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Tannins of *Coriaria japonica* A. GRAY. II.[1] Coriariins C, D, E and F, New Dimeric and Monomeric Hydrolyzable Tannins

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Three new dimeric hydrolyzable tannins, named coriariins C (**3**), D (**4**) and E (**5**), and a new monomeric tannin, coriariin F (**6**), have been isolated from the leaves of *Coriaria japonica* A. GRAY along with rugosin B (**7**), gemin D (**8**) and strictinin, and the structures of the new tannins have been established upon the basis of chemical and spectroscopic evidence.

Keywords——tannin; ellagitannin; dimeric hydrolyzable tannin; Coriariaceae; Rosaceae; *Coriaria japonica*; coriariin C; coriariin D; coriariin E; coriariin F

The isolation of nine hydrolyzable tannins including coriariins A (**1**) and B (**2**), from the leaves of *Coriaria japonica* A. GRAY (Coriariaceae), and the structure elucidation of **1** and **2**, were reported previously.[1] We now report the isolation of seven additional tannins including three new dimeric hydrolyzable tannins named coriariins C (**3**), D (**4**), E (**5**) and a new monomeric tannin named coriariin F (**6**) from the leaves, and the structures of these new tannins.

A portion of the *n*-butanol extract of the leaves was chromatographed over Toyopearl HW-40 and afforded coriariins C (**3**) and D (**4**). Another portion of the extract was submitted to column chromatography on Sephadex LH-20 and then to centrifugal partition chromatography (CPC),[2] and the fractions containing tannins were further purified by column chromatography on Sephadex LH-20 and Toyopearl HW-40, to give coriariins E (**5**) and F (**6**), along with rugosin B (**7**),[3] gemin D (**8**)[4] and strictinin.[5]

Coriariin F (**6**), $C_{34}H_{26}O_{23} \cdot 7H_2O$, $[\alpha]_D$ +82°, was obtained as an off-white amorphous powder. The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum of **6** (in acetone-d_6 + D_2O) indicates that coriariin F forms an anomer mixture in a ratio of 3 : 2 (α : β) as shown by the dual peaks of each proton; the signals of a galloyl group (δ 7.06, 1.2H, s; 7.05, 0.8H, s) and a valoneoyl group (δ 7.161, 6.49, 6.24, 0.6H each, s; 7.155, 6.48, 6.25, 0.4H each, s) are observed. The chemical shifts and the coupling constants of glucose protons (Table I) show close similarity to those of gemin D (**8**)[4]; the chemical shift of H-2 of the α-anomer of **6** indicates that the hydroxyl group at C-2 of the glucose core is not acylated, and those of H-4, H_a-6 and H_b-6 show that the hexahydroxydiphenoyl (HHDP) part of the valoneoyl group in **6** is located at *O*-4 and *O*-6 of the glucose core.[3,6] Thus the galloyl group should be at *O*-3. The circular dichroic (CD) spectrum of 6 shows a distinctive positive Cotton effect in the short-wavelength region ($[\theta]_{225}$ $+11.9 \times 10^4$), indicating *S*-configuration[7] of the biphenyl moiety of the valoneoyl group. Coriariin F was produced through rugosin B (**7**), by partial hydrolysis of rugosin A (**9**) with tannase. These results led to the structure **6**, 3-*O*-galloyl-4,6-*O*-[(*S*)-valoneoyl]-D-glucose, for coriariin F.

Coriariin C (**3**), $C_{89}H_{62}O_{57} \cdot 14H_2O$, $[\alpha]_D$ +99°, was obtained as a light brown amorphous powder. The ^{1}H-NMR spectrum of **3** (in acetone-d_6) shows the presence of four galloyl groups (δ 7.01, 6.99, 6.968 and 6.965, 2H each, s), a dehydrodigalloyl (DHDG) group (δ 7.23,

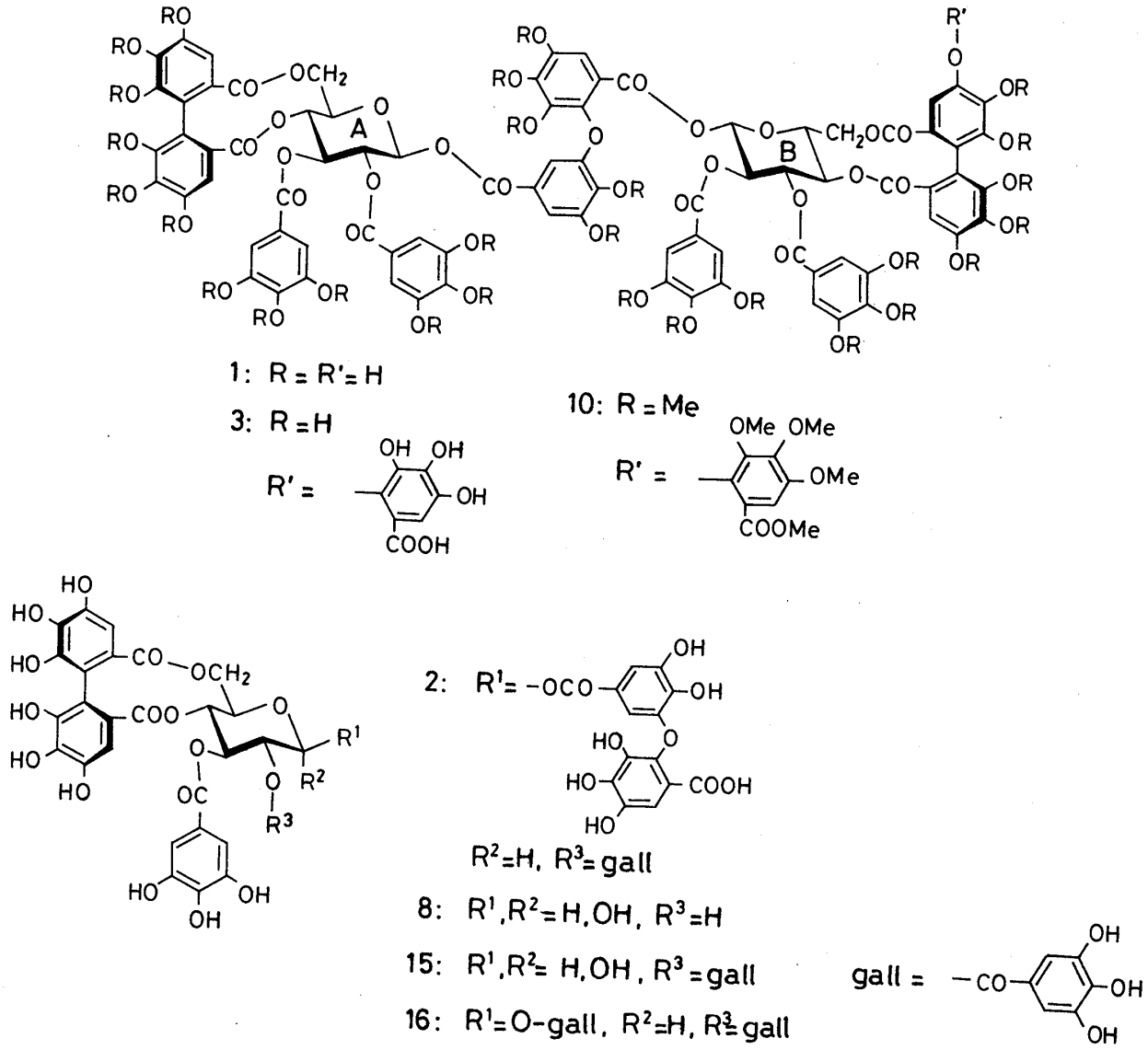

Chart 1

1H, d, J=2 Hz; 7.17, 1H, s; 6.68, 1H, d, J=2 Hz). a valoneoyl group and an HHDP group (δ 7.15, 6.66, 6.46, 6.45 and 6.36, 1H each, s) in **3**. The signals of two β-glucopyranose cores (Table II) of *C1* conformation are also observed. The chemical shifts of the glucose protons, which are similar to those of coriariin A (**1**),[1] indicate that the location of each polyphenolic group is analogous to that in **1**. Thus, the structure in which a valoneoyl group substitutes for one of the HHDP groups in **1** was assigned for coriariin C (**3**).

Treatment of **3** with dimethyl sulfate and potassium carbonate afforded hentriaconta-*O*-methylcoriariin C monomethyl ester (**10**), $C_{121}H_{126}O_{57}$, $[\alpha]_D$ +31°, which was methanolyzed to methyl tri-*O*-methylgallate (**11**), dimethyl hexamethoxydiphenate (**12**), dimethyl ester of penta-*O*-methyldehydrodigallic acid [=methyl 2-(2,3-dimethoxy-5-methoxycarbonylphenoxy)-tri-*O*-methylgallate] (**13**), trimethyl octa-*O*-methylvaloneate (**14**) and D-glucose. This result also shows the presence of galloyl, HHDP, DHDG and valoneoyl groups, and D-glucose cores in **3**. Partial hydrolysis of **3** afforded rugosin B (**7**), coriariin B (**2**), and a small amount of tellimagrandin I (**15**), which can be regarded as a hydrolysis product of **2**. This result clearly indicates the location of each acyl group on the glucose cores of **3**.

Therefore, coriariin C has the structure **3**, in which the free carboxyl group of the DHDG

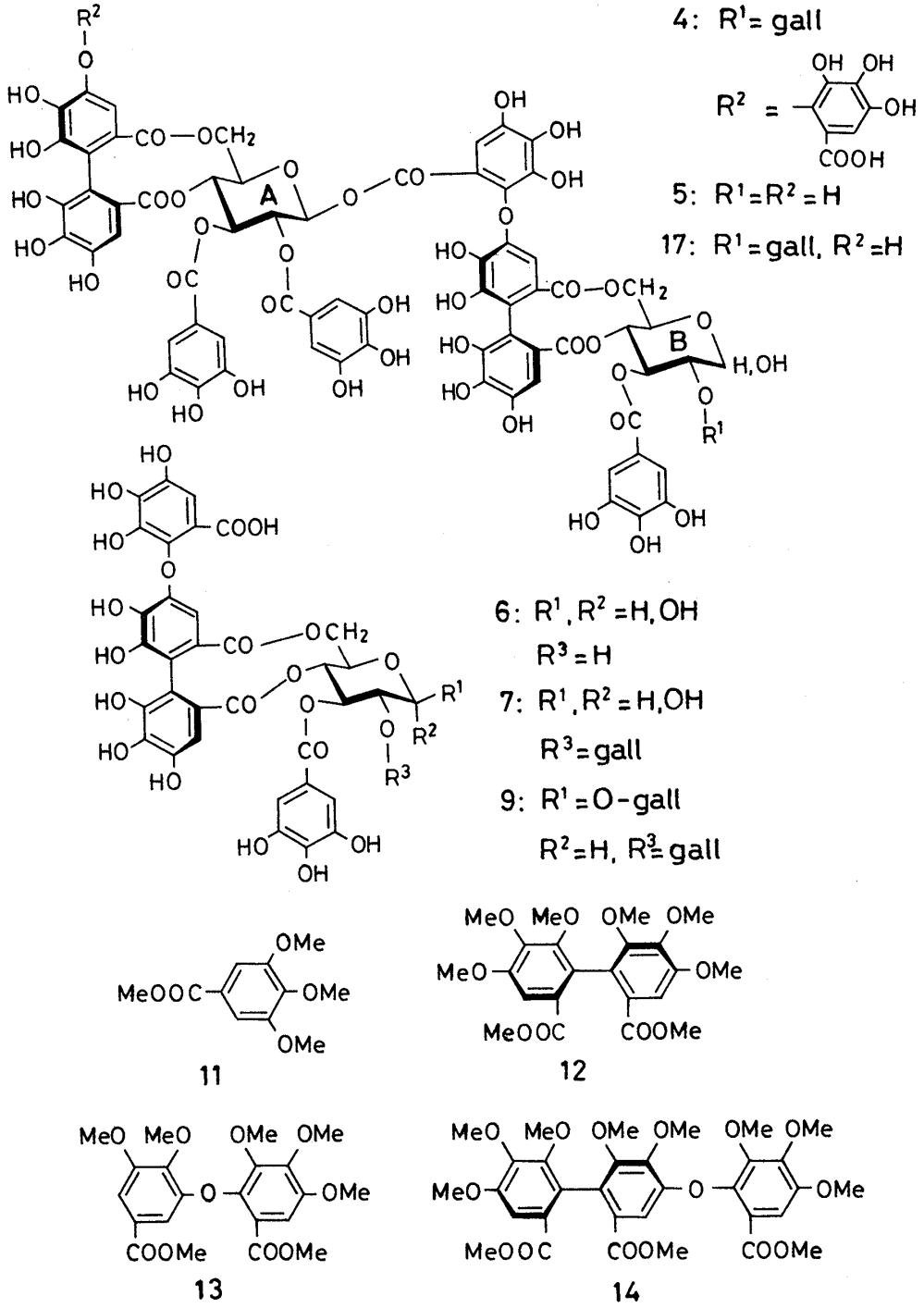

Chart 2

group of **2** forms an ester linkage with the anomeric hydroxyl group of **7**. The *S*-configurations of the HHDP group and the valoneoyl group in **3** are indicated by the productions of **2** and **7** upon partial hydrolysis. The positive Cotton effect around 230 nm which shows amplitude ($[\theta]_{231}$ $+35.1\times10^4$) corresponding to the sum of that of rugosin A (**9**) ($[\theta]_{227}$ $+18.6\times10^4$) and that of tellimagrandin II (**16**) ($[\theta]_{234}$ $+13.5\times10^4$), also substantiates the *S*-configurations of these two groups. Coriariin C is the first example of a dimeric tannin which has both valoneoyl and DHDG groups in the molecule.

Coriariin D (**4**), $C_{82}H_{58}O_{53}\cdot7H_2O$, $[\alpha]_D$ $+117°$, has been obtained as a light brown amorphous powder. Although coriariin D shows complicated peaks in its ^{1}H-NMR spectrum

TABLE I. ^{1}H-NMR Spectral Data for the Glucose Moiety in Coriariin F (**6**) (400 MHz, in acetone-d_6 + D_2O, J in Hz)

	α-Anomer[a]	β-Anomer[a]
H-1	5.21 (d, J=4)	4.71 (d, J=7.5)
H-2	3.81 (dd, J=4, 10)	3.6[b]
H-3	5.47 (t, J=10)	5.30 (t, J=10)
H-4	4.90 (t, J=10)	4.93 (t, J=10)
H-5	4.51 (dd, J=6.5, 10)	4.06 (dd, J=6.5, 10)
H_a-6	5.15 (dd, J=6.5, 13)	5.17 (dd, J=6.5, 13)
H_b-6	3.65 (d, J=13)	3.71 (d, J=13)

a) The ratio of anomers, α : β is 3 : 2. *b*) H-2 of the β-anomer overlaps the HDO signals at around 3.6 ppm.

TABLE II. ^{1}H-NMR Spectral Data for the Glucose Moiety in Coriariin C (**3**) (200 MHz, in acetone-d_6, J in Hz)

	Glucose core A[a]	Glucose core B[b]
H-1	6.10 (d, J=8)	6.01 (d, J=8)
H-2	5.55 (dd, J=8, 10)	5.51 (dd, J=8, 10)
H-3	5.82 (t, J=10)	5.76 (t, J=10)
H-4	5.19 (t, J=10)	5.10 (t, J=10)
H-5	4.52 (dd, J=6, 10)	4.42 (dd, J=6, 10)
H_a-6	5.33 (dd, J=6, 13)	5.25 (dd, J=6, 13)
H_b-6	3.84 (d, J=13)	3.69 (d, J=13)

a) Left glucose core of the formula **3** in Chart 1. *b*) Right glucose core of the formula **3** in Chart 1.

TABLE III. ^{1}H-NMR Spectral Data for the Glucose Moiety in Coriariin D (**4**) (400 MHz, in acetone-d_6, J in Hz)

	α-Anomer[a]	β-Anomer[a]
Glucose core A[b]		
H-1	6.13 (d, J=8)	6.12 (d, J=8)
H-2	5.54 (dd, J=8, 10)	5.52 (dd, J=8, 10)
H-3	5.78 (t, J=10)	5.78 (t, J=10)
H-4	5.12 (t, J=10)	5.11 (t, J=10)
H-5	4.47 (dd, J=6.5, 10)	4.45 (dd, J=6.5, 10)
H_a-6	5.26 (dd, J=6.5, 13)	5.25 (dd, J=6.5, 13)
H_b-6	3.75 (d, J=13)	3.75 (d, J=13)
Glucose core B[c]		
H-1	5.56 (d, J=3.5)	5.10 (d, J=8)
H-2	5.16 (dd, J=3.5, 10)	5.29 (dd, J=8, 10)
H-3	5.88 (t, J=10)	5.62 (t, J=10)
H-4	5.04 (t, J=10)	5.06 (t, J=10)
H-5	4.65 (dd, J=6.5, 10)	4.26 (dd, J=6.5, 10)
H_a-6	5.21 (dd, J=6.5, 13)	5.22 (dd, J=6.5, 13)
H_b-6	3.66 (d, J=13)	3.74 (d, J=13)

a) The ratio of anomers, α : β is 3 : 2. *b*) Left glucose core of the formula **4** in Chart 2. *c*) Right glucose core of the formula **4** in Chart 2.

(in acetone-d_6) due to formation of an anomeric mixture in a ratio of 3 : 2 (α : β), the signals of two valoneoyl groups (δ 7.17, 1H, s; 7.14, 0.6H, s; 7.13, 0.4H, s; 6.48, 0.6H, s; 6.47, 1H, s; 6.46, 0.4H, s; 6.34, 0.6H, s; 6.33, 0.4H, s; 6.223, 0.6H, s; 6.217, 0.4H, s) and four galloyl groups (δ 7.09, 1.2H, s; 7.08, 0.8H, s; 7.023, 1.2H, s; 7.017, 1.2H, s; 7.01, 0.8H, s; 6.99, 2H, s; 6.98, 0.8H, s) are observed. A pair of doublets (δ 6.13, 0.6H, d, J=8 Hz; 6.12, 0.4H, d, J=8 Hz) of an anomeric proton indicates that one of the two anomeric hydroxyl groups is acylated and β-oriented, and the signals of the other glucose protons (Table III) form a pattern analogous to that of rugosin E (**17**).[8] Thus, the structure **4**, in which a valoneoyl group substitutes for the HHDP group of **17**, is assigned.

Partial hydrolysis of coriariin D (**4**) afforded rugosin B (**7**), and quantitative analysis by high-performance liquid chromatography (HPLC) showed that 1 mol of **4** gives approximately 2 mol of **7**. Therefore, the structure **4** of coriariin D, in which the carboxyl group of **7** forms an ester linkage with the β-anomeric hydroxyl group of another molecule of **7**, has been established. The results of partial hydrolysis, and the positive Cotton effect in the short-

TABLE IV. ^{1}H-NMR Spectral Data for the Glucose Moiety in Coriariin E (**5**) (400 MHz, in acetone-d_6, J in Hz)

	α-Anomer[a]	β-Anomer[b]
Glucose core A[b]		
H-1	6.14 (d, J=8)	6.15 (d, J=8)
H-2	5.55 (dd, J=8, 10)	5.55 (dd, J=8, 10)
H-3	5.81 (t, J=10)	5.81 (t, J=10)
H-4	5.17 (t, J=10)	5.17 (t, J=10)
H-5	4.50 (dd, J=6.5, 10)	4.50 (dd, J=6.5, 10)
H_a-6	5.33 (dd, J=6.5, 13)	5.33 (dd, J=6.5, 13)
H_b-6	3.82 (d, J=13)	3.82 (d, J=13)
Glucose core B[c]		
H-1	5.25 (d, J=3.5)	4.75 (d, J=7.5)
H-2	3.82 (dd, J=3.5, 10)	3.62 (dd, J=7.5, 10)
H-3	5.49 (t, J=10)	5.32 (t, J=10)
H-4	4.89 (t, J=10)	4.93 (t, J=10)
H-5	4.52 (ddd, J=1, 6.5, 10)	4.08 (dd, J=6.5, 10)
H_a-6	5.19 (dd, J=6.5, 13)	5.20 (dd, J=6.5, 13)
H_b-6	3.63 (dd, J=1, 13)	3.69 (d, J=13)

a) The ratio of anomers, α:β is 3:2. *b*) Left glucose core of the formula **5** in Chart 2. *c*) Right glucose core of the formula **5** in Chart 2.

wavelength region of the CD spectrum, of which the amplitude ($[\theta]_{224}$ $+26.9\times10^4$) is twice that of rugosin B ($[\theta]_{220}$ $+14.3\times10^4$), indicate the *S*-configuration of the two valoneoyl groups in **4**.

Coriariin E (**5**), $C_{68}H_{50}O_{44}\cdot10H_2O$, $[\alpha]_D$ +91°, forms a light brown amorphous powder. The fast atom bombardment mass spectrum (FAB-MS) of **5** shows the $[M+Na]^+$ ion at m/z 1593. The formation of an anomeric mixture in a ratio of 3:2 (α:β) is indicated by the dual peaks for each proton in the ^{1}H-NMR spectrum (in acetone-d_6); protons of three galloyl groups (δ 7.05, 2H, s; 7.03, 1.2H, s; 7.02, 0.8H, s; 6.980, 0.8H, s; 6.978, 1.2H, s), a valoneoyl group and an HHDP group (δ 7.15, 6.671, 6.465, 6.442, 6.233, 0.6H each, s; 7.14, 6.674, 6.467, 6.437, 6.231, 0.4H each, s), and of two glucose cores adopting the *C1* conformation (Table IV) are observed. A pair of doublets of an anomer proton at δ 6.15 (0.4H, d, J=8 Hz) and 6.14 (0.6H, d, J=8 Hz) indicate that one of the anomeric hydroxyl groups in **5** is acylated and β-oriented, and the other anomeric hydroxyl group is not acylated, as shown by a pair of doublets at δ 5.25 (0.6H, d, J=3.5 Hz, α-anomer) and 4.75 (0.4H, d, J=7.5 Hz, β-anomer). The chemical shifts of the signals of H-2 (δ 3.82, 0.6H, dd, J=3.5, 10 Hz, α-anomer; δ 3.62, 0.4H, dd, J=8, 10 Hz, β-anomer), which couple with the signals of H-1 at higher field (δ 5.25 and 4.75), indicate that the hydroxyl group at C-2 of the glucose core having the free anomeric hydroxyl group, is not acylated. The chemical shifts of H-4, H_a-6 and H_b-6 of the two glucose cores (Table IV) show that the HHDP group and the valoneoyl group are located at *O*-4 and *O*-6 of the glucose cores, by analogy with those of tellimagrandin II (**16**)[6] and gemin D (**8**).[4]

The large amplitude of the positive Cotton effect in the short-wavelength region ($[\theta]_{229}$ $+19.1\times10^4$) of the CD spectrum of **5** indicates that both the HHDP group and the valoneoyl group have the *S*-configuration. The production of tellimagrandin I (**15**) and coriariin F (**6**) upon partial hydrolysis of coriariin E, combined with the results described above, leads to the structure **5** of coriariin E.

Among the tannins isolated from *C. japonica*, seven tannins, namely 1,2,3-tri-*O*-galloyl-β-D-glucose,[1] tellimagrandins I[1] and II,[1] and rugosins A,[1] B, D[1] and E,[1] have been isolated from *R. rugosa*.[3,8] The results obtained by the present investigation may provide a chemical basis for estimating the taxonomical relationship of Coriariaceae and Rosaceae.

Experimental

Optical rotations were measured on a JASCO DIP-4 polarimeter. Ultraviolet (UV) spectra were recorded on a Hitachi 200-10 spectrophotometer and infrared (IR) spectra on a JASCO A-102 spectrometer. FAB-MS were recorded on a JEOL JMS-D300 machine and electron impact mass spectra (EI-MS) on a Shimadzu LKB-9000 GC-MS spectrometer. CD spectra were recorded on a JASCO J-500A spectropolarimeter equipped with a DP-501 data processor. ^{1}H-NMR spectra were measured on a Hitachi R-22FTS (90 MHz), a JEOL FX-200 (200 MHz) or a Bruker AM-400 (400 MHz) instrument, with tetramethylsilane as an internal standard; chemical shifts are given in δ values (ppm). Gas liquid chromatography (GLC) was performed on a Hitachi 163 gas chromatograph equipped with a glass column (3 mm × 2 m) packed with 2.5% OV-17 on Chromosorb W. HPLC was run on a column of YMC A312 (ODS, 6 × 150 mm, Yamamura Chemical Laboratories Co., Ltd., Kyoto, Japan), with 0.1 M KH_2PO_4 aq.–0.1 M H_3PO_4 aq.–ethanol–ethyl acetate (10 : 10 : 2 : 1, by volume), at 40 °C in an oven. Detection was effected by UV absorption measurement at 254 nm. Analytical and preparative thin layer chromatography (TLC) were performed on Avicel SF (Funakoshi) cellulose plates with the following solvent systems; (A) *n*-butanol–*n*-propanol–H_2O (2 : 1 : 3, upper layer), (B) 7% acetic acid and (C) *n*-butanol–*n*-propanol–H_2O (4 : 1 : 5, upper layer), or on Kieselgel PF_{254} (Merck) plates with the following solvent systems; (D) benzene–acetone (5 : 1), (E) benzene–acetone (3 : 1) and (F) benzene–acetone (14 : 1). Spots were visualized under UV irradiation (254 nm), or by spraying the plates with $FeCl_3$ or $NaNO_2$ aq.–acetic acid reagent (for TLC on the cellulose plates). Sephadex LH-20 (100 μm, Pharmacia Fine Chemicals) and Toyopearl HW-40 (fine grade, Toyo Soda Mfg.) were used for column chromatography. CPC was performed on a centrifugal partition chromatograph, model L-90 (Sanki Engineering Ltd., Nagaoka-kyo, Kyoto, Japan), equipped with twelve column cartridges,[2] and developed with *n*-butanol–*n*-propanol–H_2O (4 : 1 : 5, normal-phase development) at 1000 rpm. Solvents were removed by evaporation under reduced pressure at below 40 °C.

Isolation of Tannins——A portion (6 g) of the *n*-butanol extract[1] obtained from the leaves of *Coriaria japonica* was chromatographed over Toyopearl HW-40 (2.2 × 70 cm), developing with ethanol–H_2O (7 : 3, fractions 1—200), and then ethanol–acetone–H_2O (13 : 1 : 6, fractions 201—300). Fractions of 12 g each were collected, yielding coriariin D (**4**, 85 mg, from fractions 176—194), coriariin C (**3**, 119 mg, from fractions 225—270) and coriariin A (**1**, 88 mg, from fractions 289—310). Another portion (40 g) of the *n*-butanol extract was chromatographed over Sephadex LH-20 (6 × 26 cm) with ethanol–H_2O (7 : 3) and then acetone–H_2O (7 : 3) as eluants. An aliquot (2.4 g) of the acetone–H_2O eluate was submitted to CPC, and afforded six fractions [fr. I, 0.14 g; fr. II, 0.3 g; fr. III, 0.75 g; fr. IV, 0.51 g; fr. V, 0.25 g; fr. VI (from the stationary phase), 0.27 g]. Fr. II (3.3 g), obtained from 26.6 g of the acetone–H_2O eluate, was further purifield by column chromatography on Sephadex LH-20 (ethanol) to afford rugosin B (**7**, 423 mg). Fr. V (2.8 g) of CPC was chromatographed over Sephadex LH-20 (2.2 × 70 cm) with ethanol–H_2O (7 : 3, fractions 1—134) and ethanol–acetone–H_2O (13 : 1 : 6, fractions 135—180), and 10 g fractions were colected. Combined fractions 151—180 gave coriariin E (**5**, 335 mg), and combined fractions 34—47 (815 mg) were submitted to column chromatography on Toyopearl HW-40 (1.1 × 70 cm) with ethanol–H_2O (2 : 8) and then ethanol–H_2O (3 : 7) as eluants. Coriariin F (**6**, 42 mg) was obtained from the ehtnaol–H_2O (2 : 8) eluate, and the ethanol–H_2O (3 : 7) eluate afforded gemin D (**8**, 142 mg) and strictinin[5] (104 mg).

Coriariin F (6)——An off-white amorphous powder, TLC (cellulose), *Rf* 0.43 (solvent system A), $[\alpha]_D$ +82° (c = 0.1, MeOH). *Anal.* Calcd for $C_{34}H_{26}O_{23} \cdot 7H_2O$: C, 43.97; H, 4.34. Found: C, 44.15; H, 4.22. UV λ_{max}^{MeOH} nm (log ε): 221 (4.84), 261 (4.53). IR ν_{max}^{KBr} cm^{-1}: 1730—1700 (ester carbonyl). CD (MeOH) [θ] (nm): +11.9 × 10^4 (225), +4.1 × 10^4 (238), −3.6 × 10^4 (260), +2.0 × 10^4 (285).

Partial Hydrolysis of Rugosin A (9) with Tannase——An aqueous solution (9 ml) of rugosin A (90 mg) was treated with tannase at 37 °C for 3.5 d. The resulting solution was acidified to pH 2 with 1% citric acid and then evaporated. The residue was chromatographed over Sephadex LH-20 (1.1 × 41 cm), with ethanol as an eluant, to give coriariin F (**6**, 26 mg).

Coriariin C (3)——A light brown amorphous powder, TLC (cellulose), *Rf* 0.43 (solvent system A), $[\alpha]_D$ +99° (c = 0.1, MeOH). *Anal.* Calcd for $C_{89}H_{62}O_{57} \cdot 14H_2O$: C, 46.57; H, 3.95, Found: C, 46.63; H, 4.15. UV λ_{max}^{MeOH} nm (log ε): 220 (5.24), 277 (4.93). IR ν_{max}^{KBr} cm^{-1}: 1740—1710 (ester carbonyl). CD (MeOH) [θ] (nm): +35.0 × 10^4 (231), −5.0 × 10^4 (263), +6.9 × 10^4 (285).

Methylation of Coriariin C (3)——A mixture of **3** (51 mg), dimethyl sulfate (125 μl) and potassium carbonate (260 mg) in dry acetone (3 ml) was stirred for 24 h at room temperature, and then refluxed for 1.5 h, and filtered. The resulting filtrate was evaporated. The residue was purified by preparative TLC on silica gel (solvent system D, developed twice) to give hentriaconta-*O*-methylcoriariin C monomethyl ester (**10**, 24 mg) as a white amorphous solid, TLC (silica gel), *Rf* 0.55 (solvent system E), $[\alpha]_D$ +31° (c = 0.1, acetone). *Anal.* Calcd for $C_{121}H_{126}O_{57}$: C, 58.31; H, 5.10. Found: C, 58.14; H, 5.39. IR ν_{max}^{KBr} cm^{-1}: 1760—1730 (ester carbonyl). EI-MS *m/z*: 614, 570 (octa-*O*-methylvaloneoyl); 422, 404 (penta-*O*-methyldehydrodigalloyl, hexamethoxydiphenoyl); 212, 197, 195 (tri-*O*-methylgalloyl). ^{1}H-NMR (200 MHz, acetone-d_6) δ: 7.22 (6H, s), 7.20 (2H, s) (tri-*O*-methylgalloyl); 7.38 (1H, s), 7.36 (1H, d, J = 2 Hz), 6.79 (1H, d, J = 2 Hz) (penta-*O*-methyldehydrodigalloyl); 7.28 (1H, s), 6.95 (1H, s), 6.77 (2H, s), 6.55 (1H, s) (octa-*O*-methylvaloneoyl and hexamethoxydiphenoyl); 6.23, 6.18 (1H each, d, J = 8 Hz, H-1 of both glucose cores), 5.89, 5.85 (1H each, t, J = 10 Hz, 2 × H-3), 5.63, 5.57 (1H each, dd, J = 8, 10 Hz, 2 × H-2), 5.31, 5.20 (1H each, t,

$J=10$ Hz, 2×H-4), 5.31, 5.18 (1H each, dd, $J=6$, 10 Hz, 2×H_a-6), 4.59, 4.48 (1H each, dd, $J=6$, 13 Hz, 2×H-5), 4.03—3.64 (32×OMe). The H_b-6 proton signals of both glucose cores overlap with the signals of the methoxyl groups.

Methanolysis of Hentriaconta-*O*-methylcoriariin C Monomethyl Ester (10)——A mixture of **10** (1 mg) in absolute methanol (0.5 ml) and 1% sodium methoxide (0.5 ml) was left to stand overnight at room temperature, then neutralized with acetic acid, and evaporated. The residue was partitioned between chloroform and H_2O. The chloroform layer was evaporated and the residue was purified by preparative TLC (silica gel, solvent system F) to give methyl tri-*O*-methylgallate (**11**), dimethyl hexamethoxydiphenate (**12**), dimethyl ester of penta-*O*-methyldehydrodigallic acid (**13**) and trimethyl octa-*O*-methylvaloneate (**14**), which were shown to be identical with authentic samples[1,3] by EI-MS and TLC. The aqueous layer afforded glucose, which was identified by GLC of the trimethylsilyl ether.

Partial Hydrolysis of Coriariin C (3)——An aqueous solution (10 ml) of coriariin C (20 mg) in a sealed tube was kept in a water bath (60 °C) for 63 h. The reaction mixture was concentrated and chromatographed over Sephadex LH-20 (1.1×33 cm), with ethanol–methanol (9 : 1) as an eluant, and 600-drop fractions were collected. Combined fractions 96—135 afforded coriariin B (**2**, 3 mg) and combined fractions 61—80 were further purified by preparative TLC (cellulose, solvent system B) to give rugosin B (**7**, 3 mg) and tellimagrandin I (**15**, 1.8 mg).

Coriariin D (4)——A light brown amorphous powder, TLC (cellulose), *Rf* 0.47 (solvent system A), $[\alpha]_D$ +117° ($c=0.1$, MeOH). *Anal.* Calcd for $C_{82}H_{58}O_{53}\cdot 7H_2O$: C, 48.82; H, 3.60. Found: C, 48.95; H, 3.87. UV λ_{max}^{MeOH} nm (log ε): 220 (5.15), 274 (4.82). IR ν_{max}^{KBr} cm^{-1}: 1740—1710 (ester carbonyl). CD (MeOH) [θ] (nm): $+25.6\times10^4$ (225), $+8.3\times10^4$ (240), -6.6×10^4 (259), $+9.1\times10^4$ (284).

Partial Hydrolysis of Coriariin D (4)——(1) An aqueous solution (8 ml) of **4** (16 mg) in a sealed tube was kept in a water bath (60 °C) for 22 h. The reaction mixture was concentrated and submitted to preparative TLC (cellulose, solvent system B) to afford rugosin B (**7**, 5 mg).

(2) An aqueous solution (1 ml) of **4** (2 mg) in a sealed tube was kept in a water bath (60 °C) for 21 h, and the reaction mixture was analyzed by HPLC, which demonstrated the production of 1.7 mol of **7** from 1 mol of **4**.

Coriariin E (5)——A light brown amorphous powder, TLC (cellulose), *Rf* 0.42 (solvent system A), $[\alpha]_D$ +91° ($c=0.1$, MeOH). *Anal.* Calcd for $C_{68}H_{50}O_{44}\cdot 10H_2O$: C, 46.64; H, 4.03. Found: C, 46.90; H, 4.05. FAB-MS *m/z*: 1593 ($[M+Na]^+$). UV λ_{max}^{MeOH} nm (log ε): 221 (5.11), 261 (4.80). IR ν_{max}^{KBr} cm^{-1}: 1730—1710 (ester carbonyl). CD (MeOH) [θ] (nm): $+19.1\times10^4$ (229), -5.8×10^4 (260), $+6.7\times10^4$ (282).

Partial Hydrolysis of Coriariin E (5)——An aqueous solution (12.5 ml) of **5** (25 mg) in a sealed tube was kept in a water bath (65 °C) for 27 h, and then evaporated. The residue was submitted to preparative TLC (cellulose, solvent system C) to yield coriariin F (**6**, 12 mg) and tellimagrandin I (**15**, 10 mg).

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