C-NMR (acetone-d_6+D_2O) δ 38.1 (B-ring C-3″), 63.8 (Glc C-6), 64.3 (Glc C-3), 65.8 (Glc C-4), 71.2 (Glc C-2), 72.8 (Glc C-5), 78.4 (B-ring C-2″), 90.2 (Glc C-1), 107.9 (HHDP C-3′), 110.5 (HHDP C-3), 111.0 (2C) (galloyl C-2, 6), 111.8 (A-ring C-3′), 113.1, 115.1, 117.0 (HHDP C-1, 1′, A-ring C-1′), 120.3 (galloyl C-1), 123.4 (B-ring C-5″), 124.9 (A-ring C-2′), 125.1 (HHDP C-2), 125.8 (HHDP C-2′), 136.5 (A-ring C-5′), 137.8 (2C) (HHDP C-5, 5′), 139.7 (galloyl C-4), 144.5, 145.0 (2C), 145.1, 145.5, 145.8 (HHDP C-4, 4′, 6, 6′, A-ring C-4′, 6′), 146.0 (2C) (galloyl C-3, 5), 149.1 (B-ring C-4″), 162.0, 164.5, 164.8, 166.1, 166.3, 167.4, 168.3 (ester carbonyl).

Phyllanthusiin F (**6**): An off-white amorphous powder. $[\alpha]_D$ −16° (*c*=1.0, MeOH). ESI-MS *m/z*: 642 $(M+NH_4)^+$. HR ESI-MS *m/z*: 642.1344 $(M+NH_4)^+$, Calcd for $C_{26}H_{24}O_{18}+NH_4$, 642.1306. UV λ_{max} (MeOH) nm (log ε): 230 (4.37), 280 (4.22). ^{1}H-NMR (acetone-d_6+D_2O) δ 7.15 (2H, s, galloyl-H), 7.01 (1H, s, A-ring H-3′), 6.21 (1H, br s, Glc H-1), 5.26 (1H, br s, Glc H-2), 4.97 (1H, m, Glc H-4), 4.61 (1H, s, B-ring H-1″), 4.57 (1H, dd, *J*=7, 12 Hz, B-ring H-4″), 4.52 (1H, m, Glc H-3), 4.28 (1H, dd, *J*=6, 7 Hz, Glc H-5), 4.21 (1H, dd, *J*=7, 11 Hz, Glc H-6), 3.96 (1H, dd, *J*=6, 11 Hz, Glc H-6), 2.34 (1H, dd, *J*=7, 12 Hz, B-ring H-3″), 2.17 (1H, br t, *J*=12 Hz, B-ring H-3″). ^{13}C-NMR (acetone-d_6+D_2O) δ 46.6 (B-ring C-3″), 61.7 (Glc C-3),

62.76 (Glc C-6), 62.80 (B-ring C-1″), 70.4 (Glc C-2), 71.0 (Glc C-4), 74.7 (B-ring C-4″), 77.9 (Glc C-5), 78.4 (B-ring C-2″), 92.3 (Glc C-1), 110.1 (2C) (galloyl C-2, 6), 110.9 (A-ring C-3′), 116.8 (B-ring C-5″), 117.7 (A-ring C-2′), 118.8 (A-ring C-1′), 120.5 (galloyl C-1), 135.3 (A-ring C-5′), 139.4 (galloyl C-4), 146.0 (2C) (galloyl C-3, 5), 146.9 (A-ring C-4′), 149.6 (A-ring C-6′), 165.31 (galloyl C-7), 165.28 (A-ring C-7′), 174.2 (B-ring C-7″).

Partial Hydrolysis of 2 and 3 An aqueous solution (2 ml) of **2** (or **3**; each 1 mg) was heated in a boiling-water bath for 1.5 h. The reaction mixture was analyzed by HPLC [YMC Pack A_{312} octadecyl silica (ODS), 6 mm i.d.×150 mm; 0.05 M phosphate buffer–CH_3CN (82 : 12 v/v); 40 °C; flow rate 1.3 ml/min; detection 280 nm] to show the peaks due to corilagin (**4**) and ellagic acid.

Methylation of 2 and 3 A mixture of **2** (17 mg), $(CH_3)_2SO_4$ (0.12 ml) and K_2CO_3 (100 mg) in acetone (5 ml) was stirred overnight at room temp., and then refluxed for 8 h. After removal of the inorganic material by centrifugation, the supernatant was evaporated to dryness *in vacuo*. The product was purified by preparative TLC (SiO_2, light petroleum–benzene–acetone 1 : 2 : 1 v/v) to yield the tridecamethyl derivative of **2**, a pale yellowish amorphous powder, $[\alpha]_D$ −128° (c=0.8, acetone), ^{1}H-NMR (acetone-d_6) δ 7.30 (2H, s, galloyl-H), 7.22 , 6.91 (each 1H, s, HHDP-H), 7.17 (1H, s, A-ring H-3′), 6.87 (1H, br s, Glc H-1), 6.42 (1H, d, J=1 Hz, B-ring H-5″), 5.49 (1H, m, Glc H-4), 5.43 (1H, m, Glc H-3), 5.40 (1H, br s, Glc H-2), 5.29 (1H, d, J=1 Hz, B-ring H-2″), 5.29 (1H, t, J=1 Hz, B-ring H-3″), 5.16 (1H, t, J=11 Hz, Glc H-6), 4.81 (1H, br dd, J=8, 11 Hz, Glc H-5), 4.40 (1H, dd, J=8, 11 Hz, Glc H-6), 3.94, 3.90, 3.89, 3.88, 3.85, 3.83, 3.70, 3.65, 3.50 (each 3H, s, OMe), 3.86, 3.68 (each 6H, s, OMe).

Geraniinic acid C (**3**) (16 mg) was methylated in a way similar to that described above to give nona-*O*-methylcorilagin (**4a**) (1.0 mg) and the tridecamethyl derivative of **3** (4.7 mg), a pale yellowish amorphous powder, $[\alpha]_D$ −102° (c=0.7, acetone), ^{1}H-NMR (acetone-d_6) δ 7.31 (2H, s, galloyl-H), 7.14 , 6.92 (each 1H, s, HHDP-H), 7.14 (1H, s, A-ring H-3′), 6.97 (1H, br s, Glc H-1), 6.48 (1H, d, J=1 Hz, B-ring H-5″), 5.74 (1H, d, J=6 Hz, B-ring H-2″), 5.57 (1H, m, Glc H-4), 5.36 (1H, m, Glc H-3), 5.31 (1H, br s, Glc H-2), 5.18 (1H, t, J=11 Hz, Glc H-6), 5.11 (1H, br d, J=6 Hz, B-ring H-3″), 4.82 (1H, br dd, J=8, 11 Hz, Glc H-5), 4.40 (1H, dd, J=8, 11 Hz, Glc H-6), 3.94, 3.91, 3.89, 3.88, 3.87, 3.84, 3.80, 3.70, 3.65, 3.50, 3.43 (each 3H, s, OMe), 3.68 (6H, s, OMe).

Methanolysis of Tridecamethyl Derivatives of 2 and 3 The tridecamethyl derivatives of **2** and **3** (each 8 mg) were separately methanolyzed with 1% NaOMe (0.1 ml) in methanol (2 ml) at room temp. for 10 h. After acidification with a few drops of HOAc, the solvent was removed *in vacuo*. The residue was re-dissolved in acetone and purified by preparative TLC (SiO_2, benzene–acetone 15 : 1) to give methyl tri-*O*-methylgallate (1 mg) and dimethyl hexamethoxydiphenate (2 mg), $[\alpha]_D$ +21° (c=1.1, acetone).

Partial Hydrolysis of 7 An aqueous solution (1 ml) of **7** (1 mg) was incubated at 37 °C with 2 drops of tannase prepared as in the literature.[10] Reversed-phase HPLC (LiChrospher RP-18, 4 mm i.d.×250 mm; 0.01 M phosphate buffer–CH_3CN 9 : 1 v/v; 40 °C; flow rate 1.0 ml/min; detection 280 nm) of the reaction mixture showed the production of **6** (t_R 5.85 min) after 15 min.

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