Tannins of Theaceous Plants. III.[1] Camelliatannins A and B, Two New Complex Tannins from *Camellia japonica* L.

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Two new complex tannins, camelliatannins A (1) and B (2), were isolated from the leaves of *Camellia japonica* L. (Theaceae). The structures of these tannins, each consisting of a *C*-glucosidic ellagitannin and (−)-epicatechin (9), were established by means of chemical degradation, synthesis from casuariin (4) and 9, and rotating frame Overhauser enhancement spectroscopy (ROESY). Gemin D (3), 4, pedunculagin (5) and 2,3-(*S*)-hexahydroxydiphenoyl-D-glucose (6) were also isolated from the leaves.

Keywords tannin; complex tannin; *C*-glucosidic ellagitannin; casuariin; epicatechin; camelliatannin A; camelliatannin B; *Camellia japonica*; Theaceae; ROESY

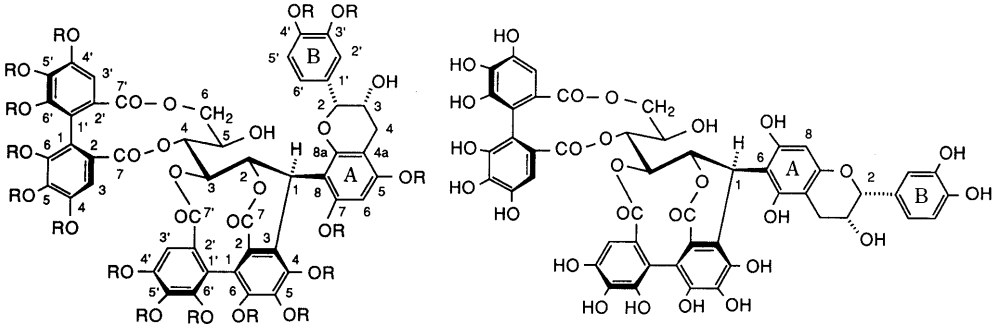
Isolation and structure elucidation of several dimeric and monomeric hydrolyzable tannins including camelliin B, which has a macrocyclic structure, from flowers of *Camellia japonica* L. were reported previously.[1,2] Further investigation of tannins of this species has led to the isolation of six compounds from the leaves. This paper deals with two new tannins named camelliatannins A (**1**) and B (**2**),[3] which belong to the category of complex tannins,[4] each consisting of a hydrolyzable tannin unit and a condensed tannin unit.

Results and Discussion

Fresh leaves of *Camellia japonica* were homogenized in aqueous acetone, and the concentrated filtrate from the homogenate was extracted with Et_2O, EtOAc and *n*-BuOH, successively. The *n*-BuOH extract was subjected to centrifugal partition chromatography (CPC),[5] and the fractions from CPC were further subjected to column chromatography on Toyopearl HW-40 and/or MCI-gel CHP-20P, which afforded camelliatannins A and B, along with gemin D (**3**),[2] casuariin (**4**),[6] pedunculagin (**5**)[6,7] and 2,3-(*S*)-hexahydroxydiphenoyl-D-glucose (**6**).[7-9]

Camelliatannin A (**1**) was obtained as an off-white powder. The positive-ion and negative-ion fast-atom bombardment mass spectra (FAB-MS) showed the $[M+H]^+$ ion peak at *m/z* 1057 and $[M-H]^-$ ion peak at *m/z* 1055, respectively. These ion peaks and the microanalytical data indicated that **1** has the molecular formula $C_{49}H_{36}O_{27}$. Methylation of **1** afforded a hexadeca-*O*-methyl derivative (**7**). The constituent sugar of **1** was glucose, as shown by its liberation upon the treatment of **1** with diluted sulfuric acid.

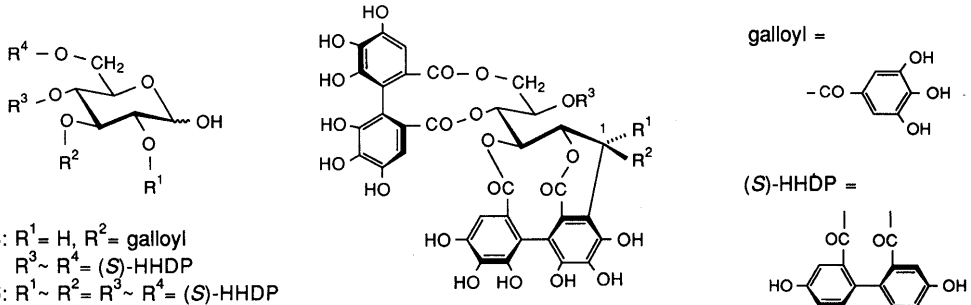
The proton nuclear magnetic resonance (^{1}H-NMR)



1: R=H
7: R=Me

2

Chart 1



3: R^1= H, R^2= galloyl
R^3~ R^4= (*S*)-HHDP
5: R^1~ R^2= R^3~ R^4= (*S*)-HHDP
6: R^1~ R^2= (*S*)-HHDP
R^3= R^4= H

4: R^1= OH, R^2= R^3= H
8: R^1= H, R^2= OH, R^3= galloyl

galloyl =

(*S*)-HHDP =

Chart 2

spectrum (500 MHz, in acetone-d_6 + D_2O) showed that **1** consists of two hexahydroxydiphenoyl (HHDP) groups (one forms a *C*-glucosidic HHDP group) [δ 6.65, 6.47 and 6.26 (1H each, s)], a glucose moiety in open-chain form [δ 4.71 (br s, H-1), 4.93 (br s, H-2), 4.99 (br d, J=3 Hz, H-3), 5.07 (br dd, J=3, 7 Hz, H-4), 3.81 (d-like, J=7 Hz, H-5), 4.48 (br d, J=12 Hz, H-6) and 3.38 (br d, J=12 Hz, H-6)] and an epicatechin residue [δ 7.18 (br s, H-2'), 6.93 (br d, J=8 Hz, H-5'), 6.83 (br d, J=8 Hz, H-6'), 5.91 (br s, A-ring H), 5.03 (br s, H-2), 4.24 (br s, H-3), 2.85 (br dd, J=3.5, 16 Hz, H-4), 2.73 (br d, J=16 Hz, H-4)]. The presence of the epicatechin residue was proved by the release of (−)-epicatechin (**9**) upon the treatment of **1** with acetic acid.[10] The chemical shifts of the glucose protons indicate that O-2, O-3, O-4 and O-6 of the glucose residue in **1** are acylated, and O-5 is unacylated. Although the precise coupling constants of the glucose protons are obscured by broadening of the peaks, the splitting patterns observed for H-3—H-6 of the glucose residue in **1** are very similar to those of the corresponding protons in several *C*-glucosidic tannins, such as **4** and stachyurin (**8**),[6] both of which have two HHDP groups at O-2/O-3 and O-4/O-6. This spectral similarity suggests that the locations of the two HHDP groups on the glucose moiety of **1** are the same as those of **4** and **8**. The circular dichroism (CD) spectrum of **1** showed a positive Cotton effect with a large amplitude in the short-wavelength region ($[\theta]_{234}$ $+2.2\times10^5$), indicating[9] the (*S*)-configuration for both of the HHDP groups. These findings suggest that **1** consists of **4** (or its epimer at C-1 of the glucose core) and **9**.

Although most of the signals in the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **1** are superimposable on the combined ^{13}C signals of **4** and **9** (Table I), differences of the chemical shifts were observed for several signals between **1** and the sum of **4** and **9**. The presence of a C–C bond between glucose C-1 and epicatechin C-8 (or C-6) in **1** is indicated by the large upfield shifts of the signals of these two carbons, relative to the corresponding carbon signals of **4**. The chemical shift (δ 80.3) of the glucose C-2 signal of **1** is analogous to those of the corresponding signals of the complex tannins in which the orientation of glucose H-1 is the same as that in **8**,[11] and suggests that the stereostructure at glucose C-1 in **1** is the same as that in these complex tannins.

TABLE I. ^{13}C-NMR Spectral Data for **1**, **2**, **4** and **9**

Carbons	**1**[a,b]	**2**[c]	**4**[a,b]	**9**[a,d]
Glucose residue				
C-1	38.2	38.1	67.7	
C-2	80.3	81.5	76.9	
C-3	76.5	76.4	70.7	
C-4	75.8	75.9	77.1	
C-5	69.2	68.6	68.4	
C-6	67.1	67.9	68.1	
Hexahydroxydiphenoyl				
C-1,1'	115.4, 115.6	115.4, 115.8	115.1, 115.9	
	115.7, 116.9	115.9, 117.0	116.3, 116.6	
C-2,2'	122.2, 124.2	122.4, 124.0	120.5, 125.5	
	125.9, 127.2	125.6, 127.4	127.4, 127.6	
C-3,3'	105.2, 107.4	105.8, 107.3	105.1, 106.9	
	108.6, 128.0	108.9, 128.1	108.3, 115.9	
C-4,4'	145.0,[e] 145.2[e]	145.1,[f] 145.2[f]	145.0, 145.1	
	145.2,[e] 145.4[e]	145.2,[f] 145.7[f]	145.7, 146.2	
C-5,5'	134.9, 135.8	135.2, 135.9	134.8, 135.6	
	136.3, 137.5	136.5, 137.6	136.5, 138.4	
C-6,6'	142.7,[e] 143.3[e]	143.1,[f] 143.2[f]	143.6, 143.8	
	144.2,[e] 144.2[e]	144.3,[f] 144.4[f]	144.3, 144.5	
C-7,7'	167.2, 167.8	167.9, 168.7	164.7, 168.6	
	169.1, 170.4	169.6, 170.6	169.3, 170.2	
Epicatechin moiety				
C-2	79.4	79.0		79.2
C-3	66.5	66.6		66.7
C-4	29.1	29.3		28.7
C-4a	99.6	100.1		99.5
C-5	156.4	155.6		157.4
C-6	96.6	107.2		95.9
C-7	155.9	155.6		157.3
C-8	105.2	96.5		95.3
C-8a	153.9	155.2		156.8
C-1'	132.0	131.9		131.6
C-2'	115.0	115.2		115.0
C-3'	145.0[e]	145.2[f]		145.2
C-4'	144.3[e]	144.3[f]		145.1
C-5'	115.7	115.4		115.3
C-6'	119.4	119.2		119.0

125.7 MHz, in acetone-d_6 + D_2O. *a*) Recorded at ambient temperature. *b*) The assignments are based on the (one-bond) ^{1}H–^{13}C heteronuclear shift correlation spectrum. *c*) Recorded at 40 °C. *d*) The assignments are based on the one-bond and long-range ^{1}H–^{13}C heteronuclear shift correlation spectra. *e,f*) The values with the same superscript may be interchanged.

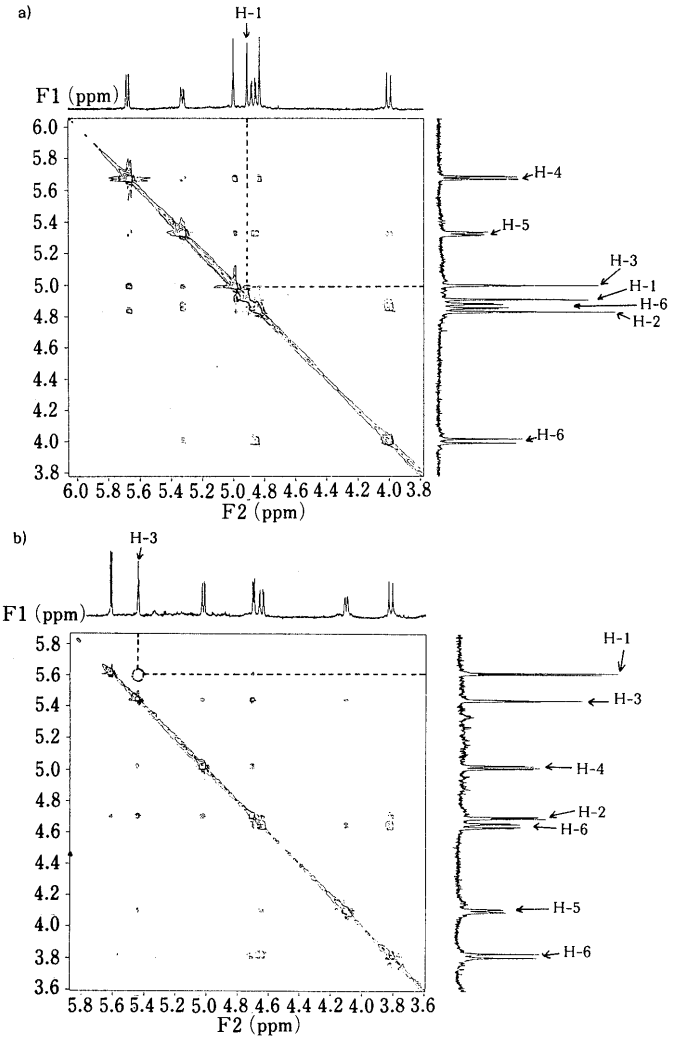


Fig. 1. The ROESY Spectra of a) Stachyurin (**8**) and b) Casuariin (**4**)

In acetone-d_6 + D_2O, 27 °C. The regions of the glucose protons are shown. The dotted circle in the spectrum of **4** (b) indicates the absence of the cross peak between H-1 and H-3.

The rotating frame Overhauser enhancement spectroscopy (ROESY) spectrum of **8** showed a cross peak due to the nuclear Overhauser effect (NOE) between glucose H-1 and H-3 (Fig. 1a), indicating the α-orientation of H-1 as reported recently,[12] while this cross peak was absent in the spectrum of **4**, which is the C-1 epimer of degalloylated **8** (Fig. 1b).

Since the glucose protons H-1 and H-2 in the ^{1}H-NMR spectrum of **1** are somewhat broadened, the coupling constant between these two protons is not clear enough for determining the orientation of the hydrogen on C-1. However, the ROESY spectrum of **1** (Fig. 2) showed the presence of an NOE between H-1 and H-3. Therefore, H-1 in **1** is α-oriented.

The ROESY spectrum of **1** also showed an NOE between H-1 of the glucose residue and H-2′ of the epicatechin residue. Molecular models of the two possible structures for **1** (one has a bond between epicatechin C-8 and glucose C-1, and the other between epicatechin C-6 and glucose C-1) show that only the former structure allows approach of the B-ring of the epicatechin residue to glucose H-1 (Fig. 2). The H-2 signal (δ 5.03) of the epicatechin moiety in **1** showed a downfield shift, relative to the corresponding signals of **9** (δ 4.89). This downfield shift is analogous to that observed for the corresponding H-2 signal (δ 4.96) of the lower epicatechin moiety in procyanidin B-2 (**10**),[13] which possesses a C-4—C-8 linkage. As noted for the glucose protons, the signals of most of the other protons in the ^{1}H-NMR spectrum of **1** are also broadened, and this broadening is attributable to the presence of the C-8 substituted epicatechin residue. Namely, the "folded" structure of **1** may induce not only restricted rotation[14] around the epicatechin-glucose linkage, but also hindrance of the conformational change of the ellagitannin residue.

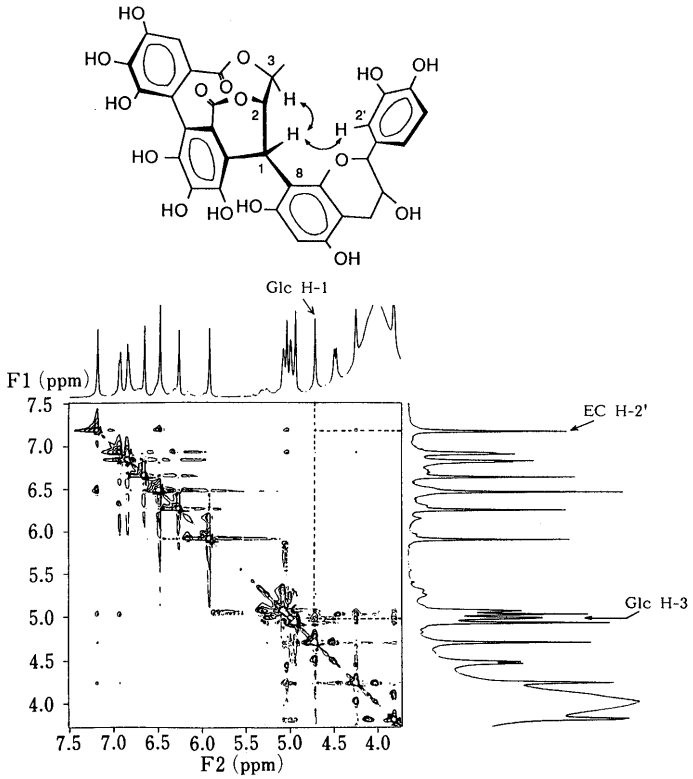


Fig. 2. The ROESY Spectrum of Camelliatannin A (**1**)

In acetone-d_6+D_2O, 30 °C. Glc and EC respectively represent glucose and epicatechin moieties in **1**.

Camelliatannin B (**2**) was obtained as an off-white powder. The positive-ion FAB-MS of **2** showed the $[M+H]^+$ ion peak at *m/z* 1057, which is consistent with the molecular formula $C_{49}H_{36}O_{27}$. The presence of glucose and an epicatechin moiety in the molecule of **2** was shown by their formation upon the treatment of **2** with diluted sulfuric acid or ethanolic acetic acid.

The ^{1}H-NMR spectrum (500 MHz, at 40 °C, in acetone-d_6+D_2O) showed that **2** has two HHDP groups (one has a *C*-glucosidic linkage) [δ 6.80, 6.53 and 6.47 (1H each, s)], a glucose moiety in the open-chain form [δ 4.66 (d, *J*=1 Hz, H-1), 4.82 (dd, *J*=1, 2.5 Hz, H-2), 5.21 (t, *J*=2.5 Hz, H-3), 5.27 (dd, *J*=2.5, 8 Hz, H-4), 4.12 (ddd, *J*=1, 3, 8 Hz, H-5), 4.73 (dd, *J*=3, 12 Hz, H-6) and 3.83 (dd, *J*=1, 12 Hz, H-6)] and an epicatechin moiety [δ 7.01 (d, *J*=1.5 Hz, H-2′), 6.79 (dd, *J*=1.5, 8.5 Hz, H-6′), 6.74 (d, *J*=8.5 Hz, H-5′), 5.98 (br s, A-ring H), 4.78 (br s, H-2), 4.15 (m, H-3), 2.82 (br dd, *J*=3.5, 16 Hz, H-4), 2.67 (br d, *J*=16 Hz, H-4)]. The CD spectrum of **2** showed a positive Cotton effect ($[\theta]_{236}$ $+2.3\times10^5$) reflecting the (*S*)-configuration of the two HHDP groups.[9] These two (*S*)-HHDP groups in **2** are at O-2/O-3 and O-4/O-6 as indicated by the chemical shifts and the coupling constants of the glucose protons. The ^{13}C-NMR spectrum of **2** was closely similar to that of **1** (Table I). These findings indicate that **2** is also composed of **4** (or its C-1 epimer) and **9**.

The orientation of glucose H-1 in **2** is also α, since the coupling constant between H-1 and H-2 is similar to that of **8**. The presence of an NOE between H-1 and H-3 of the glucose residue, which was shown by a cross peak in the ROESY spectrum of **2** (Fig. 3), also substantiated α-orientation of H-1.

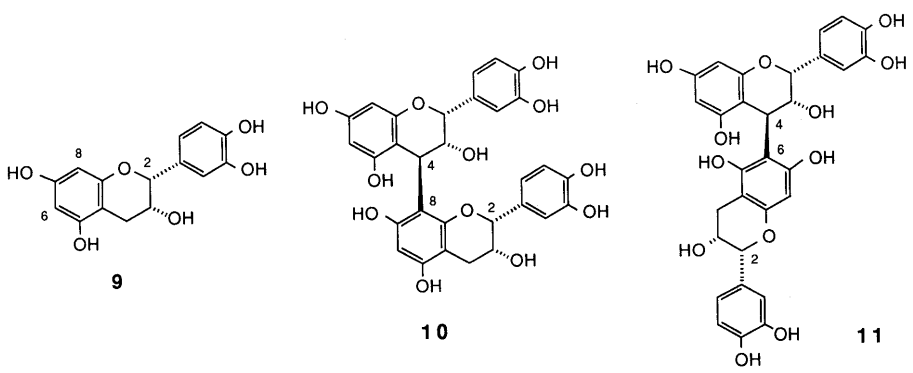


Chart 3

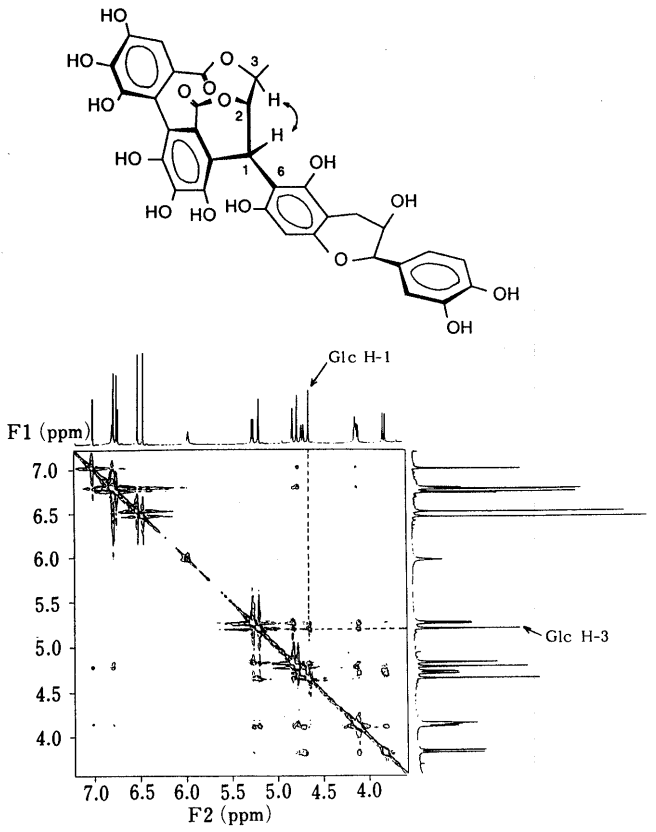


Fig. 3. The ROESY Spectrum of Camelliatannin B (**2**)
In acetone-d_6 + D_2O, 40 °C. Glc: glucose moiety in **2**.

This ROESY spectrum, however, did not show any cross peaks between the protons of the epicatechin moiety and those of the other parts of the molecule (glucose and HHDP). Unlike in **1**, the downfield shift of H-2 of the epicatechin moiety [relative to the corresponding proton of **9** (δ 4.89)] was not observed in **2**, and this absence of the downfield shift is analogous to that of H-2 in the C-6 substituted epicatechin (the lower half) of procyanidin B-5 (**11**) (δ 4.84).[13] These spectral data indicate C-6 substitution in the epicatechin moiety in **2**. Among the ^1H signals of **2**, only H-8 of the epicatechin moiety showed distinctive broadening due to the presence of the glucose-epicatechin linkage, and this supports the "unfolded" structure **2** having the less-hindered C-6-substituted epicatechin.

The structures **1** and **2** of camelliatannins A and B, thus assigned to be complex tannins,[4] were confirmed by acid-catalyzed condensation of **4** and **9**, followed by fractionation of the products by gel-column chromatography, which afforded **1** and **2**. Biogenetically, these two complex tannins may have been formed by the C–C oxidative coupling of these two constituent units.

Experimental

Optical rotations were measured on a JASCO DIP-4 polarimeter. Ultraviolet (UV) and infrared (IR) spectra were recorded on a Hitachi 200-10 spectrophotometer and a JASCO A-102 spectrometer, respectively. ^1H- and ^{13}C-NMR spectra were recorded on a Varian VXR-500 instrument (500 MHz for ^1H-NMR and 125.7 MHz for ^{13}C-NMR) in acetone-d_6 or in acetone-d_6 containing D_2O (*ca.* 3%). Chemical shifts are given in δ values (ppm), based on those of the ^1H and ^{13}C signals of acetone-d_6 (δ_H 2.04; δ_C 29.8) in the solvents. CD spectra were recorded on a JASCO J-500A spectrometer, equipped with a DP-501N data processor. FAB-MS were recorded on a JEOL JMS-D300 mass spectrometer. Gas liquid chromatography (GLC) was performed on a Hitachi 163 gas chromatograph equipped with a CITI G-250 WCOT column (1.2 mm × 40 m). The injection temperature and column temperature were 200 °C and 180 °C, respectively. Normal-phase high-performance liquid chromatography (HPLC) was performed on a Merck Superspher SI60 column (4 × 125 mm) with *n*-hexane–MeOH–tetrahydrofuran–formic acid (55 : 33 : 11 : 1) containing oxalic acid (450 mg/l) (flow rate, 1.5 ml/min). Reversed-phase HPLC was performed on a LiChrospher RP-18 (5 μm) column (4 × 250 mm) at 40 °C, with solvent system (A) 10 mM H_3PO_4–10 mM KH_2PO_4–MeOH (2 : 2 : 1) (flow rate, 1.1 ml/min), (B) 10 mM H_3PO_4–10 mM KH_2PO_4–EtOH–EtOAc (17 : 17 : 4 : 2) (flow rate, 1.2 ml/min), or (C) 10 mM H_3PO_4–10 mM KH_2PO_4–MeCN (9 : 9 : 2) (flow rate, 1.0 ml/min). Detection was effected with a Shimadzu SPD-6A spectrophotometer at 280 nm. CPC was performed using a CPC apparatus (model L-90, Sanki Engineering, Nagaoka-kyo), which contains 12 partition cell cartridges (type 1000E).

Isolation of Tannins from Leaves of *Camellia japonica* Fresh leaves (1.8 kg) of *Camellia japonica*, collected at the Herbal Garden of Okayama University in March 1988, were homogenized in 70% acetone (13 l). The concentrated filtrate (1.6 l) from the homogenate was extracted with Et_2O, EtOAc and *n*-BuOH, successively, and each solvent was removed by evaporation at below 40 °C. A portion (20 g) of the *n*-BuOH extract (85 g) was subjected to CPC with *n*-BuOH–*n*-PrOH–H_2O (4 : 1 : 5, v/v; normal-phase development→reversed-phase development), to separate six fractions (fr. I—III for the normal-phase development, and fr. IV—VI for the reversed-phase development). Fraction II (1.5 g) was chromatographed on Toyopearl HW-40F with 20% EtOH and then with 40% EtOH, to give **3** (20 mg), **4** (13 mg) and **5** (321 mg). Fraction V (1.1 g) from CPC was chromatographed on MCI-gel CHP-20P with H_2O and then with 20% MeOH. The H_2O eluate (296 mg) was further separated on a column of Toyopearl HW-40F with 40% EtOH→60% EtOH, to give **1** (109 mg) and **6** (25 mg). The 20% MeOH eluate from the column of MCI-gel (378 mg) was further chromatographed on Toyopearl HW-40SF with 70% EtOH, and then on MCI-gel CHP-20P with 10% MeOH→20% MeOH), to give **2** (12 mg).

Camelliatannin A (1) An off-white amorphous powder, $[\alpha]_D$ +68° (c = 1.2, MeOH). *Anal.* Calcd for $C_{49}H_{36}O_{27}\cdot 7H_2O$: C, 49.75; H, 4.26. Found: C, 49.77; H, 4.24. Positive-ion FAB-MS: m/z 1057 ($[M+H]^+$). Negative-ion FAB-MS: m/z 1055 ($[M-H]^-$). UV λ_{max}^{MeOH} nm (log ε): 207 (4.99), 232 (sh, 4.83), 280 (sh, 4.34). IR ν_{max}^{KBr} cm^{-1}: 1720, 1610. CD (MeOH): $[\theta]_{285}$ +2.8 × 10^4, $[\theta]_{262}$ −6.1 × 10^4, $[\theta]_{234}$ +2.2 × 10^5, $[\theta]_{206}$ −1.2 × 10^5. ^1H-NMR: see text. ^{13}C-NMR: see Table I.

Camelliatannin B (2) An off-white amorphous powder, $[\alpha]_D$ +138° (c = 0.6, MeOH). *Anal.* Calcd for $C_{49}H_{36}O_{27}\cdot 8H_2O$: C, 49.00; H, 4.33. Found: C, 48.50; H, 3.67. Positive-ion FAB-MS: m/z 1057 ($[M+H]^+$). UV λ_{max}^{MeOH} nm (log ε): 207 (4.99), 232 (sh, 4.84), 2.80 (sh, 4.34). IR ν_{max}^{KBr} cm^{-1}: 1720, 1610. CD (MeOH): $[\theta]_{285}$ +2.2 × 10^4, $[\theta]_{263}$ −4.5 × 10^4, $[\theta]_{236}$ +2.3 × 10^5, $[\theta]_{202}$ −1.4 × 10^5. ^1H-NMR: see text. ^{13}C-NMR: see Table I.

Degradation of 1 and 2 1) A solution of **1** (2 mg) in 1 N H_2SO_4 (0.2 ml) in a sealed tube was heated in a boiling-water bath for 12 h. Then, the solution was neutralized with Dia-ion SA-20AP, and evaporated. The presence of glucose in the residue was shown by trimethylsilylation followed by GLC analysis. The liberation of glucose upon the treatment of camellianin B with 1 N H_2SO_4 was also proved in an analogous way.

2) A solution of **1** (1 mg) in a mixture of acetic acid and EtOH (1 : 4, v/v; 1 ml) in a sealed tube was heated in a boiling-water bath for 36 h, and the reaction mixture was analyzed by HPLC [normal-phase HPLC, t_R (retention time) 2.0 min; reversed-phase HPLC with solvent (A), t_R 29.0 min; reversed-phase HPLC with solvent (B), t_R 5.6 min], resulting in the identification of **9**. The liberation of **9**, upon the treatment of **2** with ethanolic acetic acid for 18 h, was also proved by HPLC in an analogous way.

Methylation of 1 Dimethyl sulfate (10 μl) and potassium carbonate (100 mg) were added to a solution (10 ml) of **1** (10 mg) in acetone. The mixture was stirred overnight at room temperature, and then refluxed for 5 h. After centrifugation, the supernatant was evaporated, and the residue was subjected to preparative thin layer chromatography (PTLC) on Kieselgel 60 PF_{254} (Merck) with benzene–acetone (4 : 1, developed twice), to give **7** (5 mg), $[\alpha]_D$ −13° (c = 0.6, acetone). *Anal.* Calcd for $C_{65}H_{68}O_{27}\cdot 2H_2O$: C, 59.26; H, 5.50. Found: C, 59.01; H, 5.21. ^1H-NMR (500 MHz, in acetone-d_6): δ 7.27 [d, J = 2 Hz, H-2′ of the epicatechin (EC) moiety], 7.15 (dd, J = 2, 8 Hz, EC H-6′), 6.96 (d, J = 8 Hz, EC H-5′), 6.92, 6.73, 6.70 (each s, HHDP H-3, H-3′), 6.22 (s, EC H-6), 5.22 (br s, EC H-2), 5.06 [dd, J = 5.5, 7 Hz, H-4 of Glc (glucose)], 4.94 (dd, J = 1, 2 Hz, Glc H-2), 4.93 (d, J = 1 Hz, Glc H-1), 4.91 (dd, J = 2, 5.5 Hz, Glc H-3),

4.45 (dd, $J=2.5$, 12.5 Hz, Glc H-6), 4.34 (m, EC H-3), 4.06, 3.94, 3.88, 3.87, 3.84, 3.83, 3.81, 3.80, 3.80, 3.75, 3.74, 3.66, 3.63, 3.59, 3.58, 3.44 (3H each, s, 16 × OMe).

Transformation of 4 and 9 into 1 and 2 A mixture of **4** (200 mg), **9** (300 mg) and *p*-toluenesulfonic acid (100 mg) in dioxane (17 ml) in a sealed tube was heated in a boiling-water bath for 5 h. Then, the solvent was evaporated off, and the residue was chromatographed over MCI-gel CHP-20P with H_2O (fr. 1)→5% MeOH (fr. 2 and fr. 3)→20% MeOH (fr. 4—6). Fraction 1 (150 mg) was mainly composed of unchanged **4**. Fraction 3 (24 mg) was repeatedly chromatographed over Toyopearl HW-40SF (with 40% EtOH and then with 25% EtOH), to give a product (1.0 mg). Fr. 5 (15 mg) was further purified in an analogous way, to give another product (0.9 mg). These products were respectively identified as **1** and **2** by ^{1}H-NMR and HPLC [normal-phase HPLC: **1**, t_R 9.1 min; **2**, t_R 8.9 min. Reversed-phase HPLC with solvent (C): **1**, t_R 3.6 min; **2**, t_R 5.2 min].

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References and Notes

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