Tannins of *Coriaria japonica* A. GRAY. III.[1] Structures of Coriariins G, H, I and J

Tsutomu HATANO,[a] Rieko YOSHIHARA,[a] Shin HATTORI,[a] Masao YOSHIZAKI,[b] Tetsuro SHINGU[c] and Takuo OKUDA*,[a]

Faculty of Pharmaceutical Sciences, Okayama University,[a] Tsushima, Okayama 700, Japan, Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University,[b] Sugitani, Toyama 930–01, Japan, and Faculty of Pharmaceutical Sciences, Kobe Gakuin University,[c] Ikawa-dani, Nishi-ku, Kobe 673, Japan. *Received November 29, 1991*

Four new hydrolyzable tannins, coriariins G, H, I and J, were isolated from the leaf of *Coriaria japonica* (Coriariaceae). Structures 1, 2 and 3, having a sedoheptulose residue, were assigned for coriariins G, H and I, respectively. Structure 4, having a depsidone-forming dehydrodigalloyl group, was assigned for coriariin J, based on the chemical correlation with coriariin B (5). The orientation of the dehydrodigalloyl group in 5 was confirmed by ^{1}H–^{13}C long-range shift-correlation spectroscopy.

Keywords tannin; hydrolyzable tannin; coriariin G; coriariin H; coriariin I; coriariin J; *Coriaria japonica*; sedoheptulose; depsidone; dehydrodigalloyl group

The leaf of *Coriaria japonica* A. GRAY (Coriariaceae) is rich in tannins.[2] We previously isolated sixteen hydrolyzable tannins from the leaf, and elucidated the structures of six new tannins among them.[1,2] Antitumor and antiviral activities of some tannins isolated from the leaf of *C. japonica* have also been revealed.[3,4] In a further investigation, we have isolated four additional new tannins named coriariins G (**1**), H (**2**), I (**3**) and J (**4**) from the leaf, and elucidated their structures.

Results and Discussion

The new tannins were isolated in the following way. Concentrated filtrate from the aqueous acetone homogenate of the leaf of *C. japonica* was extracted with $CHCl_3$, EtOAc and *n*-BuOH, successively. The *n*-BuOH extract thus obtained was chromatographed on Sephadex LH-20, and a tannin-rich fraction was fractionated by centrifugal partition chromatography (CPC).[5] Each CPC fraction was further chromatographed on Sephadex LH-20, to give coriariins G (**1**), H (**2**) and I (**3**). The EtOAc extract was similarly chromatographed on Toyopearl HW-40C, and then on MCI-gel CHP-20P. Preparative high-performance liquid chromatography (HPLC) of a fraction from the MCI-gel chromatography gave coriariin J (**4**).

Structure of Coriariin J Coriariin J (**4**) was obtained as an off-white powder. The following data suggested that coriariin J has a structure closely related to that of coriariin B (**5**).[2] The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum of **4** showed signals assignable to two galloyl groups [δ 6.99 and 6.96 (2H each, s)], a hexahydroxy-

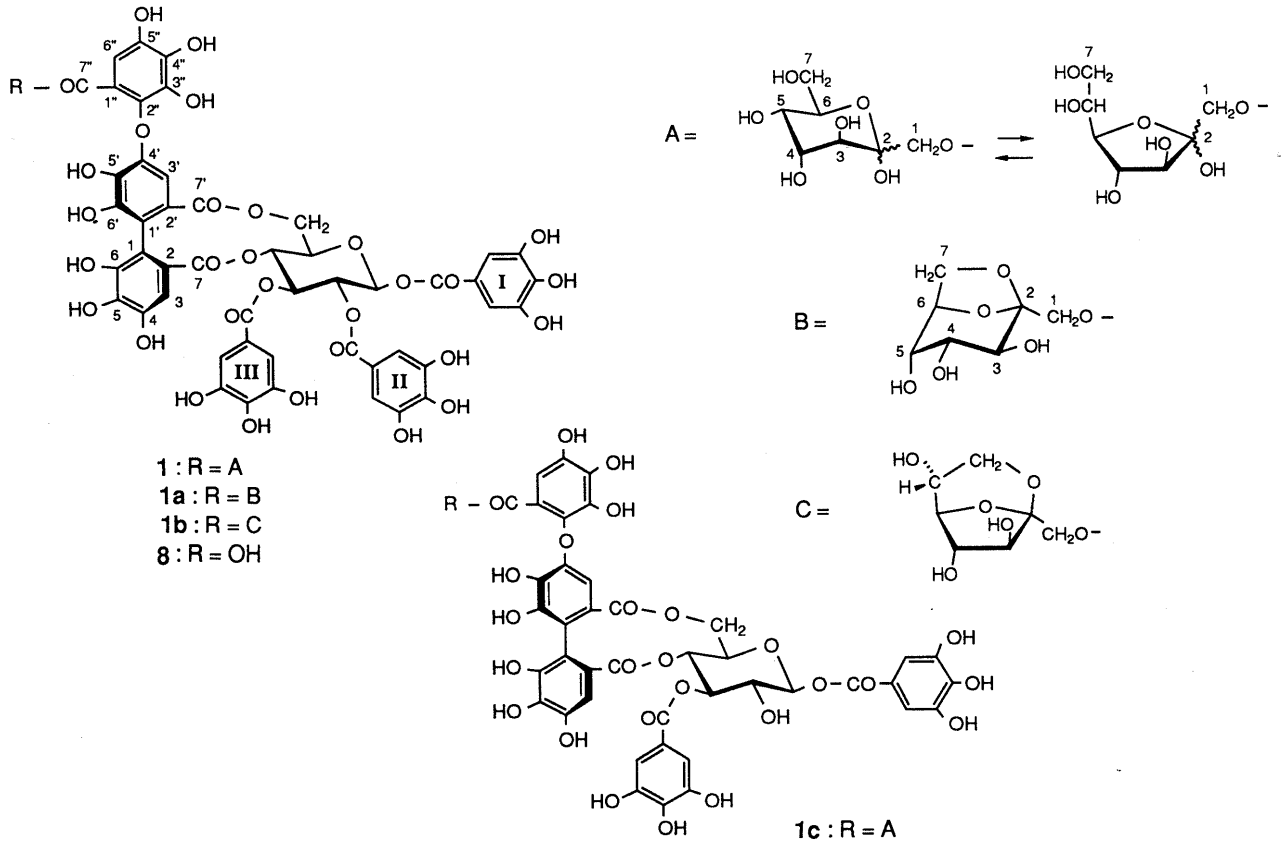


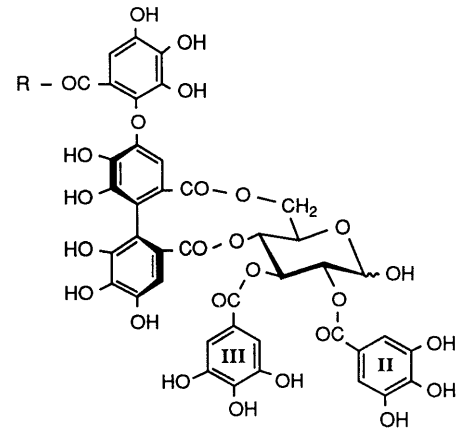
Chart 1

diphenoyl (HHDP) group [δ 6.65 and 6.46 (1H each, s)], a dehydrodigalloyl (DHDG) group [δ 7.69 (1H, d, J=2 Hz), 7.45 (1H, d, J=2 Hz) and 6.88 (1H, s)] and a β-glucopyranose core in the $^4C_1$ conformation (see Experimental). The chemical shifts of the glucose protons indicate that all of the five hydroxyl groups of the glucopyranose core are acylated. The large difference [$\Delta\delta$ 1.48 (ppm)] in the chemical shifts of the two H-6 protons of the $^4C_1$ glucopyranose core is attributable to the location of the HHDP group at O-4/O-6 of glucose.[6] The circular dichroism (CD) spectrum of **4** showed a positive Cotton effect in the short-wavelength region ($[\theta]_{224}$ $+1.2\times10^5$), indicating the *S*-configuration[7] of the HHDP group.

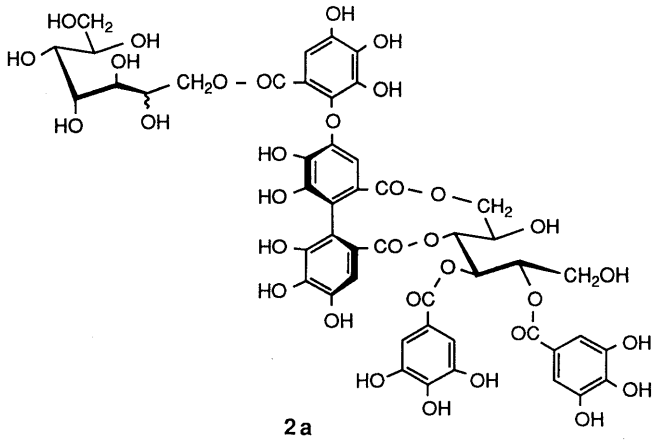
Coriariin J (**4**) was transformed into **5**, when kept in a phosphate buffer of pH 5.8 at 37 °C. The $[M+Na]^+$ ion peak of **4** at m/z 1111, indicating its molecular formula to be $C_{48}H_{32}O_{30}$, was apparent in the fast-atom bombardment mass spectrum (FAB-MS), while that of **5** was observed at m/z 1129, which is 18 mass units (H_2O) larger. Downfield shifts of H-2 and H-6 of the DHDG group in the ^{1}H-NMR spectrum of **4** (δ 7.45 and 7.69) from those of **5** (δ 6.80 and 7.21), and an upfield shift of H-6′ of the DHDG group of **4** (δ 6.88) from that of **5** (δ 7.17) suggested that the free carboxyl group in the DHDG group of **5** is depsidically[8,9] linked to the phenolic hydroxyl group at C-4 of the DHDG group in **4**.

In order to confirm the location of the depside linkage in **4**, the ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectral data of **4** and **5** were compared with each other in the following way.

Although the assignments of the ^{13}C signals of **5** were reported in a previous paper,[2] the present study revealed that the assignments for C-2 and C-6 of the DHDG group should be interchanged. The one-bond and long-range ^{1}H–^{13}C shift-correlation spectra of **5** showed cross peaks indicating the correlations summarized in Table I. The previous assignments of the signals of C-1′—C-6′ of the DHDG group are consistent with the observed correlation with H-6′ (Table I), and the chemical shifts of these carbons are practically the same as those reported for the galloyl moiety of the valoneoyl group.[10] Among the carbon signals for C-1—C-6 of the DHDG group, the carbon signal at δ 148.2 was assigned to C-3, based on the distinctive downfield shift from the oxygen-bearing carbons of the galloyl group (*i.e.*, galloyl C-3—C-5).[8] The proton signal at δ 6.80 was therefore assigned to be that of H-2, based on the cross peak of C-3—H-2 (δ_C 148.2—δ_H 6.80) in the long-range ^{1}H–^{13}C correlation spectrum. Accordingly, the proton signal at δ 7.21 which coupled with that at δ 6.80 was assigned to H-6. The cross peaks of δ_C 108.4—δ_H 6.80 and δ_C 112.2—δ_H 7.21 in the one-bond ^{1}H–^{13}C correlation spectrum thus indicated that the ^{13}C

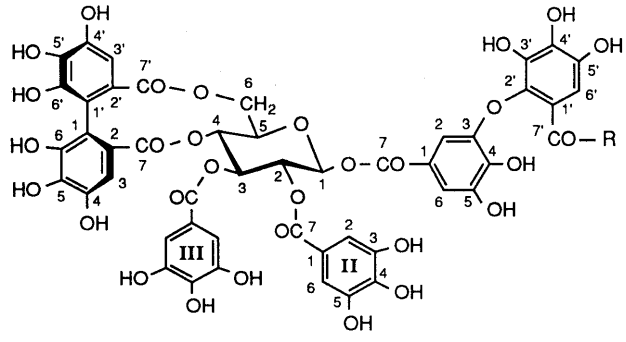


2: R = A
9: R = OH

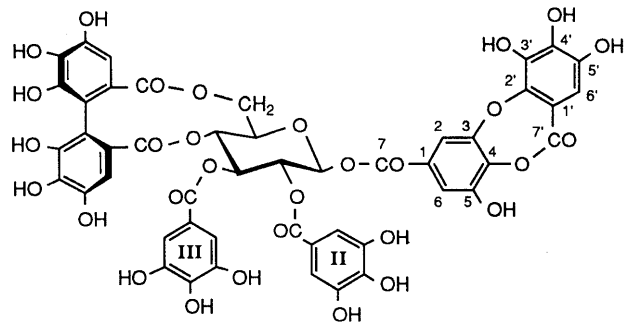


2a

Chart 2



3: R = A
3a: R = B
3b: R = C
5: R = OH



4

Chart 3

TABLE I. One-Bond and Long-Range ^1H–^{13}C Correlation Data for Coriariin B (**5**)

Carbon	δ_C	δ_H	
		Proton coupled *via* one bond	Proton coupled *via* two or three bonds
Glucose (Glc)			
C-1	93.6	6.12	5.53 (Glc H-2)
C-2	71.5	5.53	5.81 (Glc H-3)
C-3	73.0	5.81	5.53 (Glc H-2)
			5.18 (Glc H-4)[a]
C-4	70.6	5.22	5.81 (Glc H-3)
C-5	73.0	4.57	5.18 (Glc H-4)[a]
			5.32 (Glc H-6)
C-6	63.0	5.32	
		3.87	
Dehydrodigalloyl (DHDG)			
C-1	119.4		
C-2	108.4	6.80	
C-3	148.2		6.80 (DHDG H-2)
C-4	141.0		7.21 (DHDG H-6)
			6.80 (DHDG H-2)
C-5	146.5		7.21 (DHDG H-6)
C-6	112.2	7.21	
C-7	164.8		6.80 (DHDG H-2)
			7.21 (DHDG H-6)
			6.12 (Glc H-1)
C-1′	115.2		
C-2′	137.1		7.17 (DHDG H-6′)
C-3′	140.3		
C-4′	139.9		7.17 (DHDG H-6′)
C-5′	143.3		7.17 (DHDG H-6′)
C-6′	110.2	7.17	
C-7′	166.4		7.17 (DHDG H-6′)
Galloyl-II (Gall-II)[b]			
C-1	120.4		
C-2, C-6	110.1	6.98	
C-3, C-5	145.8		6.98 (Gall-II H-2, H-6)
C-4	139.1		6.98 (Gall-II H-2, H-6)
C-7	165.3		6.98 (Gall-II H-2, H-6)
			5.53 (Glc H-2)
Galloyl-III (Gall-III)[c]			
C-1	120.5		6.96 (Gall-III H-2, H-6)
C-2, C-6	110.1	6.96	
C-3, C-5	145.9		6.96 (Gall-III H-2, H-6)
C-4	139.3		6.96 (Gall-III H-2, H-6)
C-7	166.2		6.96 (Gall-III H-2, H-6)
			5.81 (Glc H-3)
Hexahydroxydiphenoyl (HHDP)			
C-1	115.5		6.45 (HHDP H-3)
C-2	125.8[d]		
C-3	107.8	6.45	
C-4	145.8		6.45 (HHDP H-3)
C-5	136.6		6.45 (HHDP H-3)
C-6	144.4[e]		
C-7	167.6		6.45 (HHDP H-3)
			5.18 (Glc H-4)
C-1′	115.6		6.64 (HHDP H-3′)
C-2′	126.4[d]		
C-3′	108.2	6.64	
C-4′	145.3		6.64 (HHDP H-3′)
C-5′	136.5		6.64 (HHDP H-3′)
C-6′	144.5[e]		
C-7′	168.0		6.64 (HHDP H-3′)
			5.32 (Glc H-6)

500 MHz for ^1H-NMR and 125.7 MHz for ^{13}C-NMR, in acetone-d_6. *a*) Based on a single cross peak attributable to the two correlations. *b*) Galloyl group at O-2 of glucose. *c*) Galloyl group at O-3 of glucose. *d, e*) Values with the same superscript may be interchanged.

signals at δ 108.4 and 112.2 should be assigned to C-2 and C-6, respectively. The remaining carbon signals of the DHDG group were easily assigned as shown in Table I, based on the correlation data. The correlations, [DHDG H-2 (δ 6.80), H-6 (δ 7.21)—DHDG C-7 (δ 164.8)] and [DHDG C-7—glucose H-1 (δ 6.12)], which were also observed in the long-range ^1H–^{13}C spectrum (Fig. 1), substantiated the reported assignment[2] of the orientation of the DHDG group in **5**, *i.e.*, the assignment of the carboxyl group in the DHDG group which is esterified with the anomeric hydroxyl group.

If the carboxyl group at C-1′ is depsidically linked to the phenolic hydroxyl group at C-4 in the DHDG group of **4**, the chemical shifts of C-1′—C-7′ in the ^{13}C-NMR spectrum of **4** are expected to be similar to those of the corresponding C-1″—C-7″ of the depsidone-forming valoneoyl group (see structure D in Table II).[11,12] In fact, the chemical shifts of the ^{13}C signals assignable to C-1′—C-7′ [δ 111.4 (C-1′), 141.3 (C-2′), 137.1 (C-3′), 143.1 (C-4′), 143.8 (C-5′), 109.9 (C-6′) and 162.6 (C-7′)] of the DHDG group in **4** are almost the same as those of C-1″—C-7″ [δ 111.4 (C-1″), 141.4 (C-2″), 137.1 (C-3″), 143.4 (C-4″), 143.8 (C-5″), 110.0 (C-6″) and 163.2 (C-7″)] of the depsidone-forming valoneoyl group in praecoxin C.[11] When the remaining DHDG signals (δ 126.8, 114.7, 153.1, 138.5, 150.2, 116.3 and 163.8) of **4** are respectively assigned to C-1—C-7, differences in the chemical shifts of DHDG carbons between **4** and **5** are analogous to the differences between the depsidone-forming valoneoyl group and the valoneoyl group (see Table II).

The distinctive downfield shifts of C-3 (4.9 ppm) and C-5 (3.7 ppm), and the upfield shifts of C-4 (2.5 ppm) and C-7′ (3.8 ppm) of the DHDG group in the ^{13}C-NMR spectrum of **4**, relative to those of **5**, are consistent with the location of the depside linkage, C-7′—O-4. The structure **4**, having a depsidone-forming DHDG group, was thus assigned for coriariin J. This structure was also substantiated by formation of **4**, upon the incubation of a solution of coriariin A (**6**) in phosphate buffer of pH 7.4, in a way analogous to the formation of a tannin having a depsidone-forming valoneoyl group from a dimeric tannin.[9,12] The HPLC detection of coriariin J in the fresh leaf homogenate strongly suggests that **4** is not an artefact, although it may be formed non-enzymatically from **6** or related oligomeric tannins in the leaf.

Structure of Coriariin G Coriariin G (**1**) was obtained as a light-brown powder. The molecular formula $C_{55}H_{46}O_{37}$ was indicated by the $[M+Na]^+$ ion peak at m/z 1321 and the $[M+K]^+$ ion peak at m/z 1337 in the FAB-MS, and supported by the microanalytical data. The presence of rugosin A (**8**)[10] in the molecule of **1** was suggested by the signals attributable to a valoneoyl group [δ 7.14—7.10 (1H), 6.48—6.46 (1H), 6.24—6.20 (1H)], three galloyl groups [δ 7.07 (2H, s), 6.99—6.98 (4H)] and a β-glucopyranose residue adopting the $^4C_1$ conformation (see Experimental), in the ^1H-NMR spectrum of **1**. The ^1H-NMR spectrum also showed complicated signals at δ 4.4—3.4, which are attributable to the protons of another sugar residue. The latter sugar in the molecule of **1** was identified as sedoheptulose, based on the formation of sedoheptulosan upon the treatment of **1** with diluted sulfuric acid. The CD spectrum of **1** showed a positive Cotton effect in the

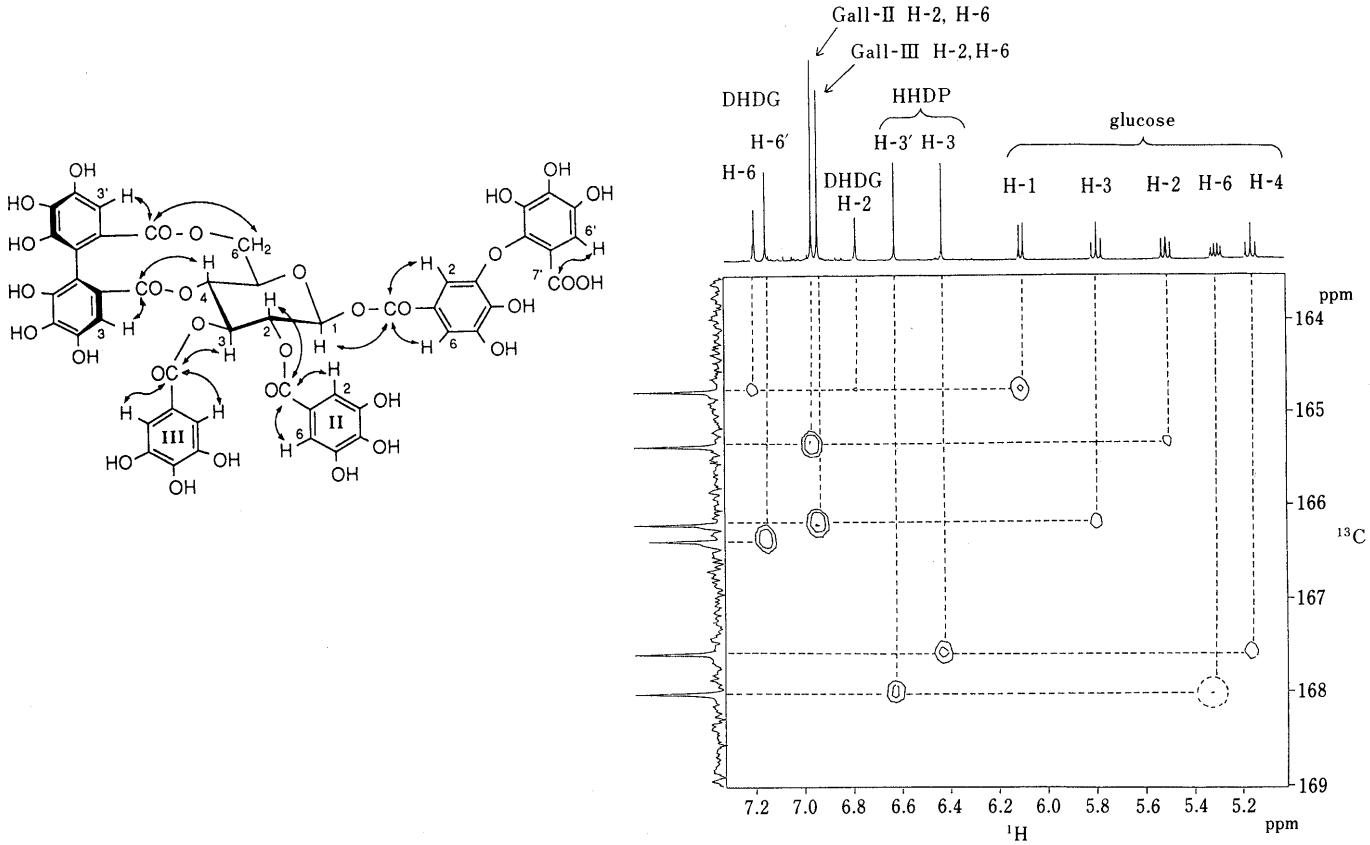


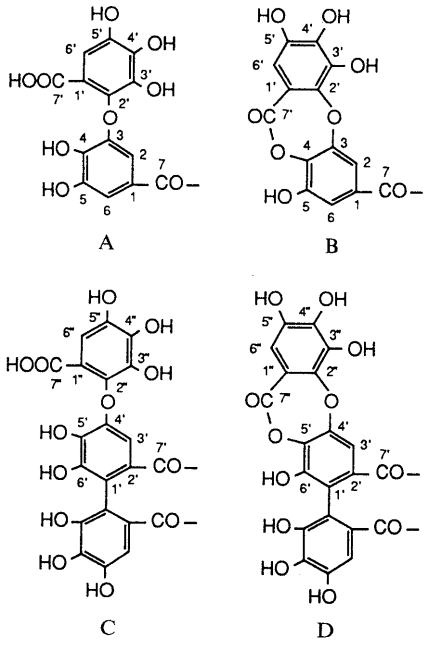
Fig. 1. ^{1}H–^{13}C Long-Range Shift-Correlation Spectrum of Coriariin B (**5**) (500 MHz for ^{1}H-NMR and 125.7 MHz for ^{13}C-NMR, in Acetone-d_6)

The spectrum was obtained after a 12 h run on a Varian HETCOR program, using 40 mg of **5**. The region corresponding to the ester carbonyl carbons is shown. The average J_{CH} value for the long-range couplings was set at 7 Hz. DHDG, dehydrodigalloyl; Gall-II, galloyl group at O-2 of glucose; Gall-III, galloyl group at O-3 of glucose; HHDP, hexahydroxydiphenoyl.

TABLE II. Changes in the ^{13}C Chemical Shifts, Accompanied by Formation of Depside Linkage ($A^{a)} \rightarrow B,^{b)}$ $C^{c)} \rightarrow D^{d)}$)

Carbon	B−A $\Delta\delta$	D−C $\Delta\delta$	Carbon
C-1	+7.4	+7.7	C-2′
C-2	+6.3	+5.9	C-3′
C-3	+4.9	+4.7	C-4′
C-4	−2.5	−1.5	C-5′
C-5	+3.7	+3.9	C-6′
C-6	+4.1	+4.5	C-1′
C-7	−1.0	−0.9	C-7′
C-1′	−3.8	−3.8	C-1″
C-2′	+4.2	+4.3	C-2″
C-3′	−3.2	−2.8	C-3″
C-4′	+3.2	+3.5	C-4″
C-5′	+0.5	+0.7	C-5″
C-6′	−0.3	+0.3	C-6″
C-7′	−3.8	−3.8	C-7″

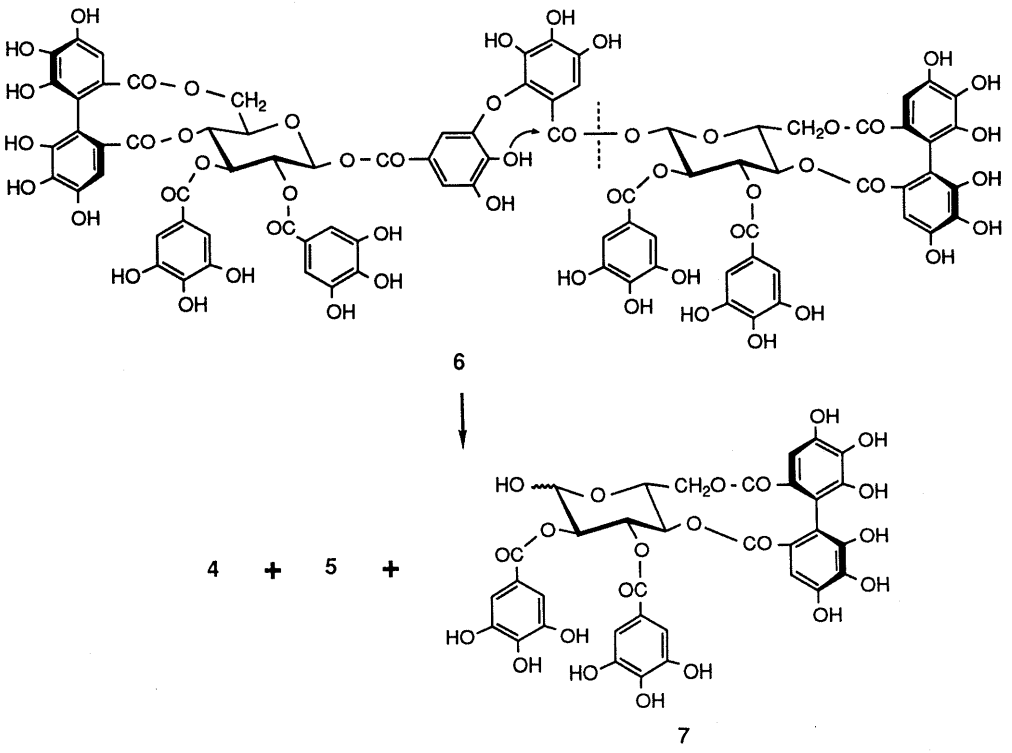
a) Dehydrodigalloyl (DHDG) group in coriariin B (**5**). *b*) Depsidone-forming DHDG group in coriariin J (**4**). *c*) Valoneoyl group in rugosin C.[10] *d*) Depsidone-forming valoneoyl group in praecoxin C.[11]



short-wavelength region ($[\theta]_{224}$ $+2.1 \times 10^5$), indicatig the *S*-configuration of the valoneoyl group.

Chemical shifts of a valoneoyl and three galloyl groups, and a glucopyranose residue in the ^{13}C-NMR spectrum of **1** (see Experimental) are analogous to those of rugosin A (**8**).[10] Among the remaining sedoheptulose carbon signals, signals at δ 97.7 (α-pyranose), 101.6 (β-furanose) and 103.4 (α-furanose) are attributable to C-2,[13] and they indicate that this sedoheptulose residue forms an equilibrium mixture[13] mostly composed of these three tautomeric forms.

The absence of the sedoheptulose protons at lower field than δ 4.4 in the ^{1}H-NMR spectrum of **1**, and this tautomerization of the sedoheptulose residue, indicate that



6

4 + 5 +

7

Chart 4

TABLE III. ^{1}H-NMR Spectral Data for Sedoheptulosan, and the Sedoheptulosan Residue in **1a** and **3a**

Proton	Sedoheptulosan	1a	3a
H-1	3.52 (d, J=12 Hz)	4.23 (d, J=12 Hz)	4.12 (d, J=12 Hz)
	3.78 (d, J=12 Hz)	4.44 (d, J=12 Hz)	4.38 (d, J=12 Hz)
H-3	3.73 (br d, J=8.5 Hz)	3.73 (d, J=8.5 Hz)	3.74 (d, J=8.5 Hz)
H-4	3.68 (dd, J=4.5, 8.5 Hz)	3.60—3.65[a]	3.64 (dd, J=4.5, 8.5 Hz)
H-5	3.81 (m)	3.84 (m)	3.82 (m)
H-6	4.52 (br d, J=5 Hz)	4.58 (br d, J=5 Hz)	4.51 (br d, J=5 Hz)
H-7	3.64 (dd, J=5, 8 Hz)	3.60—3.65[a]	3.62 (dd, J=5, 8 Hz)
	3.70 (d, J=8 Hz)	3.60—3.65[a]	3.69 (d, J=8 Hz)

500 MHz, in acetone-d_6+D_2O. *a*) Overlapped with each other.

the hydroxyl groups at C-3—C-6 of the sedoheptulose residue are not acylated. Therefore, the free carboxyl group of rugosin A is esterified with a hydroxyl group at C-1 or C-7 of sedoheptulose in the molecule of **1**.

Treatment of coriariin G (**1**) with polyphosphoric acid afforded a dehydrate **1a**, along with rugosin A (**8**) and another dehydrate **1b**, which were isolated from the products mixture. The FAB-MS of **1a** showed the $[M+Na]^+$ ion peak at m/z 1303, corresponding to the molecular formula $C_{55}H_{44}O_{36}$. The ^{1}H-NMR spectrum of **1a** (see Experimental and Table III) indicated that **1a** consists of **8** and 2,7-anhydrosedoheptulopyranose (*i.e.*, sedoheptulosan).

Comparison of the chemical shifts of protons of the sedoheptulosan residue in **1a** with those of the protons of sedoheptulosan revealed that two H-1 signals of **1a** were distinctively shifted downfield [δ 4.23, 4.44 (**1a**)←δ 3.52, 3.78 (sedoheptulosan)]. Therefore, the carboxyl group at C-1″ of the valoneoyl group is esterified with the hydroxyl group at C-1 of the sedoheptulosan residue in **1a**. The structure **1** for coriariin G was thus assigned. Compound **1b** was shown by the ^{1}H-NMR spectrum to be the ester of rugosin A with 2,7-anhydrosedoheptulofuranose between the carboxyl group at C-1″ of the valoneoyl group in the former and the hydroxyl group at C-1 of the latter (see Experimental).

Structure of Coriariin H Coriariin H (**2**) was obtained as an off-white powder. The ^{1}H-NMR spectrum showed the signals of two galloyl groups [δ 7.04—7.03 (2H) and 7.00—6.99, 6.95—6.94 (2H)], a valoneoyl group [δ 7.17—7.10 (1H), 6.47—6.44 (1H) and 6.24—6.21 (1H)], and a glucopyranose residue (δ 5.84—3.67, see Experimental). Chemical shifts of these signals are analogous to those of rugosin B (**9**).[10] The spectrum also showed signals at δ 4.4—3.4, suggesting the presence of a sedoheptulose residue in the molecule of **2**. The presence of sedoheptulose in the molecule of **2** was confirmed by the formation of sedoheptulosan upon the treatment of **2** with diluted sulfuric acid. The *S*-configuration of the valoneoyl group was indicated by the positive Cotton effect in the short-wavelength region ($[\theta]_{225}$ $+1.9\times10^5$).

Degalloylation of **1** with tannase[14] afforded **2**, along with **1c**. The FAB-MS of **2** showed the $[M+Na]^+$ ion peak at m/z 1169, which is 152 mass units (one galloyl group) smaller than that of **1**. Therefore, one of the three galloyl groups in **1** was eliminated upon the formation of **2** from **1**.

The reduction of **2** with $NaBH_4$[15] afforded **2a**, which no longer shows the equilibration between the tautomers. Hydrolysis of **2a** yielded glucitol, together with D-*glycero*-D-*gluco*- and D-*glycero*-D-*manno*-heptitols, indicating that the anomeric hydroxyl group of the glucose residue in **2** is unacylated.

Based on these findings, structure **2** was assigned for coriariin H. The presence of the rugosin B molecule in the structure of coriariin H was also substantiated by the formation of **9** upon the partial hydrolysis of **2** with poly-

phosphoric acid. Compound **1c** is shown by the upfield shift of the glucose H-2 signal in its ^{1}H-NMR spectrum from that of **1** [δ 3.97 (**1c**)←5.58 (**1**)], to have been formed by the elimination of the galloyl group at O-2 of glucose in **1**.

Structure of Coriariin I Coriariin I (**3**) was obtained as a light-brown powder. The molecular formula $C_{55}H_{46}O_{37}$ of **3** was indicated by the $[M+Na]^+$ ion peak at m/z 1321 in the FAB-MS and the microanalytical data. The ^{1}H-NMR spectrum of **3** (400 MHz, in acetone-d_6) showed the signals of two galloyl groups [δ 7.10—6.98 (2H) and 6.97 (2H)], an HHDP group [δ 6.66—6.65 (1H) and 6.45 (1H)], a DHDG group [δ 7.24—7.17 (2H), 6.80—6.76 (1H)] and a β-glucopyranose residue adopting the $^4C_1$ conformation (see Experimental). The chemical shifts of these signals are almost the same as those of coriariin B (**5**). The spectrum also showed sedoheptulose proton signals at δ 4.4—3.4. The presence of the sedoheptulose moiety in the molecule of **3** was evidenced by the formation of sedoheptulosan upon the treatment of **3** with diluted sulfuric acid. The CD spectrum of **3** showed a positive Cotton effect in the short-wavelength region ($[\theta]_{228}$ $+1.5\times10^5$), indicating the *S*-configuration of the HHDP group.

The chemical shifts of the sedoheptulose C-2 signals in the ^{13}C-NMR spectrum of **3** are almost the same as those of the corresponding signals of **1**. These data suggest the structure **3** for coriariin I, in which the carboxyl group at C-1′ of **5** is esterified with the hydroxyl group at C-1 of sedoheptulose.

Treatment of coriariin I (**3**) with polyphosphoric acid afforded coriariin B (**5**), **3a** and **3b**. The FAB-MS of **3a** showed the $[M+Na]^+$ ion peak at m/z 1303, corresponding to the molecular formula $C_{55}H_{44}O_{36}$. The ^{1}H-NMR spectrum showed the signals of sedoheptulosan, along with those of the coriariin B moiety (see Experimental and Table III). The two H-1 protons of the anhydrosedoheptulose residue of **3a** were shifted downfield, relative to those of sedoheptulosan (Table III), in a way analogous to the corresponding protons of **1a**. Therefore, the carboxyl group of **5** is esterified with the hydroxyl group at C-1 of the sedoheptulosan residue in **3a**. Compound **3b** was assigned to be the ester of **5** with the hydroxyl group at C-1 of 2,7-anhydrosedoheptulofuranose, based on the similarity of the signal pattern of sedoheptulose protons in the ^{1}H-NMR spectrum of **3b** to that of **1b**. Based on these findings, structure **3** was assigned for coriariin I.

Experimental

Ultraviolet (UV) and infrared (IR) spectra were recorded on a Hitachi 200-10 spectrophotometer and a JASCO A-102 spectrometer, respectively. Optical rotations were measured on a JASCO DIP-4 polarimeter, and CD spectra were recorded on a JASCO J-500A spectropolarimeter equipped with a DP-501N data processor. FAB-MS were recorded on a JEOL JMS-D300 or VG 70-SE mass spectrometer, using 3-nitrobenzyl alcohol (3-NOBA) or triethanolamine (TEA) as the matrix agent. A small amount of NaCl, NaI or KI was added to the sample as required. Electron-impact mass spectra (EI-MS) were measured on a Shimadzu-LKB9000 GC-MS instrument. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian VXR-500 instrument (500 MHz for ^{1}H-NMR and 125.7 MHz for ^{13}C-NMR); chemical shifts were based on the solvent signals (acetone-d_6: δ_H 2.04 and δ_C 29.8), and are given in δ (ppm) values from tetramethylsilane. A Bruker AM-400 instrument was also used for the ^{1}H-NMR spectra (400 MHz). 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. Column temperature and injection temperature were set at 170 and 200 °C, respectively. Flow rate of the N_2 carrier gas was set at 50 ml/min. Analytical and preparative HPLC was performed using a Shimadzu LC-6A chromatograph, equipped with columns of (A) YMC A312 (ODS) (6 × 150 mm) and (B) YMC A324 (ODS) (10 × 300 mm), or (C) LiChrospher RP-18 (5 μm) (4 × 250 mm, Merck), in an oven at 40 °C. Solvents were (a) 0.01 M H_3PO_4–0.01 M KH_2PO_4–MeCN (3:3:2), (b) 0.01 M H_3PO_4–0.01 M KH_2PO_4–MeCN (2:2:1), (c) 0.01 M H_3PO_4–0.01 M KH_2PO_4–MeCN (17:17:6) and (d) 0.01 M H_3PO_4–0.01 M KH_2PO_4–MeCN (11:11:3). CPC was performed on a Sanki Model L-90 instrument equipped with 12 column cartridges (inner volume, 180 ml in total).

Isolation of Coriariins G (1), H (2), I (3) and J (4) from *C. japonica* Leaf Leaves of *C. japonica* A. GRAY were collected in October 1990, at Toga-mura Village, Toyama Prefecture, and were air-dried. The leaves (2.75 kg) were homogenized in 70% acetone (20 l), and then the debris was filtered off. The filtrate was concentrated *in vacuo*, and the resulting aqueous solution (2.8 l) was extracted with $CHCl_3$ (2.8 l × 3), EtOAc (2.8 l × 10), and *n*-BuOH (1.8 l × 3), successively. Each solvent was evaporated off, to yield the $CHCl_3$ (16 g), EtOAc (352 g) and *n*-BuOH (116 g) extracts.

A part (101 g) of the EtOAc extract was chromatographed on Toyopearl HW-40C (6.65 × 40 cm), with 70% EtOH–70% acetone (10:0→9:1→8:2→0:10). The eluate (14 g) with 70% acetone was further chromatographed on Toyopearl HW-40C (2.2 × 60 cm) with 70% EtOH–70% acetone (10:0→9:1→8:2→7:3), and the eluate (2 g) with 70% EtOH–70% acetone (7:3) was purified by column chromatography on MCI gel CHP-20P (75—150 μm, 2.1 × 12 cm) with aqueous MeOH (0%→20%→40%→60%). A part (100 mg) of the eluate with 60% MeOH (885 mg) was further purified by preparative HPLC [column, (A)+(B); solvent, (a)], to give coriariin J (**4**) (9.4 mg).

A part (12 g) of the *n*-BuOH extract was chromatographed on Sephadex LH-20 (4.6 × 18 cm) with 70% EtOH, to give fr. I—fr. IV. Fraction II (5.2 g) was subjected to CPC [*n*-BuOH–*n*-PrOH–H_2O (4:1:5), normal-phase development; 1000 rpm], to separate three fractions (fr. II-1—fr. II-3). A part (191 mg) of fr. II-2 (1.12 g) was chromatographed on Sephadex LH-20 (1.1 × 95 cm) with EtOH–MeOH (4:1), to give coriariin G (**1**) (98.4 mg). Fraction II-3 (729 mg) was chromatographed on Sephadex LH-20 (2.2 × 62 cm) with EtOH–MeOH (8:2→7:3), to give coriariin H (**2**) (45.2 mg) and coriariin I (**3**) (47.1 mg).

Coriariin J (4) An off-white powder, $[\alpha]_D$ +44° (c=1, acetone). FAB-MS (3-NOBA+NaCl): m/z 1111 ($[M+Na]^+$). *Anal.* Calcd for $C_{48}H_{32}O_{30}\cdot7H_2O$: C, 47.46; H, 3.82. Found: C, 47.37; H, 3.54. UV λ_{max}^{MeOH} nm (log ε): 216 (5.01), 275 (4.65). CD (MeOH): $[\theta]_{283}$ $+6.8\times10^4$, $[\theta]_{263}$ -6.8×10^4, $[\theta]_{234}$ $+1.4\times10^5$, $[\theta]_{224}$ $+1.2\times10^5$. ^{1}H-NMR (500 MHz, in acetone-d_6) δ: 7.69 (1H, d, J=2 Hz, DHDG H-6), 7.45 (1H, d, J=2 Hz, DHDG H-2), 6.99 [2H, s, galloyl at O-2 of glucose (Gall-II) H-2, H-6], 6.96 [2H, s, H-2 and H-6 of galloyl at O-3 of glucose (Gall-III) H-2, H-6], 6.88 (1H, s, DHDG H-6′), 6.65 (1H, s, HHDP H-3′), 6.46 (1H, s, HHDP H-3). Glucose protons δ: 6.28 (d, J=8.5 Hz, H-1), 5.86 (t, J=10 Hz, H-3), 5.60 (dd, J=8.5, 10 Hz, H-2), 5.36 (dd, J=6.5, 13 Hz, H-6), 5.22 (t, J=10 Hz, H-4), 4.58 (dd, J=6.5, 10 Hz, H-5), 3.88 (d, J=13 Hz, H-6). ^{13}C-NMR (125.7 MHz, in acetone-d_6) δ: 63.0 [glucose (Glc) C-6], 70.6 (Glc C-4), 71.9 (Glc C-2), 73.0 (Glc C-5), 73.2 (Glc C-3), 94.2 (Glc C-1), 107.8 (HHDP C-3), 108.2 (HHDP C-3′), 109.9 (DHDG C-6′), 110.1, 110.2 (Gall-II C-2, C-6, Gall-III C-2, C-6), 111.4 (DHDG C-1′), 114.7 (DHDG C-2), 115.5 (HHDP C-1), 115.7 (HHDP C-1′), 116.3 (DHDG C-6), 120.3 (Gall-II C-1), 120.5 (Gall-III C-1), 125.8, 126.5 (HHDP C-2 and C-2′), 126.8 (DHDG C-1), 136.5 (HHDP C-5′), 136.6 (HHDP C-5), 137.1 (DHDG C-3′), 138.5 (DHDG C-4), 139.2 (Gall-II C-4), 139.3 (Gall-III C-4), 141.3 (DHDG C-2′), 143.1 (DHDG C-4′), 143.8 (DHDG C-5′), 144.5 (HHDP C-6′, C-6), 145.2 (HHDP C-4′), 145.3 (HHDP C-4), 145.8 (Gall-II C-3, C-5), 145.9 (Gall-III C-3, C-5), 150.2 (DHDG C-5), 153.1 (DHDG C-3), 162.6 (DHDG C-7′), 163.8 (DHDG C-7), 165.4 (Gall-II C-7), 166.2 (Gall-III C-7), 167.6 (HHDP C-7), 168.0 (HHDP C-7′).

Cleavage of the Depside Linkage in Coriariin J (4) A solution of coriariin J (**4**) (5 mg) in 0.03 M KH_2PO_4–Na_2HPO_4 buffer (pH 5.8, 5 ml) was kept at 37 °C for 5 h. The solution was then concentrated to 1.5 ml, and extracted with EtOAc (1.5 ml × 3) to recover unchanged starting material, and the aqueous layer was acidified with diluted HCl (to pH 2). The acidified solution was further extracted with EtOAc (1.5 ml × 3), and the organic layer was evaporated to give coriariin B (**5**) (1 mg), which was identified by ^{1}H-NMR and co-HPLC [column, (C); solvent, (b)].

Formation of Coriariin J (4) upon Partial Degradation of Coriariin A (6) A solution of coriariin A (**6**) (2 mg) in 0.1 M KH_2PO_4–Na_2HPO_4

buffer (pH 7.4, 2 ml) was kept at 37 °C for 2 h. HPLC analysis of the reaction mixture [column, (C); solvent, (b); flow rate, 1.0 ml/min] showed the formation of coriariin J (**4**) [retention time (t_R) 10.1 min], coriariin B (**5**) (t_R 2.9 min) and tellimagrandin I (**7**) [t_R 2.6 and 2.7 min (anomer mixture)[15]].

Detection of Coriariin J (4) in the Fresh Leaf Homogenate Fresh leaves (2.56 g) of *C. japonica* was homogenized in MeOH (20 ml) immediately after collection at the Herbal Garden of Okayama University, and the debris in the homogenate was eliminated by centrifugation (3000 rpm, 10 min). The solution thus obtained was further centrifuged [12000 rpm (10000 ***g***), 5 min], and the supernatant was analyzed by HPLC [column, (C); solvent (b)], to show the presence of coriariin J (**4**) (0.02% in fresh leaf).

Coriariin G (1) A light-brown powder, $[\alpha]_D$ +100° (c=0.1, acetone). FAB-MS (TEA+NaI/KI) *m/z*: 1321 ($[M+Na]^+$) (TEA+NaI); 1337 ($[M+K]^+$) (TEA+KI). *Anal.* Calcd for $C_{55}H_{46}O_{37}\cdot 7H_2O$: C, 46.36; H, 4.24. Found: C, 46.32; H, 4.08. UV λ_{max}^{MeOH} nm (log ε): 218 (5.08), 276 (4.74). IR ν_{max}^{KBr} cm^{-1}: 1720 (ester carbonyl), 1615. CD (MeOH): $[\theta]_{280}$ $+5.3\times10^4$, $[\theta]_{258}$ -3.0×10^4, $[\theta]_{240}$ $+6.8\times10^4$, $[\theta]_{224}$ $+2.1\times10^5$. ^{1}H-NMR (500 MHz, in acetone-d_6+D_2O) δ: 7.14—7.10 [1H, valoneoyl (Val) H-6″], 7.07 [2H, s, galloyl at O-1 of glucose (Gall-I), H-2, H-6], 6.99—6.98 (4H, Gall-II H-2, H-6, Gall-III H-2, H-6), 6.48—6.46 (1H, Val H-3), 6.24—6.20 (1H, Val H-3′). Glucose protons δ: 6.14 (d, J=8 Hz, H-1), 5.81 (t, J=10 Hz, H-3), 5.58 (br t-like, J=9 Hz, H-2), 5.25 (dd, J=7, 13 Hz, H-6), 5.17 (br t, J=10 Hz, H-4), 4.49 (dd, J=7, 10 Hz, H-5), 3.78 (d, J=13 Hz, H-6). Sedoheptulose protons δ: 4.4–3.4. ^{13}C-NMR (125.7 MHz, acetone-d_6+D_2O) δ: 62.5—83.1 [sedoheptulose (Shl) C-1, C-3—C-7], 63.1 (Glc C-6), 70.6 (Glc C-4), 71.8 (Glc C-2), 72.8 (Glc C-5), 73.2 (Glc C-3), 93.5 (Glc C-1), 97.7 (Shl C-2, α-pyranose), 101.6 (Shl C-2, β-furanose), 103.4 (Shl C-2, α-furanose), 105.0—105.3 (Val C-3′), 107.7 (Val C-3), 109.8 (Val C-6″), 110.0 (Gall-II C-2, C-6), 110.1 (Gall-III C-2, C-6, Gall-I C-2, C-6), 115.1 (Val C-1″), 115.9—116.0 (Val C-1), 117.4—117.5 (Val C-1′), 119.4, 119.9, 120.1 (Gall-I C-1, Gall-II C-1, Gall-III C-1), 125.0—125.1, 125.9 (Val C-2, C-2′), 136.4—137.2 (Val C-5, C-5′, C-2″), 139.2 (Gall-III C-4), 139.4 (Gall-II C-4), 139.8 (Gall-I C-4), 140.0—140.2 (Val C-3″, C-4″), 143.3—143.4 (Val C-5″), 144.5—145.3 (Val C-4, C-6, C-6′), 145.8 (Gall-III C-3, C-5), 145.9 (Gall-II C-3, C-5), 146.1 (Gall-I C-3, C-5), 147.0—147.2 (Val C-4′), 165.0 (Gall-I C-7), 165.4—165.9 (Val C-7″), 166.0 (Gall-II C-7), 166.5 (Gall-III C-7), 168.0—168.3 (Val C-7, C-7′). The assignments of the signals in the ^{1}H- and ^{13}C-NMR spectra were based on a comparison with those for rugosin A (**8**).[10]

Coriariin H (2) An off-white powder, $[\alpha]_D$ +119° (c=0.1, acetone). FAB-MS (TEA+NaI/KI) *m/z*: 1169 ($[M+Na]^+$) (TEA+NaI), 1185 ($[M+K]^+$) (TEA+KI). *Anal.* Calcd for $C_{48}H_{42}O_{33}\cdot 6H_2O$: C, 45.94; H, 4.34. Found: C, 46.18; H, 4.26. UV λ_{max}^{MeOH} nm (log ε): 218 (5.00), 276 (4.74). IR ν_{max}^{KBr} cm^{-1}: 1720 (ester carbonyl), 1615. CD (MeOH): $[\theta]_{285}$ $+7.1\times10^4$, $[\theta]_{260}$ -5.3×10^4, $[\theta]_{238}$ $+6.7\times10^4$, $[\theta]_{225}$ $+1.9\times10^5$. ^{1}H-NMR (500 MHz, in acetone-d_6+D_2O) δ: 7.17—7.10 (1H, Val H-6″), 7.04—7.03 (2H), 7.00—6.99, 6.95—6.94 (2H in total) (Gall-II H-2, H-6, Gall-III H-2, H-6), 6.47–6.44 (1H, Val H-3), 6.24—6.21 (1H, Val H-3′). Glucose protons δ: 5.84 (t, J=10 Hz, H-3, α-anomer), 5.57 (br t, J=10 Hz, H-3, β-anomer), 5.49 (d, J=3 Hz, H-1, α-anomer), 5.23 (br t, J=9 Hz, H-2, β-anomer), 5.19—5.14 (m, H-6, α-anomer, H-6, β-anomer), 5.10—5.04 (m, H-2, H-4, α-anomer, H-4, β-anomer), 5.02 (d, J=8 Hz, H-1, β-anomer), 4.61 (dd, J=7, 10 Hz, H-5, α-anomer), 4.21 (dd, J=6.5, 10 Hz, H-5, β-anomer), 3.75 (br d, J=13 Hz, H-6, β-anomer), 3.67 (br d, J=13 Hz, H-6, α-anomer). Sedoheptulose protons δ: 4.4–3.4. ^{13}C-NMR (125.7 MHz, in acetone-d_6+D_2O) δ: 62.6—83.1 (Shl C-1, C-3—C-7), 63.7 (Glc C-6, α-anomer, C-6, β-anomer), 66.9 (Glc C-5, α-anomer), 71.1—71.3 (Glc C-3, C-4, α-anomer, C-4, β-anomer), 71.8 (Glc C-5, β-anomer), 72.9 (Glc C-2, α-anomer), 73.6 (Glc C-3, β-anomer), 74.1 (Glc C-2, β-anomer), 91.1 (Glc C-1, α-anomer), 96.5 (Glc C-1, β-anomer), 97.7 (Shl C-2, α-pyranose), 101.5 (Shl C-2, β-furanose), 103.4 (Shl C-2, α-furanose), 104.9—105.2 (Val C-3′), 107.6 (Val C-3), 109.8 (Val C-6″), 109.9 (Gall-II C-2, C-6), 110.0 (Gall-III C-2, C-6), 114.7—115.1 (Val C-1″), 115.7—115.8 (Val C-1), 117.3—117.5 (Val C-1′), 120.3—120.8 (Gall-II C-1, Gall-III C-1), 125.2—125.3, 126.0—126.1 (Val C-2, C-2′), 136.5—136.9 (Val C-5, C-5′, C-2″), 139.1 (Gall-III C-4), 139.2 (Gall-II C-4), 139.8—140.3 (Val C-3″, C-4″), 143.2—143.4 (Val C-5″), 144.3—144.6, 144.9—145.1 (Val C-6, C-6′) 145.3 (Val C-4), 145.7—145.8 (Gall-III C-3, C-5), 145.9 (Gall-II C-3, C-5), 146.9—147.2 (Val C-4′), 165.3—165.9 (Val C-7″), 166.0, 166.3 (Gall-II C-7), 166.6, 166.9 (Gall-III C-7), 168.0—168.4 (Val C-7, C-7′). The assignments of the signals in the ^{1}H- and ^{13}C-NMR spectra were based on a comparison with those for rugosin B (**9**).[10]

Coriariin I (3) A light-brown powder, $[\alpha]_D$ +90° (c=0.1, acetone). FAB-MS (3-NOBA+NaCl) *m/z*: 1321 ($[M+Na]^+$). *Anal.* Calcd for $C_{55}H_{46}O_{37}\cdot 7H_2O$: C, 46.36; H, 4.24. Found: C, 46.34; H, 3.85. UV λ_{max}^{MeOH} nm (log ε): 220 (5.05), 277 (4.72). IR ν_{max}^{KBr} cm^{-1}: 1720 (ester carbonyl), 1615. CD (MeOH): $[\theta]_{284}$ $+5.1\times10^4$, $[\theta]_{262}$ -2.1×10^4, $[\theta]_{228}$ $+1.5\times10^5$. ^{1}H-NMR (400 MHz, in acetone-d_6) δ: 7.24—7.17 (2H, DHDG H-6, H-6′), 7.10—6.98 (2H, Gall-II H-2, H-6), 6.97 (2H, Gall-III H-2, H-6), 6.80—6.76 (1H, DHDG H-2), 6.66—6.65 (1H, HHDP H-3′), 6.45 (1H, s, HHDP H-3). Glucose protons δ: 6.14 (d, J=8 Hz, H-1), 5.82 (br t, J=10 Hz, H-3), 5.53 (br t, J=9 Hz, H-2), 5.34 (dd, J=7, 13 Hz, H-6), 5.19 (br t, J=10 Hz, H-4), 4.51 (dd, J=7, 10 Hz, H-5), 3.86 (br d, J=13 Hz, H-6). Sedoheptulose protons δ: 4.4—3.4. ^{13}C-NMR (125.7 MHz, in acetone-d_6) δ: 63.0—83.3 (Shl C-1, C-3—C-7), 62.9 (Glc C-6), 70.6 (Glc C-4), 71.6 (Glc C-2), 72.9, 73.0 (Glc C-3, C-5), 93.6 (Glc C-1), 97.7—97.9 (Shl C-2, α-pyranose), 101.3—101.5 (Shl C-2, β-furanose), 103.5 (Shl C-2, α-furanose), 107.8 (DHDG C-6), 108.0—108.3 (HHDP C-3, C-3′), 109.8—110.1 (Gall-II C-2, C-6, Gall-III C-2, C-6, DHDG C-6′), 112.3 (DHDG C-2), 114.6—115.0 (DHDG C-1′), 115.6, 115.7 (HHDP C-1, C-1′), 119.3 (DHDG C-1), 120.2, 120.3 (Gall-II C-1, Gall-III C-1), 125.7, 126.3 (HHDP C-2, C-2′), 136.4, 136.6 (HHDP C-5, C-5′), 136.8—137.1 (DHDG C-2′), 139.2 (Gall-II C-4), 139.3 (Gall-III C-4), 139.9—140.3 (DHDG C-3′, C-4′), 140.7—140.9 (DHDG C-4), 143.2—143.3 (DHDG C-5′), 144.4 (HHDP C-6, C-6′), 145.2, 145.3 (HHDP C-4, C-4′), 145.8 (Gall-II C-3, C-5), 145.9 (Gall-III C-3, C-5), 146.4—146.7 (DHDG C-5), 148.1—148.3 (DHDG C-3), 164.5—165.3 (DHDG C-7, C-7′), 165.5 (Gall-II C-7), 166.2 (Gall-III C-7), 167.6 (HHDP C-7), 168.0 (HHDP C-7′). The assignments of the signals in the ^{1}H- and ^{13}C-NMR spectra were based on a comparison with those for coriariin B (**5**) (see Table I).

Identification of Constituent Sugars of Coriariins G (1), H (2) and I (3) A solution of coriariin G (**1**) (5 mg) in 0.5 M H_2SO_4 (5 ml), in a sealed tube, was heated in a boiling-water bath for 14 h, and then neutralized with Amberlite IR-410, and extracted with EtOAc. The solvent of the aqueous phase was evaporated off, and the residue was trimethylsilylated and analyzed by GLC, to reveal the presence of glucose (t_R 2.6 and 3.8 min) and sedoheptulosan (t_R 4.2 min). Coriariins H (**2**) and I (**3**) were also treated in analogous ways to show the presence of glucose and sedoheptulose in each molecule. The presence of sedoheptulosan in the hydrolyzates mixture from coriariin G (**1**), and that from coriariin I (**3**), was further confirmed by GC-MS (EI-MS) [*m/z* 480 (M^+)].

Treatment of Coriariins G (1), H (2) and I (3) with Polyphosphoric Acid A mixture of coriariin G (**1**) (40 mg) and polyphosphoric acid (0.4 g) in dioxane (40 ml), in a sealed tube, was heated in a boiling-water bath for 90 min. The reaction mixture was then concentrated and partitioned between EtOAc and water, and each solvent was evaporated off. The residue from the organic layer was dissolved in water, and the solution was passed through a BondElut C18 cartridge (Analytichem). The adsorbed compounds were eluted with aqueous MeOH (0%→20%→40%), and the eluate with 40% MeOH was further purified by preparative HPLC [column, 2×(C); solvent, (c)] to give rugosin A (**8**) (0.3 mg), which was identified by ^{1}H-NMR. The residue from the aqueous phase was purified in an analogous way, and preparative HPLC [column, 2×(C); solvent, (c)] of the eluate with 40% MeOH (8.5 mg) gave **1a** (0.7 mg), along with **1b** (0.7 mg). Coriariin I (**3**) (40 mg) was treated with polyphosphoric acid in an analogous way, to give coriariin B (**5**) (0.5 mg), **3a** (0.7 mg) and **3b** (0.7 mg).

A solution of coriariin H (**2**) (1 mg) in dioxane (1 ml) containing polyphosphoric acid (10 mg), in a sealed tube, was heated in a boiling-water bath for 1.5 h. The reaction mixture was concentrated and partitioned between EtOAc and water, and each solvent was evaporated off. The EtOAc extract was analyzed by HPLC [column, (C); solvent, (c); flow rate, 1.0 ml/min], to reveal the formation of rugosin B (**9**) [t_R 4.1 and 4.6 min (anomer mixture)].

Compound 1a An off-white powder. FAB-MS (3-NOBA+NaCl) *m/z*: 1303 ($[M+Na]^+$). ^{1}H-NMR (500 MHz, in acetone-d_6+D_2O) δ: 7.11 (1H, s, Val H-6″), 7.07 (2H, s, Gall-I H-2, H-6), 6.98 (2H, s, Gall-II H-2, H-6), 6.96 (2H, s, Gall-III H-2, H-6), 6.45 (1H, s, Val H-3), 6.20—6.19 (1H, Val H-3′). Glucose protons δ: 6.13 (d, J=8.5 Hz, H-1), 5.79 (t, J=10 Hz, H-3), 5.57 (t, J=9 Hz, H-2), 5.25 (dd, J=6.5, 13 Hz, H-6), 5.19 (t, J=10 Hz, H-4), 4.48 (dd, J=6.5, 10 Hz, H-5), 3.77 (d, J=13 Hz, H-6). Sedoheptulose protons: see Table II.

Compound 1b An off-white powder. FAB-MS (3-NOBA+NaCl) *m/z*: 1303 ($[M+Na]^+$). ^{1}H-NMR (500 MHz, in acetone-d_6+D_2O) δ: 7.15 (1H, s, Val H-6″), 7.07 (2H, s, Gall-I H-2, H-6), 6.98 (4H, Gall-II H-2, H-6, Gall-III H-2, H-6), 6.48 (1H, s, Val H-3), 6.22—6.19 (1H, Val

H-3′). Glucose protons δ: 6.14 (d, J=8.5 Hz, H-1), 5.80 (t, J=10 Hz, H-3), 5.58 (t, J=9 Hz, H-2), 5.26—5.21 (m, H-6), 5.17 (t, J=10 Hz, H-4), 4.51—4.46 (m, H-5), 3.79 (d, J=13 Hz, H-6). Sedoheptulose protons δ: 4.31 (d, J=12 Hz, H-1), 4.23 (br dd, J=3.5, 12 Hz, H-7), 4.13 (br s, H-5), 4.10 (br s, H-3), 4.04 (d, J=12 Hz, H-1), 4.03 (br s, H-6), 3.70 (br d, J=12 Hz, H-7). The H-4 signal was overlapped with the HDO signal at around δ 3.5.

Compound 3a An off-white powder. FAB-MS (3-NOBA + NaCl) m/z: 1303 ($[M+Na]^+$). ^{1}H-NMR (500 MHz, in acetone-d_6 + D_2O) δ: 7.21 (1H, d, J=2 Hz, DHDG H-6), 7.18 (1H, s, DHDG H-6′), 6.98 (2H, s, Gall-II H-2, H-6), 6.95 (2H, s, Gall-III H-2, H-6), 6.75 (1H, d, J=2 Hz, DHDG H-2), 6.64 (1H, s, HHDP H-3′), 6.45 (1H, s, HHDP H-3). Glucose protons δ: 6.11 (d, J=8.5 Hz, H-1), 5.79 (t, J=10 Hz, H-3), 5.52 (dd, J=8.5, 9.5 Hz, H-2), 5.30 (dd, J=6.5, 13.5 Hz, H-6), 5.17 (t, J=10 Hz, H-4), 4.48 (dd, J=6.5, 10 Hz, H-5), 3.83 (d, J=13.5 Hz, H-6). Sedoheptulose protons: see Table II.

Compound 3b An off-white powder. FAB-MS (3-NOBA + NaCl) m/z 1303 ($[M+Na]^+$). ^{1}H-NMR (500 MHz, in acetone-d_6 + D_2O) δ: 7.21 (1H, d, J=2 Hz, DHDG H-6), 7.19 (1H, s, DHDG H-6′), 6.98 (2H, s, Gall-II H-2, H-6), 6.95 (2H, s, Gall-III H-2, H-6), 6.72 (1H, d, J=2 Hz, DHDG H-2), 6.63 (1H, s, HHDP H-3′), 6.46 (1H, s, HHDP H-3). Glucose protons δ: 6.11 (d, J=8 Hz, H-1), 5.78 (t, J=10 Hz, H-3), 5.53 (dd, J=8, 9 Hz; H-2), 5.29 (dd, J=6.5, 13.5 Hz, H-6), 5.17 (t, J=10 Hz, H-4), 4.48 (dd, J=6.5, 10 Hz, H-5), 3.83 (d, J=13.5 Hz, H-6). Sedoheptulose protons δ: 4.24 (br s, H-5), 4.22 (dd, J=2.5, 12 Hz, H-7), 4.18 (d, J=12 Hz, H-1), 4.10 (d, J=2 Hz, H-3), 4.01 (br s, H-6), 3.97 (d, J=12 Hz, H-1), 3.65 (d, J=12 Hz, H-7), 3.50 (br s, H-4).

Tannase Treatment of Coriariin G (1) Coriariin G (20 mg) dissolved in water was treated with tannase[14] at 37°C for 3 h. The reaction mixture was then acidified (pH 2) with 1 M HCl to stop the enzyme reaction, and extracted with Et_2O and EtOAc, successively. The aqueous layer was concentrated, the passed through a Sep-pak C18 cartridge (Millipore). The adsorbed compounds were eluted with aqueous MeOH (0%→20%→40%), and the eluate with 20% MeOH and that with 40% MeOH were further purified by preparative HPLC [column, 2×(C); solvent (d)], to give **1c** (0.7 mg) and coriariin H (**2**) (0.5 mg).

Compound 1c An off-white powder. ^{1}H-NMR (500 MHz, in acetone-d_6 + D_2O) δ: 7.16 (2H), 7.06—7.04 (2H) (galloyl H-2×2 and H-6×2), 7.14—7.08 (1H, Val H-6″), 6.47—6.45 (1H, Val H-3), 6.22—6.16 (1H, Val H-3′). Glucose protons δ: 5.83 (d, J=8 Hz; H-1), 5.44 (br t, J=10 Hz, H-3), 5.20 (br dd, J=6.5, 13.5 Hz, H-6), 5.04—4.98 (m, H-4), 4.29 (dd, J=6.5, 10 Hz, H-5), 3.97 (br t, J=9 Hz, H-2), 3.72 (d, J=13.5 Hz, H-6). Sedoheptulose protons δ: 4.4–3.4.

Treatment of Coriariin H (2) with $NaBH_4$ An aqueous solution (4 ml) of coriariin H (**2**) (26 mg), cooled in an ice-bath, was treated with $NaBH_4$ (20 mg), and the solution was acidified to pH 2 with diluted H_2SO_4. The solution was then passed through a Sep-pak C18 cartridge, and the adsorbed compounds were eluted with H_2O and then with MeOH. The eluate with MeOH afforded **2a** (22 mg).

Compound 2a An off-white powder. FAB-MS (3-NOBA + NaCl) m/z: 1173 ($[M+Na]^+$). *Anal.* Calcd for $C_{48}H_{46}O_{33}\cdot 5H_2O$: C, 46.45; H, 4.54. Found: C, 46.33; H, 4.53. ^{1}H-NMR (500 MHz, in acetone-d_6 + D_2O) δ: 7.16—7.09 (1H, Val H-6″), 7.11 (2H, s), 7.03 (2H, s) (galloyl H-2×2, H-6×2), 6.85 (1H, s, Val H-3), 6.10—6.08 (1H, Val H-3′). Glucitol protons δ: 5.93 (br d, J=7.5 Hz, H-3), 5.29—5.24 (m, H-2, H-4), 4.49 (br d, J=12 Hz, H-6), 4.03 (br d, J=9 Hz, H-5), 3.96 (dd, J=4, 13 Hz, H-1), 3.81—3.77 (m, H-1, H-6). Protons of D-*glycero*-D-*gluco*- and D-*glycero*-D-*manno*-heptitols δ: 4.4–3.4.

Identification of Constituent Sugar Alcohols of 2a A solution of **2a** (3 mg) in 0.5 M H_2SO_4 (3 ml), in a sealed tube, was heated in a boiling-water bath for 15 h, and then neutralized with Amberlite IR-410 resin. The solution was extracted with EtOAc, and each solvent was evaporated off. The residue from the aqueous layer was trimethylsilylated and analyzed by GLC to reveal the prsence of glucitol (t_R 3.7 min), D-*glycero*-D-*gluco*-heptitol (t_R 10.3 min) and D-*glycero*-D-*manno*-heptitol (t_R 10.8 min). The identity of the GLC peak of trimethylsilylated glucitol was further confirmed by GC-MS (EI-MS) m/z: 599 ($[M-CH_3]^+$), 524 $\{[M-Si(CH_3)_3OH]^+\}$.

Acknowledgments The authors thank Dr. Y. Takeda, Tokushima University, for measurements of the FAB spectra of coriariins G and H. The Varian VXR-500 instrument used in this study is the property of the SC-NMR Laboratory of Okayama University. This study was supported in part by a Grant-in-Aid for Scienctific Research from the Ministry of Education, Science and Culture of Japan.

References

1) Part II: T. Hatano, S. Hattori and T. Okuda, *Chem. Pharm. Bull.*, **34**, 4533 (1986).
2) T. Hatano, S. Hattori and T. Okuda, *Chem. Pharm. Bull.*, **34**, 4092 (1986).
3) K. Miyamoto, N. Kishi, R. Koshiura, T. Yoshida, T. Hatano and T. Okuda, *Chem. Pharm. Bull.*, **35**, 814 (1989).
4) K. Fukuchi, H. Sakagami, T. Okuda, T. Hatano, S. Tanuma, K. Kitajima, Y. Inoue, S. Inoue, S. Ichikawa, M. Nonoyama and K. Konno, *Antiviral Res.*, **11**, 285 (1989).
5) T. Okuda, T. Yoshida, T. Hatano, K. Mori and T. Fukuda, *J. Liq. Chromatogr.*, **13**, 3637 (1990).
6) C. K. Wilkins and B. A. Bohm, *Phytochemistry*, **15**, 211 (1976).
7) T. Okuda, T. Yoshida, T. Hatano, T. Koga, N. Toh and K. Kuriyama, *Tetrahedron Lett.*, **23**, 3937 (1982).
8) E. Haslam, *Fortschr. Chem. Org. Naturst.*, **41**, 1 (1982).
9) T. Yoshida, T. Hatano, T. Kuwajima and T. Okuda, *Heterocycles*, **33**, 463 (1992).
10) T. Hatano, N. Ogawa, T. Yasuhara and T. Okuda, *Chem. Pharm. Bull.*, **38**, 3308 (1990).
11) T. Hatano, K. Yazaki, A. Okonogi and T. Okuda, *Chem. Pharm. Bull.*, **39**, 1689 (1991).
12) T. Yoshida, O. Namba, L. Chen, Y.-Z. Liu and T. Okuda, *Chem. Pharm. Bull.*, **38**, 3296 (1990).
13) T. Okuda, S. Saito, M. Hayashi, N. Nagakura and M. Sugiura, *Chem. Pharm. Bull.*, **24**, 3226 (1976).
14) T. Yoshida, K. Tanaka, X.-M. Chen and T. Okuda, *Chem. Pharm. Bull.*, **37**, 920 (1989).
15) T. Hatano, T. Yoshida and T. Okuda, *J. Chromatogr.*, **435**, 285 (1988).