[Chem. Pharm. Bull. 34(10)4092—4097(1986)]

Tannins of *Coriaria japonica* A. GRAY. I. Coriariins A and B, New Dimeric and Monomeric Hydrolyzable Tannins

TSUTOMU HATANO, SHIN HATTORI and TAKUO OKUDA*

Faculty of Pharmaceutical Sciences, Okayama University, Tsushima, Okayama 700, Japan

(Received April 14, 1986)

Two new hydrolyzable tannins, named coriariins A and B, have been isolated from the leaves of *Coriaria japonica* A. GRAY along with 1,2,3-tri-*O*-galloyl-*β*-D-glucose, geraniin, tellimagrandins I (**1**) and II (**2**), and rugosins A, D and E. The structure **3** of coriariin A, which is a dimer of **2**, and the structure **4** of coriariin B, a related monomer, have been established on the basis of spectroscopic and chemical evidence.

Keywords——coriariin A; coriariin B; tellimagrandin I; tellimagrandin II; tannin; hydrolyzable tannin; ellagitannin; dimeric hydrolyzable tannin; *Coriaria japonica*; Coriariaceae

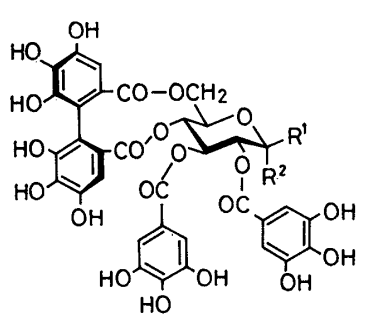
Although *Coriaria japonica* A. GRAY (Doku-utsugi in Japanese, Coriariaceae), which grows in the northern part of Japan, is well known as a poisonous plant containing toxic sesquiterpene lactones such as coriamyrtin[1] and tutin,[1] as well as a 3-heptulose named coriose,[2] the species of *Coriaria* are also rich in tannin[3] (the name is derived from the Latin word "coriarius," meaning tanner). However, little is known about the tannins in these species, except for some polyphenols related to tannin such as ellagic acid[4] and its methyl derivative.[5] As a preliminary investigation confirmed that the leaf of *C. japonica* is rich in tannin, having a very high relative affinity to methylene blue (RMB) value[6] (0.69) of the total extract, we investigated the tannins of this plant.

Results and Discussion

The homogenate of the leaves of *C. japonica* in aqueous acetone was concentrated and extracted with chloroform, ethyl acetate and *n*-butanol, successively. The ethyl acetate extract gave, upon column chromatography on Sephadex LH-20, 1,2,3-tri-*O*-galloyl-*β*-D-glucose,[7] geraniin,[8] tellimagrandins I (**1**)[9] and II (**2**),[9] rugosins A[7] and E,[10] and two new hydrolyzable tannins named coriariins A (**3**) and B (**4**). Coriariin A was also isolated from the *n*-butanol extract along with rugosin D.[10]

Coriariin B (**4**), $C_{48}H_{34}O_{31} \cdot 6H_2O$, $[\alpha]_D$ +66°, was obtained as a pale yellow amorphous powder. The ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum of **4** (in acetone-d_6) shows the presence of two galloyl groups (δ 7.00 and 6.98, 2H each, s), a hexahydroxydiphenoyl (HHDP) group (δ 6.66 and 6.48, 1H each, s), a dehydrodigalloyl (DHDG) group (δ 7.23, 1H, d, J=2 Hz; 7.18, 1H, s; 6.80, 1H, d, J=2 Hz) and a *β*-glucose core in C1 conformation. The presence of these groups was confirmed by examination of the ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum (Table I). The HHDP group in **4** is presumed to be linked to O-4 and O-6 of the glucose core, based on the analogy of the chemical shifts of H-4 (δ 5.20) and H_a-6 (δ 5.35) to those of **2**,[11] and also on the shift difference between H_a-6 and H_b-6 (δ 3.84). Therefore, the DHDG group and two galloyl groups should be on O-1—O-3 of glucose. Partial hydrolysis of **4** with trifluoroacetic acid gave tellimagrandin I (**1**), establishing

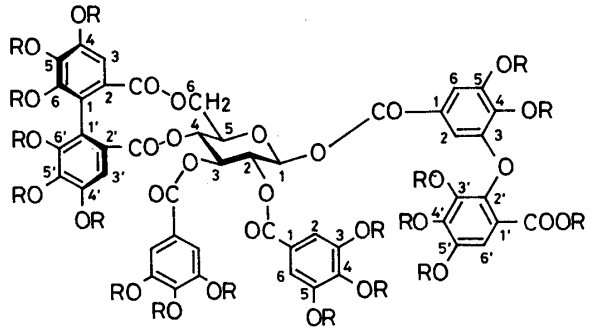
NII-Electronic Library Service



1: R^1, R^2 = H, OH

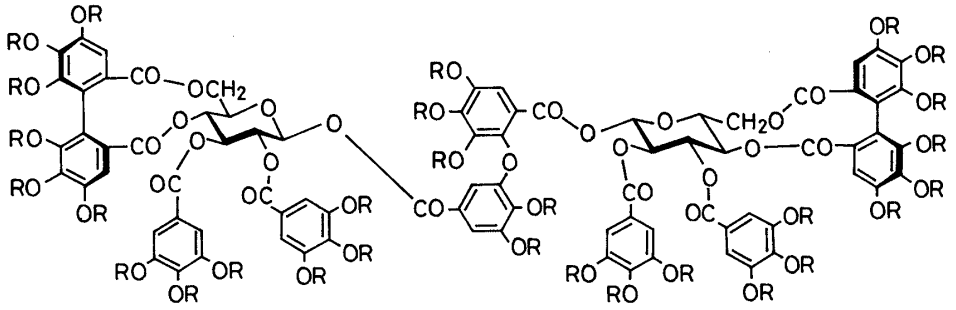
2: R^1 = –OCO– (OH, OH, OH)

R^2 = H



4: R = H

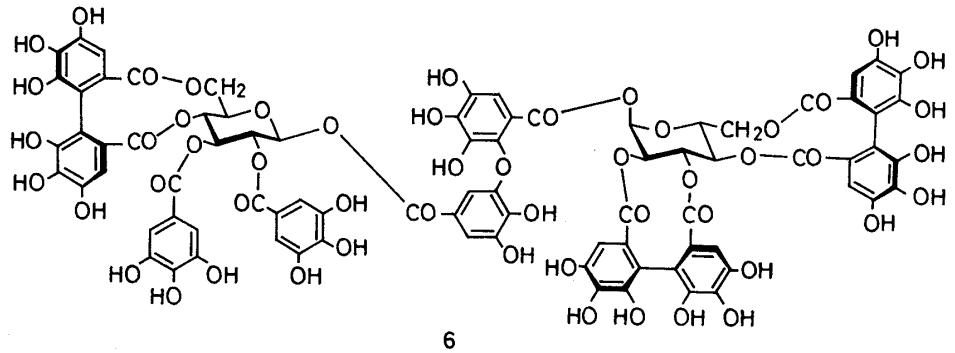
5: R = Me



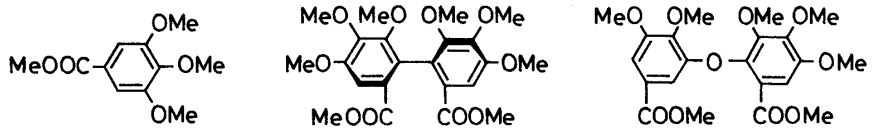
3: R = H

7: R = Me

Chart 1



6



8 9 10

Chart 2

the location of the DHDG group on O-1, and the *S*-configuration of the HHDP group. The positive Cotton effect at 233 nm in the circular dichroic (CD) spectrum of **4** also indicates the *S*-configuration[12] for the HHDP group in **4**. Methylation of **4** with dimethyl sulfate and potassium carbonate afforded heptadeca-*O*-methylcoriariin B monomethyl ester (**5**), $C_{66}H_{70}O_{31} \cdot H_2O$, which is identical with a degradative product obtained upon methylation of

NII-Electronic Library Service

TABLE I. ^{13}C-Chemical Shifts of Coriariins A and B and Tellimagrandin II

Carbon	Coriariin A (**3**)[a]	Coriariin B (**4**)[b]	Tellimagrandin II (**2**)[c]
Galloyl[d]			
C-1	119.8 (4C)	121.3 (2C)	120.7, 120.6, 120.0
C-2,6	110.3 (8C)	111.0 (4C)	110.5, 110.3, 110.2
C-3,5	145.9 (8C)	146.7 (4C)	146.1, 145.9, 145.7
C-4	139.8 (2C)	140.1 (2C)	139.8, 139.3, 139.1
	139.6 (2C)		
HHDP[d]			
C-1,1′	116.1 (4C)	116.4, 116.3	115.8, 115.6
C-2,2′	125.9 (2C)	127.3, 126.7	126.6, 126.0
	125.4 (2C)		
C-3,3′	108.2 (4C)	109.2 (2C)	108.3, 108.0
C-4,4′,6,6′	145.2 (4C)	146.1 (2C)	145.2, 144.4
	144.6 (4C)	145.3 (2C)	
C-5,5′	136.8 (2C)	137.4 (2C)	136.6 (2C)
	136.5 (2C)		
DHDG[d]			
C-1(1′)	118.7 (115.8)	120.3 (115.9)	
C-2(2′)	112.5 (138.0)	113.2 (138.1)	
C-3(3′)	148.1 (141.3)	149.1 (141.1)	
C-4(4′)	141.8 (140.4)	141.9 (140.8)	
C-5(5′)	145.9 (143.3)	147.3 (144.2)	
C-6(6′)	107.8 (110.3)	108.8 (111.0)	
Ester C=O			
	168.8 (2C)	169.1, 168.6	168.1, 167.6
	168.0 (2C)	167.6, 167.3	166.3, 165.5
	167.0 (2C)	166.4, 165.9	165.5, 165.0
	165.5 (2C)		
	165.1, 162.6		
Glucose			
C-1	93.6, 93.1	94.3	93.8
C-2	71.7 (2C)	72.0	71.8
C-3	73.5 (2C)	73.5	73.3
C-4	70.8 (2C)	71.1	70.8
C-5	72.8 (2C)	73.5	73.1
C-6	63.3 (2C)	63.5	63.1

a) 50.1 MHz, in acetone-d_6–D_2O, with dioxane (67.4 ppm) as an internal standard. *b*) 22.6 MHz in acetone-d_6. *c*) 50.1 MHz in acetone-d_6. *d*) The numbers of the carbons of these groups are in accord with those of formula **4** in Chart 1.

gemin A (**6**).[13] Therefore coriariin B is assigned the structure **4**, including the orientation of the DHDG group.

Coriariin A (**3**), $C_{82}H_{58}O_{52} \cdot 12H_2O$, $[\alpha]_D$ +91°, the main tannin of the leaves, forms an off-white amorphous powder, and this molecular formula is supported by the fast atom bombardment mass spectrum (FAB-MS) of **3** (*m/z* 1898 for the ion $[M+Na]^+$). Methylation of **3** with dimethyl sulfate and potassium carbonate afforded nonacosa-*O*-methylcoriariin A (**7**), $C_{111}H_{116}O_{52} \cdot 2H_2O$, which was methanolyzed to yield methyl tri-*O*-methylgallate (**8**), dimethyl hexamethoxydiphenate (**9**), dimethyl penta-*O*-methyldehydrodigallate (**10**) and D-glucose.

The ^{1}H-NMR spectrum of **3** shows fifteen aromatic protons assignable to four galloyl groups (δ 7.039, 7.036, 6.991 and 6.985, 2H each, s), two HHDP groups (δ 6.68, 1H, s; 6.65, 1H, s; 6.51, 2H, s) and a DHDG group (δ 7.27, 1H, d, J=2 Hz; δ 7.18; 1H, s; δ 6.70, 1H, d, J=2 Hz). The protons of the two glucose cores which show the β-configuration and the C1

NII-Electronic Library Service

conformation, appeared as six pairs of peaks. The chemical shifts of H-4 (δ 5.30 and 5.24) and H_a-6 (δ 5.37 and 5.35) of both glucose cores indicate that each of the two glucopyranose rings has an HHDP group on O-4 and O-6. The ^{13}C-NMR spectrum of coriariin A (**3**) also indicates the presence of galloyl, HHDP, DHDG groups and two glucose cores (Table I). Although the two anomeric carbon signals show a small difference of chemical shift (δ 93.6 and 93.1), all of the other glucose core signals overlap with the signals of the corresponding carbons in the other glucose core, indicating that the location of the polyphenolic groups on the two glucose cores are identical.

The CD spectrum of **3** shows a positive Cotton effect in the short wavelength region, the amplitude of which is approximately twice that of **2**,[12] indicating that both of the HHDP groups have the *S*-configuration.[12] Partial degradation of coriariin A (**3**) in hot water afforded tellimagrandin I (**1**) and coriariin B (**4**), and analysis by high-performance liquid chromatography (HPLC) showed that 1 mol of **3** gave approximately 1 mol each of **1** and **4**. Therefore coriariin A is assigned the structure **3**, in which the carboxyl group of coriariin B (**4**) is esterified by the anomeric hydroxyl group of **1**. HPLC analysis showed that coriariin B is not an artifact, as its peak was found in the homogenate of fresh leaves.

Biogenetically, coriariin A is assumed to be produced through C–O oxidative coupling between the galloyl group on O-1 in 2 mol of tellimagrandin II (**2**), which is fairly widely distributed in plants.[14] We have hitherto found two types of dimeric ellagitannins, one being dimers which have a valoneoyl group (presumably produced by the C–O oxidative coupling of an HHDP group in one monomer with a galloyl group in the other monomer) (*e.g.*, rugosins D[10] and E[10]), and the other being dimers having a DHDG group [*e.g.*, gemin A (**6**)[13] and agrimoniin[15]]. *Coriaria japonica* is the first example of a species which contain both types of dimeric ellagitannins. This plant is also one of the few reported examples of a species containing tannins having a glucose core of C1 conformation such as **1**—**4**, as well as tannins having a glucose of 1C conformation[16] as represented by geraniin.[8]

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. CD spectra were recorded on a JEOL J-20C spectropolarimeter. FAB-MS was recorded on a JEOL JMS-HX100 spectrometer and electron impact mass spectra (EI-MS) on a Shimadzu LKB-9000 GC-MS spectrometer. ^{1}H- and ^{13}C-NMR spectra were measured on a Hitachi R22-FTS spectrometer (90 MHz for ^{1}H-NMR and 22.6 MHz for ^{13}C-NMR) and a JEOL FX-200 spectrometer (200 MHz for ^{1}H-NMR and 50.1 MHz for ^{13}C-NMR), with tetramethylsilane as an internal standard unless otherwise mentioned; 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. Normal-phase HPLC was performed on a column of Nomura Develosil 60-5 (4 × 150 mm), developing with hexane–methanol–tetrahydrofuran–formic acid (55 : 33 : 11 : 1, by volume) containing oxalic acid (450 mg/l), and reversed-phase HPLC on a column of YMC A312 (ODS, 6 × 150 mm, Yamamura Chemical Laboratories Co., Ltd., Kyoto, Japan) with 0.1 M H_3PO_4 aq.–0.1 M KH_2PO_4 aq.–ethanol–ethyl acetate (17 : 17 : 4 : 2) at 40 °C. Detection was effected by UV absorption measurement at 254 nm or 280 nm. Analytical and preparative thin layer chromatography (TLC) were performed on Avicel SF (Funakoshi) cellulose plates (0.3 mm) developing with 7% acetic acid, or on Kieselgel PF_{254} (Merck) plates with the following solvent systems: (A) light petroleum–chloroform–acetone (8 : 7 : 3, by volume), (B) light petroleum–chloroform–acetone (4 : 6 : 3), (C) benzene–acetone (14 : 1) and (D) benzene–acetone (10 : 1). Light petroleum refers to that fraction boiling in the range of 75—120 °C. The plates were visualized by UV irradiation (254 nm) or by spraying with $FeCl_3$ or $NaNO_2$ aq.–acetic acid spray reagents. Sephadex LH-20 (100 μm, Pharmacia Fine Chemicals) and Toyopearl HW-40 (fine grade, Toyo Soda Mfg.) were used for column chromatography. Solvents were removed by evaporation under reduced pressure below 40 °C.

Isolation of Tannins from *Coriaria japonica*——The dried leaves (100 g) of *C. japonica* were homogenized in a mixture of acetone–water (7 : 3, v/v, 1.6 l) and the homogenate was filtered. After evaporation of the acetone, the aqueous solution was extracted with chloroform (3 × 200 ml), ethyl acetate (10 × 100 ml) and *n*-butanol (6 × 100 ml), successively. A portion (2.2 g) of the ethyl acetate extract (16 g) was chromatographed over Sephadex LH-20

NII-Electronic Library Service

(2.2 × 43 cm) with ethanol and methanol (ethanol, fractions 1—290; 20% methanol in ethanol, fractions 291—580; 50% methanol in ethanol, fractions 581—750; methanol, fractions 750—1000), collecting 500-drop fractions, to isolate the following compounds: 1,2,3,-tri-*O*-galloyl-β-D-glucose (49 mg) from fractions 45—67, geraniin (67 mg) from fractions 146—172, tellimagrandin I (**1**, 204 mg) from fractions 190—260, tellimagradin II (**2**, 96 mg) from fractions 340—370, rugosin E (83 mg) from fractions (832—852) and coriariin A (**3**, 33 mg) from fractions 873—877. Fractions 431—470 were further fractionated on a Toyopearl HW-40 column (1.1 × 80 cm) developing with methanol–water (7 : 3) to give rugosin A (15 mg) and coriariin B (**4**, 19 mg). A portion (3.2 g) of the *n*-butanol extract (10 g) was chromatographed over Toyopearl HW-40 (2.2 × 46 cm) with ehtnaol–water (7 : 3, fractions 1—190), and ethanol–acetone–water (13 : 1 : 6, fractions 191—500), collecting 12 g fractions, to yield rugosin D (33 mg) from fractions 320—331, and coriariin A (313 mg) from fractions 361—439.

Coriariin B (4)——An off-white amorphous powder, TLC (cellulose) *Rf* 0.37, $[\alpha]_D$ +66° (*c*=0.1, acetone). *Anal.* Calcd for $C_{48}H_{34}O_{31}\cdot 6H_2O$: C, 47.45; H, 3.82. Found: C, 47.30; H, 4.03. UV λ_{max}^{MeOH} nm (log ε): 222 (4.96), 277 (4.62). IR ν_{max}^{KBr} cm^{-1}: 1740—1710 (ester carbonyl). CD (MeOH) [θ] (nm): +12.7 × 10^4 (233), −2.0 × 10^4 (265), +2.7 × 10^4 (285). ^{1}H-NMR (90 MHz, in acetone-d_6) δ: 7.21 (1H, d, *J*=2 Hz), 7.19 (1H, s), 6.83 (1H, d, *J*=2 Hz) (DHDG); 7.00, 6.98 (2H each, s, 2 × galloyl); 6.66, 6.47 (1H each, s, HHDP); 6.13 (1H, d, *J*=8 Hz, H-1 of glucose), 5.82 (1H, t, *J*=10 Hz, H-3), 5.52 (1H, dd, *J*=8, 10 Hz, H-2), 5.35 (1H, dd, *J*=5, 13 Hz, H_a-6), 5.20 (1H, t, *J*=10 Hz, H-4), 4.50 (1H, dd, *J*=5, 10 Hz, H-5), 3.84 (1H, d, *J*=13 Hz, H_b-6).

Methylation of Coriariin B (4)——A mixture of **4** (13 mg), dimethyl sulfate (36 μl) and potassium carbonate (80 mg) in dry acetone (0.9 ml) was stirred for 22 h at room temperature, and then refluxed for 1.5 h. The reaction mixture was filtered and the filtrate was evaporated to give a syrupy residue. Preparative TLC (silica gel) using solvent system (B), followed by further development twice with solvent system (D), gave haptadeca-*O*-methylcoriariin B monomethyl ester (**5**, 7 mg), which was identified by direct comparison with an authentic specimen produced from gemin A (**6**)[13] ($[\alpha]_D$, EI-MS, ^{1}H-NMR and TLC).

Partial Hydrolysis of Coriariin B (4)——Coriariin B (**4**, 20 mg) in a mixture of water (10 ml) and trifluoroacetic acid (1 ml) was kept in a boiling water bath for 2 h. The hydrolyzate was purified by preparative TLC (cellulose) to give tellimagrandin I (**1**, 3 mg), which was identified by direct comparison with an authentic sample ($[\alpha]_D$, ^{1}H-NMR, normal-phase and reversed-phase HPLC, TLC).

Coriariin A (3)——An off-white amorphous powder, TLC (cellulose) *Rf* 0.27, $[\alpha]_D$ +91° (*c*=0.1, acetone). *Anal.* Calcd for $C_{82}H_{58}O_{52}\cdot 12H_2O$: C, 47.09; H, 3.95. Found: C, 47.02; H, 4.08. FAB-MS *m/z*: 1898 ($[M+Na]^+$). UV λ_{max}^{MeOH} nm (log ε): 224 (5.20), 280 (4.92). IR ν_{max}^{KBr} cm^{-1}: 1740—1710 (ester carbonyl). CD (MeOH) [θ] (nm): +28.4 × 10^4 (230), −3.8 × 10^4 (261), +6.0 × 10^4 (282). ^{1}H-NMR (200 MHz, in acetone-d_6 + D_2O) δ: 7.27 (1H, d, *J*=2 Hz), 7.18 (1H, s), 6.70 (1H, d, *J*=2 Hz) (DHDG); 7.039, 7.036, 6.991, 6.985 (2H each, s, 4 × galloyl); 6.68 (1H, s), 6.51 (2H, s) (2 × HHDP); 6.12, 6.06 (1H each, d, *J*=8 Hz, H-1 of both glucose cores), 5.83, 5.81 (1H each, t, *J*=10 Hz, 2 × H-3), 5.61, 5.59 (1H each, dd, *J*=8, 10 Hz, 2 × H-2), 5.37, 5.35 (1H each, dd, *J*=6, 14 Hz, 2 × H_a-6), 5.26, 5.21 (1H each, t, *J*=10 Hz, 2 × H-4), 4.51, 4.47 (1H each, dd, *J*=6, 10 Hz, 2 × H-5). The H_b-6 signals of both glucose cores (*ca.* 3.8 ppm) overlap with the peak of HDO.

Methylation of Coriariin A (3)——A mixture of **3** (100 mg), dimethyl sulfate (0.3 ml) and potassium carbonate (500 mg) in dry acetone (7 ml) was stirred for 24 h at room temperature, and then refluxed for 2 h. After filtration, the reaction mixture was concentrated and separated by preparative TLC (silica gel) using solvent system (A) to give nonacosa-*O*-methylcoriariin A (**7**, 55 mg), as colorless crystals (from methanol), mp 202 °C, $[\alpha]_D$ +35° (*c*=0.8, chloroform). *Anal.* Calcd for $C_{111}H_{116}O_{52}\cdot 2H_2O$: C, 57.51; H, 5.22. Found: C, 57.68; H, 5.14. EI-MS *m/z*: 422, 404, 360, 212, 197, 195. ^{1}H-NMR (200 MHz, in acetone-d_6) δ: 7.40 (1H, s), 7.38 (1H, d, *J*=2 Hz), 6.86 (1H, d, *J*=2 Hz) (penta-*O*-methyldehydrodigalloyl); 7.21 (8H, 4 × tri-*O*-methylgalloyl); 7.02 (1H, s), 6.96 (1H, s), 6.77 (2H, s), (2 × hexamethoxydiphenoyl); 6.26, 6.23 (1H each, d, *J*=8 Hz, H-1 of both glucose cores), 5.90, 5.86 (1H each, t, *J*=10 Hz, 2 × H-3), 5.63, 5.62 (1H each, dd, *J*=8, 10 Hz, 2 × H-2), 5.31, 5.27 (1H each, dd, *J*=6, 14 Hz, 2 × H_a-6), 5.30, 5.24 (1H each, t, *J*=10 Hz, 2 × H-4), 4.62, 4.54 (1H each, dd, *J*=6, 10 Hz, 2 × H-5), 3.95—3.64 (29 × OMe). The H_b-6 protons of both glucose cores overlap with the signals of the methoxyl groups.

Methanolysis of Nonacosa-*O*-methylcoriariin A (7)——A mixture of **7** (4 mg) and 1% sodium methoxide (0.5 ml) in absolute methanol (5 ml) was left to stand for 8 h at room temperature. The mixture was then neutralized with acetic acid, and evaporated. The residue was partitioned between chloroform and water. The chloroform layer was evaporated and the residue was purified by preparative TLC (silica gel) using solvent system (C) to give methyl tri-*O*-methylgallate (**8**, 1.3 mg), dimethyl hexamethoxydiphenate (**9**, 0.4 mg) and dimethyl penta-*O*-methyldehydrodigallate (**10**, 0.6 mg), which were identified by direct comparison with authentic samples[13] by EI-MS, TLC and GLC (oven temperature: 170, 250 and 270 °C, respectively). The aqueous layer gave glucose, which was identified by GLC of the trimethylsilyl ether.

Partial Hydrolysis of Coriariin A (3)——(1) An aqueous solution (15 ml) of **3** (120 mg) in a sealed tube was kept in a water bath (55 °C) for 17 h. The reaction mixture was concentrated and chromatographed over Sephadex LH-20 using 20% methanol in ethanol as an eluant to give tellimagrandin I (**1**, 28 mg) and coriariin B (**4**, 12 mg).

(2) An aqueous solution (1.4 ml) of **3** (1.4 mg) in a sealed tube was kept in a water bath (50 °C) for 18 h, and the reaction mixture was analyzed by reversed-phase HPLC, which showed the production of 1.2 mol of **1** and 0.7 mol of

NII-Electronic Library Service

4 from 1 mol of **3**.

Detection of Coriariin B (4) in Fresh Leaves——Fresh leaves (1 g) of *C. japonica*, collected at Mt. Hira, Shiga Prefecture, Japan, were homogenized in methanol (20 ml) within 1 d after collection. After centrifugation, the supernatant liquor was analyzed by normal-phase and reversed-phase HPLC. The peak of **4** was detected in both systems.

Acknowledgements We thank Assoc. Prof. Y. Takeda and Mr. K. Kida, Faculty of Pharmaceutical Sciences, Tokushima University, for the 200 MHz ^{1}H-NMR and 50.1 MHz ^{13}C-NMR spectra, and Dr. K. Fukushima, Research Institute for Chemobiodynamics, Chiba University, for FAB-MS.

References

1) T. Okuda and T. Yoshida, *Chem. Pharm. Bull.*, **15**, 1955 (1967).
2) T. Okuda and K. Konishi, *Tetrahedron*, **24**, 6907 (1968).
3) R. Hegnauer, "Chemotaxonomie der Pflanzen," Band 3, Birkhäuser Verlag, Basel, Stuttgart, 1964, p. 562.
4) T. Kariyone, K. Kashiwagi and S. Mizutani, *Yakugaku Zasshi*, **57**, 800 (1937).
5) T. Okuda, *Chem. Pharm. Bull.*, **9**, 178 (1961).
6) T. Okuda, K. Mori and T. Hatano, *Chem. Pharm. Bull.*, **33**, 1424 (1985).
7) T. Okuda, T. Hatano, K. Yazaki and N. Ogawa, *Chem. Pharm. Bull.*, **30**, 4230 (1982).
8) T. Okuda, T. Yoshida and T. Hatano, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 9.
9) T. Okuda, T. Yoshida, M. Ashida and K. Yazaki, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1765.
10) T. Okuda, T. Hatano and N. Ogawa, *Chem. Pharm. Bull.*, **30**, 4234 (1982).
11) C. K. Wilkins and B. A. Bohm, *Phytochemistry*, **15**, 211 (1976).
12) T. Okuda, T. Yoshida, T. Hatano, T. Koga, N. Toh and K. Kuriyama, *Tetrahedron Lett.*, **23**, 3937 (1982).
13) T. Yoshida, T. Okuda, M. U. Memon and T. Shingu, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 315.
14) *a*) T. Okuda, T. Yoshida, K. Mori and T. Hatano, *Heterocycles*, **15**, 1323 (1981); *b*) T. Okuda, T. Yoshida, T. Hatano, K. Yazaki and M. Ashida, *Phytochemistry*, **21**, 2871 (1982); *c*) E. A. Haddock, R. K. Gupta, S. M. K. Al-Shafi, K. Layden, E. Haslam and D. Magnolato, *ibid.*, **21**, 1049 (1982).
15) T. Okuda, T. Yoshida, M. Kuwahara, M. U. Memon and T. Shingu, *Chem. Pharm. Bull.*, **32**, 2165 (1984).
16) E. A. Haddock, R. K. Gupta and E. Haslam, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 2535.

NII-Electronic Library Service