Gallotannins Having a 1,5-Anhydro-D-glucitol Core and Some Ellagitannins from *Acer* Species[1)]

Tsutomu HATANO,[a] Shin HATTORI,[a] Yoshitaka IKEDA,[a] Tetsuro SHINGU[b] and Takuo OKUDA*,[a]

Faculty of Pharmaceutical Sciences, Okayama University,[a] Tsushima, Okayama 700, Japan and Faculty of Pharmaceutical Science, Kobe Gakuin University,[b] Ikawadani, Nishi-ku, Kobe 673, Japan. *Received February 2, 1990*

Tannins of two *Acer* species were investigated. Basides acertannin (1), gallotannins 2 and 3, having three and four galloyl groups on their 1,5-anhydro-D-glucitol cores, were obtained from the leaves of *Acer ginnala*. The estimation of their tanning activity by the *RMBG* (relative affinity to methylene blue based on the affinity of geraniin) determination method revealed that the tanning activities of 2 and 3 are high, while that of 1, which has only two galloyl groups, is low. Two isomers (2a and 2b) of 2, and three isomers (3a, 3b and 3c) of 3 were respectively separated from each other after methylation. Their structures, in which all of the acyl groups (galloyl group, digalloyl group and/or trigalloyl group) are linked exclusively to O-2 and O-6 of the 1,5-anhydro-D-glucitol core, were assigned. Fractionation of the constituents of leaves of *Acer saccharum* afforded two ellagitannins, geranin (10) and davidiin (11), and also chlorogenic acid and quercitrin.

Keywords tannin; gallotannin; acertannin; 1,5-anhydro-D-glucitol; ellagitannin; geraniin; davidiin; *Acer ginnala*; *Acer saccharum*; tanning activity

Isolation of a polyphenolic component of a rather small molecule, named acertannin (**1**), from *Acer ginnala* was reported in 1922,[2)] and its structure, 2,6-di-*O*-galloyl-1,5-anhydro-D-glucitol, was established recently.[3,4)] The presence of 1,5-anhydro-D-glucitols having three galloyl groups (**2**) in this plant was also reported[4)] although the two isomers, 6-*O*-digalloyl-2-*O*-galloyl-1,5-anhydro-D-glucitol (**2a**) and 2-*O*-digalloyl-6-*O*-galloyl-1,5-anhydro-D-glucitol (**2b**), were not separated.

We have been investigating tannins of some *Acer* species, and previously reported on ellagitannins of *Acer nikoense*.[5)] Upon further studies on the tannins of these species, **2a** and **2b** from *A. ginnala* have been separated from each other after methylation. The methylation also facilitated elucidation of their structures, since the equilibration, which is caused by the migration[6)] of depsidically linked galloyl groups between *meta*- and *para*-hydroxyl groups of the galloyl groups attached directly to the sugar core (Chart 1), was absent in the methylated derivatives.

Besides the above compounds, 1,5-anhydroglucitols having four galloyl groups (**3**) have been newly obtained from *A. ginnala*, and three isomers, 2-*O*-galloyl-6-*O*-trigalloyl-1,5-anhydro-D-glucitol (**3a**), 2,6-bis-*O*-digalloyl-1,5-anhydro-D-glucitol (**3b**) and 6-*O*-galloyl-2-*O*-trigalloyl-1,5-anhydro-D-glucitol (**3c**), were separated from each other in an analogous way.

We report here on these galloylated 1,5-anhydro-D-glucitols from *A. ginnala*, and also on ellagitannins from *A. saccharum*.

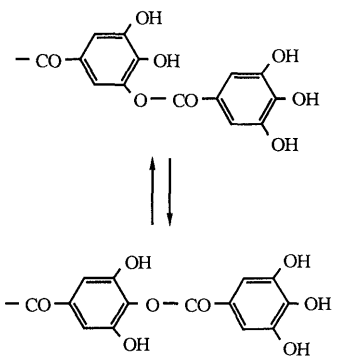


Chart 1

Results and Discussion

Gallotannins of *A. ginnala* Acertannin (**1**) was crystallized out from the concentrated filtrate obtained from a homogenate of leaves of *A. ginnala*. The aqueous mother liquor of **1** was extracted with diethyl ether and ethyl acetate successively, and the ethyl acetate extract was subjected to column chromatography on Sephadex LH-20, to afford **2** and **3**. Methanolysis of **2** and **3** in a manner inducing preferential cleavage of the depside linkage[7)] afforded **1** and methyl gallate (**4**) in molar ratios of 1:1 and 1:2, respectively. Therefore, **2** and **3** have the structures in which one or two additional galloyl groups are depsidically linked to galloyl groups of **1** (Chart 2). Upon estimation of their tanning activity by the *RMBG* (relative affinity to methylene blue based on the affinity of geraniin) determination method,[8)] **2** and **3** showed high *RMBG* values (**2**, 0.84; **3**, 0.90), while **1**, having only two galloyl groups, showed a low value (0.08). Therefore, **2** and **3** are genuine tannin components in the leaves of this plant, while **1** is not, in spite of its name, acertannin.[9)]

Methylation of **2** afforded a mixture containing two octamethyl derivatives **5** and **6**. These two were separated from each other by preparative thin layer chromatography (PTLC) on silica gel. As described below, this methylation occurred preferentially on the *para*-hydroxyl groups of the galloyl groups attached directly to the anhydroglucitol core, in a manner similar to the methylation of methyl digallate.[6a)] Methylation of **3**, followed by PTLC of the reaction mixture, afforded the decamethyl derivatives **7**, **8** and **9**.

Compounds **5** and **6** showed their molecular ions at *m/z* 732 in the electron-impact mass spectra (EI-MS). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **5** showed six aromatic protons assignable to a tri-*O*-methylgalloyl (TMG) group [δ 7.33 (2H, s)] and a penta-*O*-methyl-*m*-digalloyl group (PMDG) [δ 7.62, 7.54 (each d, J=2 Hz) and 7.49 (2H, s)], along with protons of a 1,5-anhydroglucitol core and of eight methoxyl groups (see Experimental). The H-2 and two H-6 protons of the anhydroglucitol core appeared at lower field (H-2, δ 4.94; H-6, δ 4.69 and 4.48), relative to the other anhydroglucitol

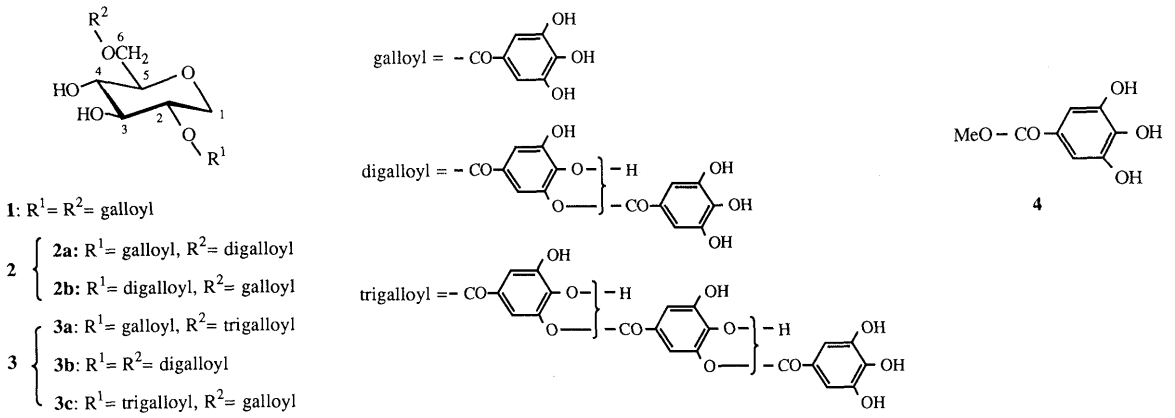


Chart 2

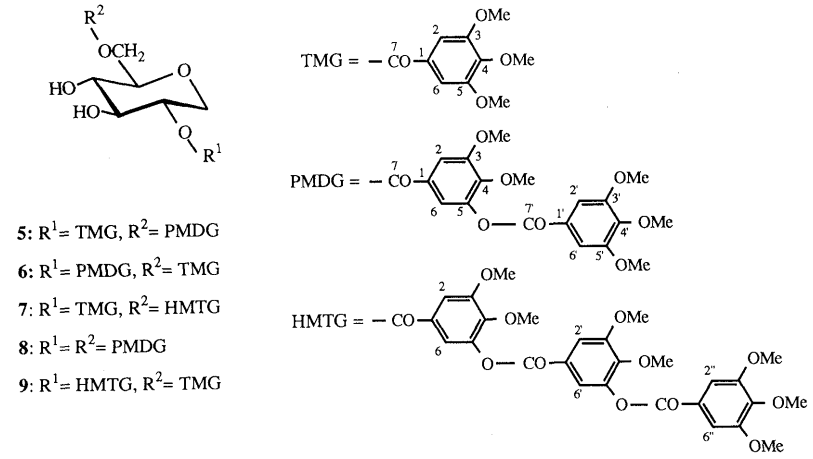


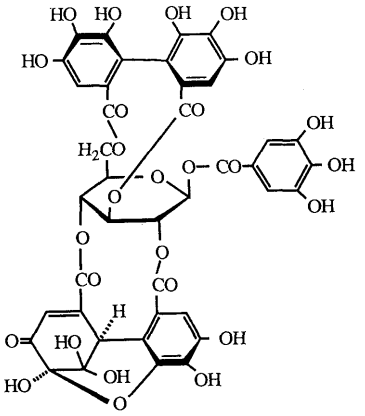
Chart 3

protons, indicating that these two acyl groups (TMG and PMDG groups) in **5** are at O-2 and O-6 on the anhydroglucitol core. The ^{1}H-NMR spectrum of **6** also showed the presence of a TMG group [δ 7.34 (2H, s)], a PMDG group [δ 7.63, 7.54 (each d, J=2 Hz) and 7.49 (2H, s)], and a 1,5-anhydroglucitol core (see Experimental) in the molecule of **6**. The chemical shifts of the H-2 and two H-6 protons (H-2, δ 4.96; H-6, δ 4.67 and 4.46) of the anhydroglucitol core indicated that the two acyl groups in **6** are also on O-2 and O-6. Therefore, **5** and **6** are octamethyl derivatives of **2a** (or **2b**) and **2b** (or **2a**).

The ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum of **6** showed a downfield shift of the C-2 signal (δ 73.64) among the anhydroglucitol carbon signals, relative to the C-2 signal of **5** (δ 73.41). The signal of C-6 of the anhydroglucitol core of **5** (δ 65.35) also showed a downfield shift, relative to the corresponding signal of **6** (δ 65.17). These downfield shifts, which are analogous to those induced by the substitution of digalloyl groups for galloyl groups in some gallotannins,[6a] indicate that the PMDG group in **6** is at O-2 on its anhydroglucitol core, and this group in **5** is at O-6. Therefore, compounds **5** and **6** were assigned to be octamethyl derivatives of **2a** and **2b**, respectively.

Among the anhydroglucitol protons in the ^{1}H-NMR spectrum of **6**, the H-2 signal of its anhydroglucitol core showed a slight downfield shift, relative to the corresponding signal of **5** (δ 4.94→4.96), and the H-6 signals of **5** showed analogous downfield shifts (δ 4.67→4.69, δ 4.46→4.48), relative to those of **6**. The hydroxyl proton at C-3 of the anhydroglucitol core is also susceptible to the substition of PMDG group for TMG group at O-2 [δ 4.77 (**5**)→4.85 (**6**)]. On the other hand, the chemical shift of OH at C-4 of the anhydroglucitol core is less influenced by the substitution at O-6. These differences in the chemical shifts, therefore, can be utilized for discrimination of the location of the acyl group having a depside linkage from that of the TMG group.

Each isolated compound, **7**, **8** and **9**, derived from **3**, showed a molecular ion at m/z 912 in the EI-MS. The ^{1}H-NMR spectrum of **7** showed eight aromatic protons assignable to a TMG group [δ 7.34 (2H, s)] and a hepta-*O*-methyl-*m*-trigalloyl (HMTG) group [δ 7.77, 7.71, 7.63, 7.58 (each d, J=2 Hz) and 7.51 (2H, s)], along with protons of a 1,5-anhydroglucitol core and of ten methoxyl groups (see Experimental). Two H-6 protons and H-2 of the anhydroglucitol core of **7** appeared at lower field [δ 4.68, 4.48 (H-6); 4.93 (H-2)], relative to the other anhydroglucitol protons, indicating that the two acyl groups (TMG and HMDG groups) in **7** are at O-2 and O-6 on its anhydroglucitol core. The ^{1}H-NMR spectrum of **9** also showed signals of a TMG group [δ 7.34 (2H, s)] and an HMDG group [δ 7.76, 7.71, 7.63, 7.57 (each d, J=2 Hz) and 7.51 (2H, s)]. The chemical shifts of the two H-6 protons and H-2 [δ 4.67, 4.46 (H-6); δ 4.95 (H-2)] of the anhydroglucitol core in **9** indicate that the two acyl groups are on O-2 and O-6 of its 1,5-anhydroglucitol core. The H-2 signal of the anhydroglucitol core of **9** showed a slight



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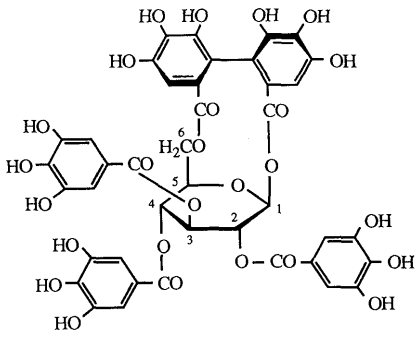

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Chart 4

downfield shift, relative to the corresponding signal of **7** (δ 4.93→4.95), and the H-6 signals of **7** showed analogous downfield shifts (δ 4.67→4.68, δ 4.46→4.48) relative to those of **9**. The hydroxyl proton at C-3 also showed a downfield shift attributable to substitution of an HMTG group for a TMG group [δ 4.76 (**7**)→4.90 (**9**)]. Therefore, **7** and **9** are decamethyl derivatives of **3a** and **3c**, respectively. The remaining decamethyl derivative **8** showed ^{1}H signals due to two PMDG groups [δ 7.62, 7.61, 7.54, 7.52 (1H each, d, J=2 Hz), 7.49, 7.48 (2H each, s)] along with the signals of its 1,5-anhydro-D-glucitol core. The chemical shifts of H-2 (δ 4.95) and two H-6 (δ 4.68, 4.47) signals, which appeared at lower field, relative to the other anhydroglucitol protons, indicate that the two PMDG groups are at O-2 and O-6 on the anhydroglucitol core. Therefore, **8** is the decamethyl derivative of **3b**.

Ellagitannins of *A. saccharum* The ethyl acetate extract of a homogenate of leaves of *A. saccharum* was chromatographed on Sephadex LH-20, to give two ellagitannins, geraniin (**10**)[10] and davidiin (**11**),[11] along with chlorogenic acid and quercitrin.

Although geraniin has been reported to be distributed widely in Dicotyledonous plants including those of Aceraceae,[4b,5,12] davidiin has previously been found only in *Davidia involculata*,[11a] which is a rare species, and is the sole species belonging to Davidiaceae. The occurrence of davidiin in an Aceraceous plant, as found in the present study, may be suggestive of some correlation between these two families in the plant systematics.

Experimental

Optical rotations were measured on a JASCO DIP-4 polarimeter. Ultraviolet (UV) and infrared (IR) spectra were respectively recorded on a Hitachi 200-10 spectrophotometer and a JASCO A-102 spectrometer. ^{1}H-NMR spectra were recorded with a Bruker AM-400 spectrometer (400 MHz), and ^{13}C-NMR spectra were recorded with JEOL FX-200 spectrometer (50.1 MHz). A Hitachi R22-FTS spectrometer (90 MHz for ^{1}H-NMR and 22.6 MHz for ^{13}C-NMR) and a Varian VXR-500 instrument (500 MHz for ^{1}H-NMR and 125.7 MHz for ^{13}C-NMR) were also used for measurements ^{1}H- and ^{13}C-NMR spectra. Chemical shifts are given in δ values (ppm) from tetramethylsilane. EI-MS were recorded on a Shimadzu LKB-9000 instrument. Thin layer chromatography (TLC) was performed on Kieselgel PF_{254} (Merck) using solvent systems (a) light petroleum (refers to the fraction boiling in the range of 85—120 °C)–chloroform–acetone (4:6:3, v/v), (b) benzene–acetone (4:1), (c) *n*-hexane–tetrahydrofuran–acetic acid (100:100:1) and (d) benzene–acetone (3:1). High-performance liquid chromatography (HPLC) was performed on a YMC A312 (ODS) column (6×150 mm, Yamamura Chemical Laboratories) with solvent A [0.1 M H_3PO_4–0.1 M KH_2PO_4–EtOH–ethyl acetate (10:10:2:1)] or solvent B [0.05 M H_3PO_4–0.05 M KH_2PO_4–EtOH–ethyl acetate (17:17:4:2)], in an oven at 40 °C, with monitoring at 254 nm.

Purification of 1,5-Anhydro-D-glucitol Derivatives from *A. ginnala* Leaves (960 g) of *A. ginnala* were homogenized in 70% acetone (7.5 l×3), immediately after collection from the trees grown at Handayama Botanical Garden, Okayama. Concentrated filtrate obtained from the homogenate was kept in a refrigerator, and crystallized acertannin (63 g) was filtered off. The mother liquor was extracted successively with diethyl ether and ethyl acetate. A portion (4 g) of the ethyl acetate extract (46 g) was chromatographed over Sephadex LH-20 (2.2×60 cm) with 70% EtOH, to give **1** (536 mg), **2** (879 mg) and **3** (170 mg).

Estimation of Tanning Activity Tanning activity of each sample was determined by the reported method based on the binding activity to methylene blue,[8] and was expressed as *RMBG* value.

Acertannin (1)[2-4] Colorless needles, mp 165 °C, $[\alpha]_D$ +21° (c=1, acetone). *Anal.* Calcd for $C_{20}H_{20}O_{13}\cdot 2H_2O$: C, 49.38; H, 4.55. Found: C, 49.02; H, 4.46. UV λ_{max}^{MeOH} nm (log ε): 221 (4.68), 275 (4.35). IR ν_{max}^{KBr} cm^{-1}: 1690 (ester carbonyl), 1615. ^{1}H-NMR (500 MHz, acetone-d_6) δ: 7.13, 7.11 (2H each, s, 2×galloyl), 4.87 [dt, J=5.5, 10 Hz, H-2 of 1,5-anhydro-D-glucitol (AHG) core], 4.56 (d, J=12 Hz, AHG H-6), 4.35 (dd, J=5, 12 Hz, AHG H-6), 4.05 (dd, J=5.5, 10.5 Hz, AHG H-1), 3.79 (t, J=9 Hz, AHG H-3), 3.59—3.54 (m, AHG H-4 and H-5), 3.34 (t, J=10.5 Hz, AHG H-1). ^{13}C-NMR (125.7 MHz, acetone-d_6) δ: 166.83, 166.46 (galloyl C-7×2), 145.95, 145.90 (2C each, galloyl C-3×2, C-5×2), 138.90, 138.77 (galloyl C-4×2), 121.50, 121.22 (galloyl C-1×2), 109.93, 109.77 (2C each, galloyl C-2×2, C-6×2), 79.42 (AHG C-5), 76.39 (AHG C-3), 72.85 (AHG C-2), 71.49 (AHG C-4), 67.35 (AHG C-1), 64.56 (AHG C-6).

Methanolysis of 2 and 3 A solution (2.0 ml) of **2** (2.4 mg) in a 9:1 (v/v) mixture of MeOH and 0.5 M acetic acid–sodium acetate buffer (pH 6) was incubated at 37 °C for 7 h. HPLC analysis (using solvent A) of the reaction mixture showed the presence of acertannin (**1**) and methyl gallate (**4**) in a molar ratio of 1:1. Upon treatment of **3** in an analogous way, **1** and **4** were produced in a molar ratio of 1:2.

Separation after Methylation of the Isomers of 2 and 3 A mixture of **2** (200 mg), dimethyl sulfate (0.48 ml) and K_2CO_3 (1 g) in acetone (12 ml) was stirred for 24 h at room temperature, and then refluxed for 1 h. After insoluble material in the reaction mixture was filtered off, the filtrate was evaporated, and the residue thus obtained was separated by TLC using solvent systems (a) and (b), to give the octamethyl derivatives **5** (71 mg) and **6** (68 mg). Methylation of **3** in a similar way, followed by separation of the constituent isomers by TLC using solvent systems (c), (d) and (e), gave the decamethyl derivatives **7**, **8** and **9**.

Octamethyl Derivative (5) of 6-*O*-Digalloyl-2-*O*-galloyl-1,5-anhydro-D-glucitol (2a) White powder, $[\alpha]_D$ +31° (c=0.1, acetone). EI-MS m/z: 732 ([M]$^+$). IR ν_{max}^{KBr} cm^{-1}: 1730 (ester carbonyl), 1595. ^{1}H-NMR (400 MHz, acetone-d_6) δ: 7.62 (d, J=2 Hz, PMDG H-6), 7.54 (d, J=2 Hz, PMDG H-2), 7.49 (2H, s, PMDG H-2′, H-6′), 7.33 (2H, TMG H-2, H-6), 4.94 (ddd, J=5.5, 9.5, 11 Hz, AHG H-2), 4.77 (d, J=5 Hz, AHG OH at C-3), 4.72 (d, J=4.5 Hz, AHG OH at C-4), 4.69 (dd, J=2, 12 Hz, AHG H-6), 4.48 (dd, J=5.5, 12 Hz, AHG H-6), 4.10 (dd, J=5.5, 11 Hz, AHG H-1), 4.00 (3H, s, MeO), 3.94 (6H, s, MeO×2), 3.88 (3H, s, MeO), 3.88 (6H,

s, MeO × 2), 3.86 (3H, s, MeO), 3.84 (ddd, J=5, 8, 9.5, AHG H-3), 3.80 (3H, s, MeO), 3.65 (ddd, J=2, 5.5, 9.5 Hz, AHG H-5), 3.61 (ddd, J=4.5, 8, 9.5 Hz, AHG H-4), 3.41 (t, J=11 Hz, AHG H-1). ^{13}C-NMR (50.1 MHz, acetone-d_6) δ: 165.97, 165.71 [TMG C-7; PMDG C-7], 164.71 (PMDG C-7′), 154.35 (PMDG C-5), 154.26 (2C), 154.03 (2C) (TMG C-3, C-5; PMDG C-3′, C-5′), 146.46 (PMDG C-4), 144.94 (PMDG C-3), 144.30 (PMDG C-4′), 143.78 (TMG C-4), 126.11, 125.76, 124.68 (PMDG C-1, C-1′; TMG C-1), 117.76 (PMDG C-2), 112.33 (PMDG C-6), 108.53, 108.21 (2C each, PMDG C-2′, C-6′; TMG C-2, C-6), 79.42 (AHG C-5), 76.53 (AHG C-3), 73.41 (AHG C-2), 71.71 (AHG C-4), 67.36 (AHG C-1), 65.35 (AHG C-6), 60.97, 60.73, 60.45 (MeO × 3), 56.65 (5C, MeO × 5).

Octamethyl Derivative (6) of 2-*O*-Digalloyl-6-*O*-galloyl-1,5-anhydro-D-glucitol (2b) White powder, $[\alpha]_D$ +28° (c=0.1, acetone). EI-MS m/z: 732 ($[M]^+$). IR ν_{max}^{KBr} cm^{-1}: 1730 (ester carbonyl), 1595. ^{1}H-NMR (400 MHz, acetone-d_6) δ: 7.63 (d, J=2 Hz, PMDG H-6), 7.54 (d, J=2 Hz, PMDG H-2), 7.49 (2H, s, PMDG H-2, H-6), 7.34 (2H, TMG H-2, H-6), 4.96 (ddd, J=5.5, 9.5, 11.5 Hz, AHG H-2), 4.85 (d, J=5 Hz, AHG OH at C-3), 4.70 (d, J=4.5 Hz, AHG OH at C-4), 4.67 (dd, J=2, 12 Hz, AHG H-6), 4.46 (dd, J=5.5, 12 Hz, AHG H-6), 4.12 (dd, J=5.5, 11.5 Hz, AHG H-1), 3.99 (3H, s, MeO), 3.94, 3.89 (6H each, s, MeO × 4), 3.87, 3.86 (3H each, s, MeO × 2), 3.85 (ddd, J=5, 8, 9.5, AHG H-3), 3.81 (3H, s, MeO), 3.64 (ddd, J=2, 5.5, 9.5 Hz, AHG H-5), 3.59 (ddd, J=4.5, 8.5, 9.5 Hz, AHG H-4), 3.43 (t, J=11.5 Hz, AHG H-1). ^{13}C-NMR (50.1 MHz, acetone-d_6) δ: 166.32 (TMG C-7), 165.35 (PMDG C-7), 164.71 (PMDG C-7′), 154.29 (3C), 154.08 (2C) (TMG C-3, C-5; PMDG C-5, C-3′, C-5′), 146.58 (PMDG C-4), 144.89 (PMDG C-3), 144.33 (PMDG C-4′), 143.69 (TMG C-4), 126.05, 125.85, 124.62 (PMDG C-1, C-1′; TMG C-1), 117.94 (PMDG C-2), 112.48 (PMDG C-6), 108.50, 108.07 (2C each, PMDG C-2′, C-6′; TMG C-2, C-6), 79.51 (AHG C-5), 76.53 (AHG C-3), 73.64 (AHG C-2), 71.83 (AHG C-4), 67.30 (AHG C-1), 65.17 (AHG C-6), 61.00, 60.73, 60.65 (MeO × 3), 56.76, 56.68 (2C), 56.61 (2C) (MeO × 5).

Decamethyl Derivative (7) of 2-*O*-Galloyl-6-*O*-trigalloyl-1,5-anhydro-D-glucitol (3a) White powder, $[\alpha]_D$ +12° (c=0.4, acetone). EI-MS m/z: 912 ($[M]^+$). IR ν_{max}^{KBr} cm^{-1}: 1730 (ester carbonyl), 1595. ^{1}H-NMR (400 MHz, acetone-d_6) δ: 7.77 (d, J=2 Hz, HMTG H-6′), 7.71 (d, J=2 Hz, HMTG H-2′), 7.63 (d, J=2 Hz, HMTG H-6), 7.58 (d, J=2 Hz, HMTG H-2), 7.51 (2H, s, HMTG H-2″, H-6″), 7.34 (2H, TMG H-2, H-6), 4.93 (ddd, J=5.5, 9.5, 11 Hz, AHG H-2), 4.76 (d, J=4 Hz, AHG OH at C-3), 4.70 (d, J=4 Hz, AHG OH at C-4), 4.68 (dd, J=2, 12 Hz, AHG H-6), 4.48 (dd, J=5, 12 Hz, AHG H-6), 4.09 (dd, J=5.5, 11.5 Hz, AHG H-1), 4.05, 4.00 (3H each, s, MeO × 2), 3.94 (6H, s, MeO × 2), 3.93, 3.88 (3H each, s, MeO × 2), 3.87 (6H, s, MeO × 2), 3.85 (3H, s, MeO), 3.83 (in part overlapped by methoxyl signals, AHG H-3), 3.80 (3H, s, MeO), 3.67—3.57 (2H, m, AHG H-4, H-5), 3.41 (t, J=11 Hz, AHG H-1).

Decamethyl Derivative (8) of 2,6-Bis-*O*-digalloyl-1,5-anhydro-D-glucitol (3b) White powder, $[\alpha]_D$ +7° (c=0.4, acetone). EI-MS m/z: 912 ($[M]^+$). IR ν_{max}^{KBr} cm^{-1}: 1730 (ester carbonyl), 1595. ^{1}H-NMR (400 MHz, acetone-d_6) δ: 7.62, 7.61 (1H each, d, J=2 Hz, PMDG H-6 × 2), 7.54, 7.52 (1H, each, d, J=2 Hz, PMDG H-2), 7.49, 7.48 (2H each, s, PMDG H-2′, H-6′), 4.95 (ddd, J=5.5, 9.5, 11 Hz, AHG H-2), 4.84 (d, J=4 Hz, AHG OH at C-3), 4.70 (d, J=4 Hz, AHG OH at C-4), 4.68 (dd, J=2, 12 Hz, AHG H-6), 4.47 (dd, J=5.5, 12 Hz, AHG H-6), 4.11 (dd, J=5.5, 11 Hz, AHG H-1), 4.00, 3.98 (3H each, s, MeO × 2), 3.94, 3.93 (6H each, s, MeO × 4), 3.88, 3.87, 3.86, 3.85 (3H each, s, MeO × 4), 3.83 (in part overlapped by methoxyl signals, AHG H-3), 3.66—3.57 (2H, m, AHG H-4, H-5), 3.42 (t, J=11 Hz, AHG H-1).

Decamethyl Derivative (9) of 6-*O*-Galloyl-2-*O*-trigalloyl-1,5-anhydro-D-glucitol (3c) White powder, $[\alpha]_D$ +8° (c=0.4, acetone). EI-MS m/z: 912 ($[M]^+$). IR ν_{max}^{KBr} cm^{-1}: 1730 (ester carbonyl), 1595. ^{1}H-NMR (400 MHz, acetone-d_6) δ: 7.76 (d, J=2 Hz, HMTG H-6′), 7.71 (d, J=2 Hz, HMTG H-2′), 7.63 (d, J=2 Hz, HMTG H-6), 7.57 (d, J=2 Hz, HMTG H-2), 7.51 (2H, s, HMTG H-2″, H-6″), 7.34 (2H, TMG H-2, H-6), 4.95 (ddd, J=5.5, 9.5, 11 Hz, AHG H-2), 4.90 (d, J=4 Hz, AHG OH at C-3), 4.76 (d, J=4 Hz, AHG OH at C-4), 4.67 (dd, J=2, 12 Hz, AHG H-6), 4.46 (dd, J=5, 12 Hz, AHG H-6), 4.12 (dd, J=5.5, 11 Hz, AHG H-1), 4.04, 4.00 (3H each, s, MeO × 2), 3.94 (6H, s, MeO × 2), 3.93 (3H, s, MeO), 3.89 (6H, s, MeO × 2), 3.88, 3.86 (3H each, s, MeO × 2), 3.83 (in part overlapped by methoxyl signals, AHG H-3), 3.80 (3H, s, MeO), 3.63 (ddd, J=2, 5.5, 9.5 Hz, AHG H-5), 3.59 (dt, J=4, 9.5 Hz, AHG H-4), 3.42 (t, J=11 Hz, AHG H-1).

Isolation of Phenolic Constituents from *A. saccharum* Leaves (5.3 g) of *A. saccharum*, stored in a freezer, were homogenized in MeOH (500 ml and then 25 ml). After centrifugation, the combined supernatant was extracted with light petroleum (boiling in the range of 60—90 °C), and the mother liquor was concentrated to 10 ml *in vacuo*. Water was added to the concentrated solution, and extracted with ethyl acetate (60 ml × 9). The ethyl acetate extract (330 mg) thus obtained was chromatographed on Sephadex LH-20 (1.1 × 40 cm) with 70% EtOH, to separate fr. 1—3. Fraction 1 (41 mg) was further separated by HPLC using solvent B, to give chlorogenic acid (7 mg) and quercitrin (10 mg). Fraction 2 and fr. 3 afforded **10** (80 mg) and **11** (29 mg), respectively.

Davidiin (11)[11] A light brown amorphous powder, $[\alpha]_D$ +37° (c=0.7, MeOH). ^{1}H-NMR (90 MHz, acetone-d_6) δ: 7.17—7.16 (4H, galloyl × 2), 7.11 (2H, s, galloyl), 6.87—6.86 [2H, hexahydroxydiphenoyl (HHDP)], 6.12 [d, J=2.5 Hz, glu (glucose) H-1], 5.79 (t, J=7 Hz, H-3), 5.52 (dd, J=2.5, 7 Hz, H-2), 5.21 (br d, J=7 Hz, H-4), 5.0—4.3 (3H, m, H-6 × 2, H-5). Treatment of **11** with acetic anhydride and pyridine afforded pentadecaacetate, ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.75 (4H, s, 3,4,5-triacetoxybenzoyl × 2), 7.72 (2H, s, 3,4,5-triacetoxybenzoyl), 7.70, 7.45 (1H each, s, hexa-*O*-acetyl derivative of HHDP), 6.23 (d, J=2.5 Hz, glu H-1), 5.85 (t, J=6 Hz, glu H-3), 5.43 (dd, J=2.5, 6 Hz, glu H-2), 5.07 (dd, J=2, 6 Hz, glu H-4), 4.79 (t, J=11.5 Hz, glu H-6), 4.64 (br dd, J=5, 12 Hz, glu H-5), 4.51 (dd, J=5, 11 Hz, glu H-6), 2.3—2.0 (AcO × 15).

Acknowledgements We thank the staff of Kyoto Herbal Garden of Takeda Chemical Industries for the kind gift of the leaves of *A. saccharum*, and the staff of Handayama Botanical Garden for permission to collect the leaves of *A. ginnala*. We also thank Assoc. Prof. Y. Takeda and Mr. K. Kida, Faculty of Pharmaceutical Sciences, Tokushima University, for the 50.1 MHz ^{13}C-NMR spectra. The Varian VXR-500 instrument used in this study was the property of the SC-NMR Laboratory of Okayama University.

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