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Tannins and Related Polyphenols of Theaceous Plants. VIII.[1)] Camelliatannins C and E, New Complex Tannins from *Camellia japonica* Leaves

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Two new tannins, camelliatannins C (1) and E (2), were isolated from the leaves of *Camellia japonica* L. (Theaceae). They were found to be complex tannins of a new type, lacking C–C bond between glucose C-1 and the aroyl (hexahydroxydiphenoyl) group at glucose O-2.

Key words tannin; *Camellia japonica*; Theaceae; camelliatannin C; camelliatannin E

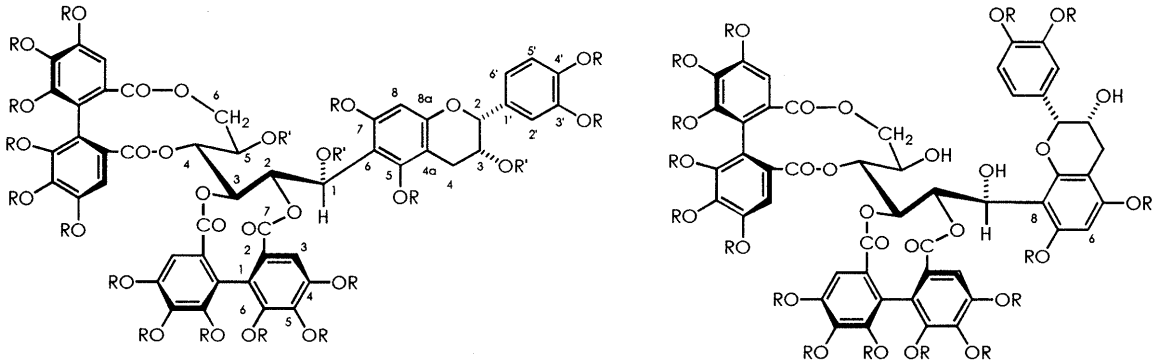
We have reported the isolation and structure elucidation of tannins of several plant species of Theaceae, including *Camellia japonica*. They include monomeric and dimeric hydrolyzable tannins,[1–4)] and complex tannins.[2,5)] The complex tannins previously isolated from *C. japonica*, and from some other plant species[6)] are regarded as condensates of *C*-glycosidic ellagitannins and flavan-3-ols,[5)] and have two C–C bonds at glucose C-1: one is that between glucose C-1 and the A-ring of the flavan-3-ol moiety, and the other is that between glucose C-1 and the aroyl [*e.g.*, hexahydroxydiphenoyl (HHDP)] group at glucose O-2. We report here the isolation of two more new tannins from *C. japonica* leaves. These tannins, named camelliatannins C (1) and E (2), are complex tannins of a new type, lacking the C–C bond between glucose C-1 and the aroyl group at glucose O-2 in each molecule.

Results and Discussion

The new tannins, **1** and **2**, were isolated in the following way. Fresh leaves of *C. japonica* were homogenized in aqueous acetone, and the concentrated filtrate obtained from the homogenate was extracted with Et_2O and EtOAc, successively. The aqueous layer was then concentrated to afford a brown residue, which was subjected to column chromatography on Diaion HP-20P, Toyopearl HW-40 and MCI-gel CHP-20, to give **1** and **2**.

Structure of Camelliatannin C Camelliatannin C (**1**) was obtained as an off-white powder. The positive-ion and negative-ion FAB-MS of **1** showed an $[M+H]^+$ ion peak at m/z 1075 and an $[M-H]^-$ ion peak at m/z 1073, respectively, corresponding to the formula $C_{49}H_{38}O_{28}$. The ^1H-NMR spectrum of **1** (500 MHz, in acetone-d_6+D_2O) showed three aromatic proton signals forming an ABX system [δ 6.99 (1H, d, $J=2$ Hz, H-2′), 6.74 (1H, d, $J=8.5$ Hz, H-5′) and 6.78 (1H, dd, $J=2$, 8.5 Hz, H-6′)], an aromatic singlet at δ 5.84 (1H, A-ring H) and four aliphatic proton signals at δ 4.78 (1H, br s, H-2), 4.17 (1H, m, H-3), 2.94 (1H, dd, $J=4.5$, 17 Hz, H-4) and 2.74 (1H, dd, $J=2.5$, 17 Hz, H-4). These signals indicate the presence of an epicatechin moiety in the molecule of **1**. The spectrum also showed four aromatic singlets assignable to two HHDP groups [δ 6.73 (1H), 6.64 (2H) and 6.53 (1H)], and sugar proton signals [δ 5.75 (1H, d, $J=2$ Hz, H-1), 5.42 (1H, dd, $J=2$, 9 Hz, H-2), 5.89 (1H, dd, $J=2$, 9 Hz, H-3), 5.53 (1H, dd, $J=2$, 8 Hz, H-4), 4.32 (1H, br d, $J=8$ Hz, H-5), 4.60 (1H, dd, $J=2.5$, 12.5 Hz, H-6) and 3.98 (1H, br d, $J=12.5$ Hz, H-6)]. The constituent sugar is glucose, as shown by the formation of glucose upon the treatment of **1** with diluted sulfuric acid for the cleavage of all of the linkages around the sugar moiety.

The chemical shifts of the glucose protons suggested that the hydroxyl groups at glucose C-2, C-3, C-4 and C-6



1: R=R'=H
1a: R=Me, R'=H
1b: R=Me, R'=$COCH_3$

2: R=H
2a: R=Me

Chart 1

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are acylated with the two HHDP groups. The coupling constants of these glucose proton signals are similar to those reported for *C*-glucosidic tannins, such as stachyurin (except for $J_{2,3}$),[5,7] suggesting that the glucose residue adopts an open-chain form. Taking the open-chain form of the glucose residue into consideration, the absence of one of the two A-ring protons of the epicatechin moiety suggests the presence of a C–C bond between glucose C-1 and epicatechin C-6 or C-8. Partial degradation of **1** under a weakly acidic condition (ethanolic acetic acid) afforded (−)-epicatechin (**3**) and casuariin (**4**)[5] (Chart 2).

Methylation of **1** with dimethyl sulfate and potassium carbonate in acetone afforded hexadecamethylate (**1a**), as revealed by sixteen methoxyl signals in the ^{1}H-NMR spectrum. Upon the successive irradiation of all of the methoxyl signals of **1a** for detecting nuclear Overhauser effects (NOEs) between the methoxyl groups and the adjacent aromatic protons, NOE of the A-ring proton (δ 6.42) of the epicatechin moiety in **1a** was observed only when one methoxyl group (δ 3.84) was irradiated (14%). If C-8 of the epicatechin moiety participates in the C–C linkage with glucose C-1, NOEs of the A-ring proton (H-6) should be observed upon the irradiation of two methoxyl signals (the methoxyl groups at O-5 and O-7) (see Fig. 1). The participation of epicatechin C-6 in the linkage with glucose was thus assigned.

The *S*-configuration of the HHDP groups in **1** was indicated by the positive Cotton effect with a large amplitude in the short-wavelength region[8] ($[\theta]_{237}+1.9\times10^{5}$) in the circular dichroism (CD) spectrum of **1**.

These findings suggest that **1** has a structure closely related to a complex tannin previously isolated from the same plant source, camelliatannin B (**5**),[5] which is also composed of 6-substituted epicatechin, glucose and two (*S*)-HHDP groups. Heating a dioxane solution of **1** in the presence of polyphosphoric acid caused its transformation into **5**. As previously reported,[5] **5** was synthesized from casuariin (**4**) and (−)-epicatechin (**3**), and therefore the 2*R*,3*R* configuration of the epicatechin residue in **1** was substantiated by this transformation. This transformation also verified the locations of the HHDP groups at O-2/O-3 and O-4/O-6 on the open-chain glucose in **1**.

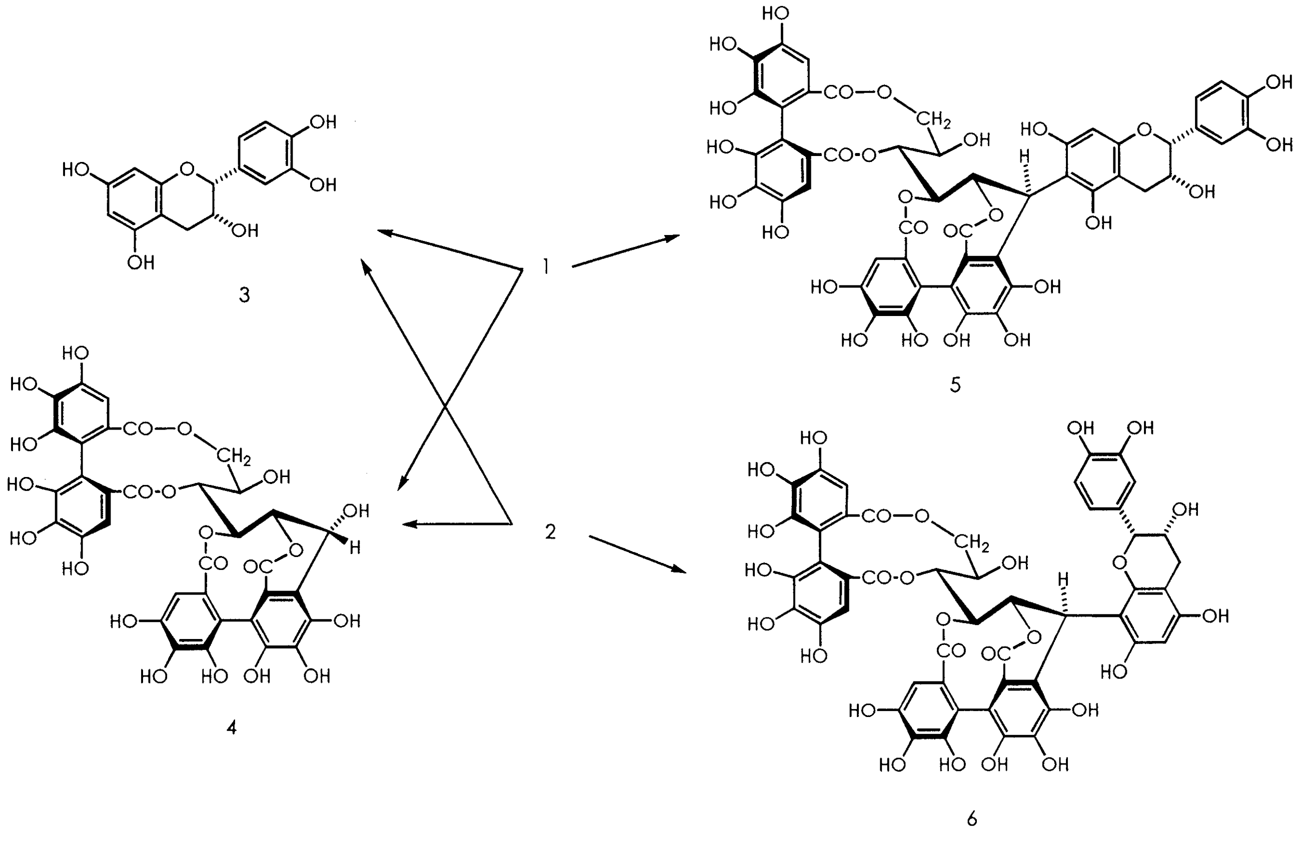
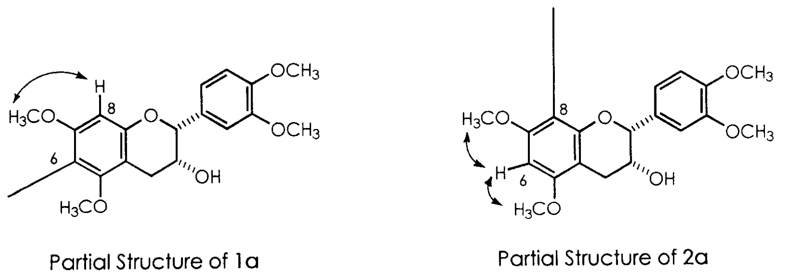


Chart 2



Partial Structure of 1a

Partial Structure of 2a

Fig. 1. Observed NOEs between A-Ring Protons and Adjacent Methoxyl Protons in the Epicatechin Residues of **1a** and **2a**

The molecular mass of **1** ($C_{49}H_{38}O_{28} = 1074$) is 18 mass units ($H_2O$) larger than that of **5** ($C_{49}H_{36}O_{27} = 1056$). The presence of four HHDP protons in the ^{1}H-NMR spectrum of **1**, instead of three HHDP protons of **5** suggests that the C–C bond between C-1 of glucose and C-3 of the HHDP group at glucose O-2/O-3 in **5** is absent in the molecule of **1**.

The ^{13}C-NMR spectrum of **1** also showed that this tannin is composed of epicatechin, two HHDP groups and glucose in an open-chain form (see Experimental). Although the spectrum showed a structural resemblance of **1** to **5**, the glucose C-1 signal at δ 68.3 in the spectrum of **1** showed a distinctive downfield shift relative to the corresponding signal of **5** (δ 38.1). This downfield shift is attributable to the presence of a hydroxyl group at glucose C-1.

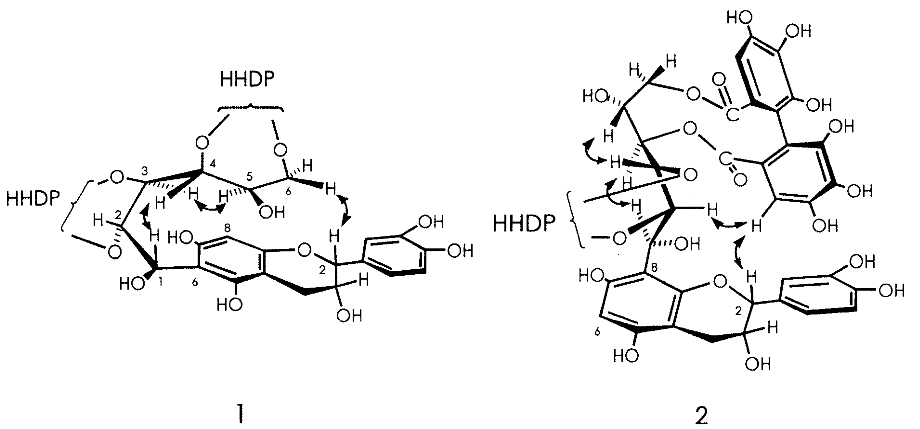
The presence of a hydroxyl group at glucose C-1 was evidenced by acetylation of **1a**, giving an acetate (**1b**). The ^{1}H-NMR spectrum of **1b** (500 MHz, in $CDCl_3$) showed signals of three acetyl groups at δ 2.12, 2.09 and 1.81 (3H each, s), and also showed downfield shifts of the signals due to H-1 and H-5 of the glucose core, and of the H-3 signal of the epicatechin residue, relative to the corresponding signals of **1a** [δ 5.60 (**1a**)→6.52 (**1b**) (glucose H-1); δ 4.45 (**1a**)→5.22 (**1b**) (glucose H-5); δ 4.29 (**1a**)→ 5.31 (**1b**) (epicatechin H-3)]. These downfield shifts clearly indicated the presence of the aliphatic hydroxyl groups at C-1 and C-5 of the glucose residue, and at C-3 of the epicatechin residue in **1**.

In order to assign the configuration at glucose C-1, rotating-frame Overhauser enhancement spectroscopy (ROESY) was applied. The ROESY spectrum of **1** showed a correlation between glucose H-6 and epicatechin H-2, indicating that the glucose moiety forms a structure folded towards the epicatechin moiety, as shown in Fig. 2, where the two protons are spatially close to each other. As for the glucose protons, correlations between H-1 and H-4, and between H-3 and H-5 were also observed in the spectrum, and the former indicated that the two protons, H-1 and H-4, are at the front side of the folded structure. On the other hand, the latter two protons, H-3 and H-5, should be at the back side, since no correlation between H-1 and H-3 was observed in the spectrum. The structure of **1** with the *S*-configuration at glucose C-1 satisfies these correlations and the dihedral angles of glucose C–H bonds defined by the coupling constants of the glucose protons.

Structure of Camelliatannin E Camelliatannin E (**2**) was also obtained as an off-white powder. The positive-ion FAB mass spectrum of **2** showed an $[M+Na]^+$ ion peak at *m/z* 1097, suggesting that **2** is an isomer of **1**. The ^{1}H-NMR spectrum of **2** (500 MHz, in acetone-$d_6 + D_2O$, 40 °C) showed signals assignable to the protons of an epicatechin moiety [δ 6.84 (1H, br s, H-2′), 6.68 (1H, br d, $J = 8$ Hz, H-6′), 6.60 (1H, d, $J = 8$ Hz, H-5′), 6.03 (1H, s, A-ring H), 4.85 (1H, br s, H-2), 4.21 (1H, m, H-3), 2.83 (H-4, in part overlapped with the HDO signal), 2.68 (1H, dd, $J = 5$, 16.5 Hz, H-4)], and two HHDP groups [δ 6.81, 6.64, 6.62 and 6.52 (1H each, s)]. The spectrum also showed signals due to an open-chain glucose residue [δ 5.73 (1H, d, $J = 2.5$ Hz, H-1), 5.34 (1H, dd, $J = 2.5$, 9 Hz, H-2), 5.94 (1H, dd, $J = 2$, 9 Hz, H-3), 5.50 (1H, dd, $J = 2$, 8 Hz, H-4), 4.26 (1H, br d, $J = 8$ Hz, H-5), 4.59 (1H, dd, $J = 3$, 12 Hz, H-6) and 3.96 (1H, dd, $J = 1.5$, 12 Hz, H-6)]. Although the presence of only one proton on the A-ring of the epicatechin moiety and the open-chain glucose core suggests the presence of a C–C bond between glucose C-1 and the epicatechin moiety, the chemical shift of the A-ring proton in the ^{1}H-NMR spectrum of **2** is noticeably different from that of **1**. These data indicated that **2** is a regio-isomer of **1**, concerning the position of the C–C bond on the epicatechin moiety.

The ^{13}C-NMR spectrum of **2** also indicated that **2** is composed of epicatechin, two HHDP groups and glucose adopting an open-chain form (see Experimental). The presence of glucose in **2** was substantiated by the formation of glucose upon the degradation of **2** with diluted sulfuric acid. Formation of **3** along with **4** was also observed upon the treatment of **2** with ethanolic acetic acid.

Methylation of **2** with dimethyl sulfate and potassium carbonate afforded the methyl derivative **2a**, which shows the signals of sixteen methoxyl groups in its ^{1}H-NMR spectrum. If the participation of epicatechin C-8 in the C–C linkage with glucose C-1 is assumed, NOEs of two methoxyl groups (those at O-5 and O-7 of epicatechin) with the A-ring proton would be expected to be observed (Fig. 1). In fact, NOE correlated spectroscopy (NOESY) of **2a** showed that two of the methoxyl groups (at δ 3.82 and 3.70) have NOEs with the A-ring proton at δ 6.35. The participation of epicatechin C-8 in the linkage with glucose C-1 was further verified by the transformation of



1 2

Fig. 2. Observed Correlations in the ROESY Spectra of Camelliatannins C (1) and E (2) Suggesting Their Conformations

2 into camelliatannin A (**6**)[5] using polyphosphoric acid. Since **6** was synthesized from **4** and (−)-epicatechin (**3**),[5] the 2*R*,3*R* configuration of the epicatechin residue in **2** was also substantiated by this transformation. The locations of the HHDP groups at O-2/O-3 and O-4/O-6 on the open-chain glucose in **2** were also indicated by this transformation.

The CD spectrum of **2** showed a positive Cotton effect in the short-wavelength region ($[\theta]_{234} + 2.0 \times 10^5$), substantiating the *S*-configuration of the HHDP groups.[8]

The coupling constants of glucose protons of **2** are practically identical with those of **1**, indicating the identity of the conformation of the glucose residue, and also of the configuration at glucose C-1 with those of **1**. The ROESY spectrum of **2** showed cross peaks due to the correlation between glucose H-1 and H-4, and that between H-3 and H-5 substantiated the *S*-configuration at glucose C-1 in a way similar to that for **1**. Structure **2** was thus assigned for camelliatannin E. The spectrum also showed correlations between an HHDP proton at δ 6.64 and glucose H-2, and between the HHDP proton and epicatechin H-2. The HHDP proton was assigned as that on the glucose O-4 side of the HHDP group at glucose O-4/O-6, based on a molecular model and on the three-bond coupling between the HHDP proton and the ester carbonyl carbon at δ_C 167.2, and that between the same ester carbonyl carbon and glucose H-4 (δ_H 5.50), shown by $^1H-^{13}C$ long-range shift-correlation spectroscopy (COSY) for **2**. A possible conformation of **2** is illustrated in Fig. 2.

The facile transformation from **1** to **5**, and that from **2** to **6**, suggested that complex tannins of a new type, such as **1** and **2**, might be precursors of the "normal" type of complex tannins,[5,6] such as **5** and **6**, and if so, complex tannins of this new type can be expected to be found in other plants containing the "normal" type of complex tannins.

Experimental

FAB-MS were recorded on a JEOL JMS-D300 or a VG 70-SE mass spectrometer. UV spectra were recorded on a Hitachi 200-10 spectrophotometer. ^1H- and ^{13}C-NMR spectra were recorded on a Varian VXR-500 instrument (500 MHz for ^1H-NMR and 126 MHz for ^{13}C-NMR) or a Bruker AM-400 (400 MHz for ^1H-NMR) spectrometer, at room temperature unless otherwise mentioned. Chemical shifts are based on those of the solvent signals (acetone-d_6, δ_H 2.04 and δ_C 29.8; $CDCl_3$, δ_H 7.26) and given in δ values. CD spectra were recorded on a JASCO J-500A spectrometer, equipped with a DP-501N data processor. Preparative TLC was performed on Merck Kieselgel $60PF_{254}$ plates. 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 column temperature and injection temperature were 180 and 200 °C, respectively. The flow-rate of the He carrier gas was 20 ml/min. HPLC was performed on a Merck LiChrospher 100 RP-18 (5 μm) column (4 × 250 mm) with 10 mM KH_2PO_4–10 mM H_3PO_4–CH_3CN (9 : 9 : 2) at 40 °C.

Isolation of Camelliatannins C (1) and E (2) Leaves (3.5 kg) of *C. japonica* L., were collected at the Herbal Garden of Okayama University, in April 1989, and were homogenized in acetone–water (7 : 3, v/v) (20 l). The debris in the homogenate was filtered off, the filtrate was concentrated to 3 l *in vacuo*, and the resulting solution was extracted with Et_2O and EtOAc, successively. The aqueous layer was then evaporated, and the residue was chromatographed over Diaion HP-20 (6.5 × 48 cm) with aqueous MeOH (0%→20%→40%→60%→80%→100%). The eluate with 20% MeOH (23.6 g) was further chromatographed over Toyopearl HW-40 (coarse grade, 2.5 × 63 cm) with 70% EtOH–70% acetone [10 : 0 (frs. I—V)→9 : 1 (fr. VI)→8 : 2 (frs. VII and VIII)→0 : 10 (fr. IX)]. Fractions II and V were respectively purified by column chromatography on MCI-gel CHP-20P (75—150 μm) and/or on Toyopearl HW-40 (superfine grade), to give camelliatannins E (**2**) (67 mg) and C (**1**) (71 mg).

Camelliatannin C (1) An off-white powder, $[\alpha]_D$ +119° (c = 1.6, MeOH). *Anal.* Calcd for $C_{49}H_{38}O_{28} \cdot 7H_2O$: C, 49.00; H, 4.33. Found: C, 48.83; H, 4.23. FAB-MS: positive-ion mode *m/z*: 1075 ($[M+H]^+$); negative-ion mode *m/z*: 1073 ($[M-H]^-$). UV λ_{max}^{MeOH} nm (log ε): 207 (4.98), 230 (sh, 4.79). CD (MeOH) $[\theta] \times 10^{-4}$ (nm): +0.5 (286), −4.4 (264), +19.1 (237), −9.0 (215). ^1H-NMR: see text. ^{13}C-NMR (126 MHz, in acetone-d_6 + D_2O) δ: 28.9 [epicatechin (EC) C-4], 66.6 (EC C-3), 67.9 [glucose (Glc) C-6], 68.3 (Glc C-1), 69.1 (Glc C-5), 72.2 (Glc C-4), 76.5 (Glc C-3), 78.6 (Glc C-2), 79.1 (EC C-2), 94.9 (EC C-8), 99.8 (EC C-4a), 103.8 (EC C-6), 106.7, 107.5, 107.9, 109.1 (HHDP C-3), 113.9, 114.4, 114.9, 116.8 (HHDP C-1), 115.1 (EC C-2′), 115.3 (EC C-5′), 119.1 (EC C-6′), 124.9, 127.2, 127.5, 127.6 (HHDP C-2), 131.9 (EC C-1′), 135.4, 135.8, 136.0, 136.8 (HHDP C-5), 143.9, 144.1, 144.3 (2C), 144.7, 145.1—145.2 (5C) (HHDP C-4 and C-6; EC C-3′ and C-4′), 153.6 (EC C-8a), 155.7 (EC C-7), 157.1 (EC C-5), 167.3, 168.9, 169.4, 169.7 (HHDP C-7). The assignments of the signals were substantiated by $^1H-^{13}C$ COSY, and $^1H-^{13}C$ long-range COSY.

Camelliatannin E (2) An off-white powder, $[\alpha]_D$ +53° (c = 1, MeOH). *Anal.* Calcd for $C_{49}H_{38}O_{28} \cdot 6H_2O$: C, 49.75; H, 4.23. Found: C, 49.52; H, 4.06. FAB-MS: positive-ion mode *m/z*: 1097 ($[M+Na]^+$). UV λ_{max}^{MeOH} nm (log ε): 208 (4.99), 231 (sh, 4.83), 260 (sh, 4.55). CD (MeOH) $[\theta] \times 10^{-4}$ (nm): +2.6 (283), −5.6 (261), +20.2 (234), +6.6 (216). ^1H-NMR: see text. ^{13}C-NMR (126 MHz, in acetone-d_6 + D_2O, 40 °C) δ: 27.8 (EC C-4), 67.1 (EC C-3), 67.8 (Glc C-6), 68.7 (Glc C-1), 69.7 (Glc C-5), 72.7 (Glc C-4), 76.8 (Glc C-3), 78.5 (Glc C-2), 79.2 (EC C-2), 96.6 (EC C-6), 99.8 (EC C-4a), 104.2 (EC C-8), 107.3, 107.8, 108.7, 108.9 (HHDP C-3), 113.5, 114.5, 115.1, 116.1 (HHDP C-1), 114.9 (EC C-2′), 115.8 (EC C-5′), 119.5 (EC C-6′), 125.6, 127.5, 127.6 (2C) (HHDP C-2), 131.0 (EC C-1′), 135.7 (2C), 136.3, 136.8 (HHDP C-5), 143.8, 144.1, 144.3, 144.5, 144.8, 145.0 (2C), 145.2 (3C) (HHDP C-4 and C-6; EC C-3′ and C-4′), 153.0 (EC C-8a), 156.3 (EC C-7), 156.7 (EC C-5), 167.2, 168.8, 169.5 (2C) (HHDP C-7). The assignments were substantiated by $^1H-^{13}C$ COSY and $^1H-^{13}C$ long-range COSY.

Methylation of Camelliatannins C (1) and E (2) A mixture of camelliatannin C (**1**) (35 mg), dimethyl sulfate (0.16 ml) and K_2CO_3 (160 mg) in acetone (5 ml) was stirred overnight at room temperature, and then refluxed for 2.5 h. After removal of the insoluble material in the mixture by centrifugation, the supernatant was evaporated, and the residue was subjected to preparative TLC with benzene–acetone (3 : 1), to give hexadeca-*O*-methylcamelliatannin C (**1a**) (17 mg). Camelliatannin E (**2**) (10 mg) was treated in an analogous way, to give hexadeca-*O*-methylcamelliatannin E (**2a**) (1 mg).

Hexadeca-*O*-methylcamelliatannin C (1a) Colorless powder, $[\alpha]_D$ +18° (c = 0.6, acetone). ^1H-NMR (400 MHz, in acetone-d_6, 24 °C) δ: 7.16, 6.99, 6.87, 6.73 [1H each, s, hexamethoxydiphenoyl (HMDP)], 7.14 [1H, d, J = 2 Hz, tetramethylepicatechin (TMEC) H-2′], 7.00 (1H, dd, J = 2, 8 Hz, TMEC H-6′), 6.91 (1H, d, J = 8 Hz, TMEC H-5′), 6.42 (1H, s, TMEC H-8), 5.81 (1H, dd, J = 2, 9 Hz, Glc H-3), 5.60 (1H, dd, J = 2, 11 Hz, Glc H-1), 5.52 (1H, dd, J = 2, 7 Hz, Glc H-4), 5.30 (1H, dd, J = 2, 9 Hz, Glc H-2), 5.06 (1H, br s, TMEC H-2), 4.95 (1H, d, J = 11 Hz, Glc OH-1), 4.87 (1H, d, J = 7 Hz, Glc OH-5), 4.68 (1H, dd, J = 2.5, 12 Hz, Glc H-6), 4.45 (1H, m, Glc H-5), 4.29 (1H, m, TMEC H-3), 4.09 (1H, dd, J = 1, 12 Hz, H-6), 4.00—3.55 (16 × MeO), 3.91 (1H, d, J = 5 Hz, TMEC OH-3), 3.07 (1H, dd, J = 4, 16.5 Hz, TMEC H-4), 2.84 (1H, dd, J = 3.5, 16.5 Hz, TMEC H-4). Hexadeca-*O*-methylcamelliatannin C (**1a**) (10 mg) was treated with acetic anhydride (0.3 ml) and pyridine (0.3 ml) overnight, and the solvent was evaporated off. The residue was purified by preparative TLC with benzene–acetone (6 : 1), to give the triacetate **1b** (5 mg). ^1H-NMR (500 MHz, in $CDCl_3$) δ: 7.00, 6.77, 6.632, 6.629 (1H each, s, HMDP), 6.93 (1H, d, J = 2 Hz, TMEC H-2′), 6.88 (1H, dd, J = 2, 8.5 Hz, TMEC H-6′), 6.82 (1H, d, J = 8.5 Hz, TMEC H-5′), 6.52 (1H, d, J = 4 Hz, Glc H-1), 6.28 (1H, s, TMEC H-8), 5.69 (1H, dd, J = 1, 9 Hz, Glc H-3), 5.61 (1H, dd, J = 4, 9 Hz, Glc H-2), 5.35 (1H, dd, J = 1, 6 Hz, Glc H-4), 5.31 (1H, m, TMEC H-3), 5.22 (1H, m, Glc H-5), 4.99 (1H, br s, TMEC H-2), 4.69 (1H, dd, J = 2.5, 12.5 Hz, Glc H-6), 4.20 (1H, dd, J = 2, 12.5 Hz, H-6), 3.94—3.58 (16 × MeO), 2.96—2.89 (2H, m, TMEC H-4), 2.12, 2.09, 1.81 (3H each, s, 3 × AcO).

Hexadeca-*O*-methylcamelliatannin E (2a) Colorless powder, $[\alpha]_D$ −4° (c = 0.9, acetone). ^1H-NMR (400 MHz, in acetone-d_6, 24 °C) δ: 7.33 (1H, d, J = 2 Hz, TMEC H-2′), 7.18, 7.07, 7.01, 6.83 (1H each, s, HMDP), 7.00 (1H, dd, $J=2$, 8 Hz, TMEC H-6'), 6.91 (1H, d, $J=8$ Hz, TMEC H-5'), 6.35 (1H, s, TMEC H-6), 5.83 (1H, dd, $J=1.5$, 8.5 Hz, Glc H-3), 5.76 (1H, dd, $J=2$, 10.5 Hz, Glc H-1), 5.51 (1H, dd, $J=1.5$, 7 Hz, Glc H-4), 5.48 (1H, dd, $J=2$, 8.5 Hz, Glc H-2), 5.46 (1H, d, $J=10.5$ Hz, Glc OH-1), 5.12 (1H, br s, TMEC H-2), 4.83 (1H, d, $J=7$ Hz, Glc OH-5), 4.55 (1H, dd, $J=2.5$, 12 Hz, Glc H-6), 4.46 (1H, m, TMEC H-3), 4.39 (1H, m, Glc H-5), 3.96 (2H, m, Glc H-6 and TMEC OH-3), 3.91—3.44 (16 × MeO), 2.96 (1H, dd, $J=5$, 17 Hz, TMEC H-4), 2.84 (1H, dd, $J=3$, 17 Hz, TMEC H-4).

Identification of the Constituent Sugar of Camelliatannins C (1) and E (2) A solution of camelliatannin C (**1**) (2 mg) in diluted H_2SO_4 (0.2 ml) in a sealed tube was heated in a boiling-water bath for 12 h. The solution was then neutralized with Diaion SA-20AP resin, and evaporated. The residue was trimethylsilylated and analyzed by GLC, to show the peaks due to α-glucose [retention time (t_R) 9.6 min] and β-glucose (t_R 12.4 min). Liberation of glucose upon the analogous treatment of camelliatannin E (**2**) was also detected by GLC.

Treatment of Camelliatannins C (1) and E (2) with Ethanolic Acetic Acid A solution (0.5 ml) of camelliatannin C (**1**) (0.5 mg) in a mixture of acetic acid and ethanol (1 : 3, 0.5 ml) in a sealed tube was heated in a boiling-water bath for 19 h, and the reaction mixture was analyzed by HPLC, to show the presence of **3** (t_R 13.3 min) and **4** (t_R 3.3 min) in the mixture. Camelliatannin E (**2**) was also treated in an analogous way and analyzed by HPLC, to show the formation of **3** and **4**.

Transformation of Camelliatannins C (1) and E (2) into Camelliatannins B (5) and A (6) A mixture of camelliatannin C (**1**) (13.5 mg) and polyphosphoric acid (50 mg) in dioxane (4 ml) in a sealed tube was heated in a boiling-water bath for 40 min. The solvent was evaporated off, and the residue was subjected to column chromatography on MCI-gel CHP-20P with $H_2O \rightarrow 10\%$ MeOH → 20% MeOH to give camelliatannin B (**5**) (1.5 mg), $[\alpha]_D$ +40° ($c=0.5$, MeOH), which was identified by comparison of its ^{1}H-NMR, UV and CD spectra with those of an authentic sample, and by co-HPLC with the authentic sample. A mixture of camelliatannin E (**2**) (10 mg) and polyphosphoric acid (70 mg) in dioxane (3 ml) was heated in a boiling-water bath for 10 min in an analogous way, and the reaction mixture was purified by column chromatography on MCI-gel CHP-20P with $H_2O \rightarrow 5\%$ MeOH → 10% MeOH to give camelliatannin A (**6**) (1 mg), $[\alpha]_D$ +60° ($c=1.2$, MeOH), which was identified by ^{1}H-NMR, UV and CD spectral comparison, and by co-HPLC with an authentic specimen.

References and Notes

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