Tannins of *Stachyurus* Species. III.[1] Stachyuranins A, B and C, Three New Complex Tannins from *Stachyurus praecox* Leaves

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Three new complex tannins, stachyuranins A (1), B (2) and C (3), were isolated from the leaves of *Stachyurus praecox* (Stachyuraceae), and their structures, each consisting of a catechin or gallocatechin residue and a monomeric hydrolyzable tannin moiety, were assigned. Structures 1 and 2 lack a C–C linkage between glucose C-1 and the aroyl group at glucose O-2, suggesting that they may be biogenetic precursors of complex tannins with the C–C linkage.

Key words tannin; *Stachyurus praecox*; Stachyuraceae; stachyuranin A, B, C

Leaves and fruits of *Stachyurus praecox* SIEB. *et* ZUCC. (Stachyuraceae) are rich in tannins,[2] and we have reported the isolation and structures of several new tannins from the leaves.[1,3] Although all of the tannins previously isolated are hydrolyzable tannins,[1,3] further investigation on the tannins of the leaf of this plant has led to the isolation of three new complex tannins, named stachyuranins A (**1**), B (**2**) and C (**3**).

Almost all of the complex tannins reported to date have a C–C linkage between glucose C-1 and the aroyl group at glucose O-2, and have been considered to be produced from *C*-glycosidic tannin and a flavan-3-ol.[4,5] However, we have reported[4] the isolation of new complex tannins with a (−)-epicatechin residue, which lack the C–C linkage between glucose C-1 and aroyl group at glucose O-2, from *Camellia japonica* leaves. Facile transformation of the new tannins into "normal" complex tannins having the C–C linkage[5] suggested that they might be precursors of the latter "normal" type of complex tannins. On the other hand, precursors of "normal" complex tannins with a (+)-catechin residue have not yet been found.

Compounds **1** and **2** found in the present study have a (+)-catechin residue, and also lack the C–C linkage. The structures of these tannins of a new type are consistent with the idea that complex tannins having the C–C linkage are not directly synthesized from *C*-glycosidic tannins and a flavan-3-ol, and suggest the presence of an alternative biogenetic pathway through tannins lacking the C–C linkage. Compound **3** is a rare example of a complex tannin with a gallocatechin residue[6] and a phenylcyclopentenone moiety,[7] indicating the diversity of tannin metabolism. This paper deals with the isolation and structure elucidation of these tannins.

Results and Discussion

The new tannins were isolated from fresh leaves of *Stachyurus praecox* in the following way. The leaves were homogenized in aqueous acetone, and the concentrated filtrate from the homogenate was extracted with EtOAc. The aqueous mother liquor was then concentrated, and subjected to column chromatography over Dia-ion HP-20, Toyopearl HW-40 and MCI-gel CHP-20P. Fractions containing new tannins were further purified by preparative HPLC, to give stachyuranins A (**1**), B (**2**) and C (**3**), along with casuarinin (**4**)[3,5] and guavin C (**5**).[6]

Structure of Stachyuranin A Stachyuranin A (**1**) was obtained as an off-white powder. When a solution of **1** in a mixture of MeOH and water (1 : 1, v/v) was left to stand at room temperature, this tannin was gradually converted into stenophyllanin A (**6**).[8] Upon heating a solution of **1** in dioxane containing polyphosphoric acid,[4] **1** was quickly converted into **6**. The molecular weight of **1** ($C_{56}H_{42}O_{32}=1226$) indicated by the $[M+Na]^+$ ion peak at *m/z* 1249 in the FAB-MS is 18 mass units (corresponding to H_2O) larger than that of **6** ($C_{56}H_{40}O_{31}=1208$).

The ^{1}H-NMR spectrum of **1** (in acetone-d_6 + D_2O) showed signals of ten aromatic protons. Among them, signals forming an ABC system [δ 6.57 (1H, d, $J=2$ Hz), 6.59 (1H, d, $J=8$ Hz) and 6.46 (1H, dd, $J=2$, 8 Hz)] and a 1H singlet at δ 6.01 are respectively assignable to H-2′, H-5′, H-6′ and H-6 of the catechin residue, and a 2H singlet at δ 7.10 is ascribable to protons of the galloyl group. The remaining four 1H singlets at δ 6.55, 6.60, 6.69 and 6.74 are due to protons of the two hexahydroxydiphenoyl (HHDP) groups (H-3 and H-3′). Since compound **6** (having a C–C linkage between C-1 of glucose and C-3 of the HHDP group at glucose O-2/O-3) shows three HHDP proton signals, the presence of the four HHDP signals indicates that **1** lacks the C–C linkage.

The ^{13}C-NMR spectrum of **1** showed four signals due to C-3 and C-3′ of two HHDP groups at δ 107.5, 107.6, 107.8 and 109.0, substantiating the absence of the C–C linkage between glucose C-1 and the HHDP group at glucose O-2/O-3. The ^{13}C-NMR spectrum also showed the glucose C-1 signal at δ 68.3, which is shifted downfield relative to the corresponding signal of **6** (δ 38.3).[8] This shift is attributable to the presence of a hydroxyl group at glucose C-1.

Complex tannins with a hydroxyl group at glucose C-1 instead of a C–C linkage between glucose C-1 and an aroyl group at glucose O-2, such as camelliatannins C (**7**) and E (**8**),[4] have recently been found. The above-mentioned data indicated that **1** also belongs to this type of complex tannin. Coupling constants of the glucose protons of **1**, including $J_{1,2}$ (2.5 Hz), are almost the same as those for **7** and **8**, indicating the (*S*)-configuration[4] of glucose C-1.

The 2*R*,3*S*-configuration for the catechin residue in **1**

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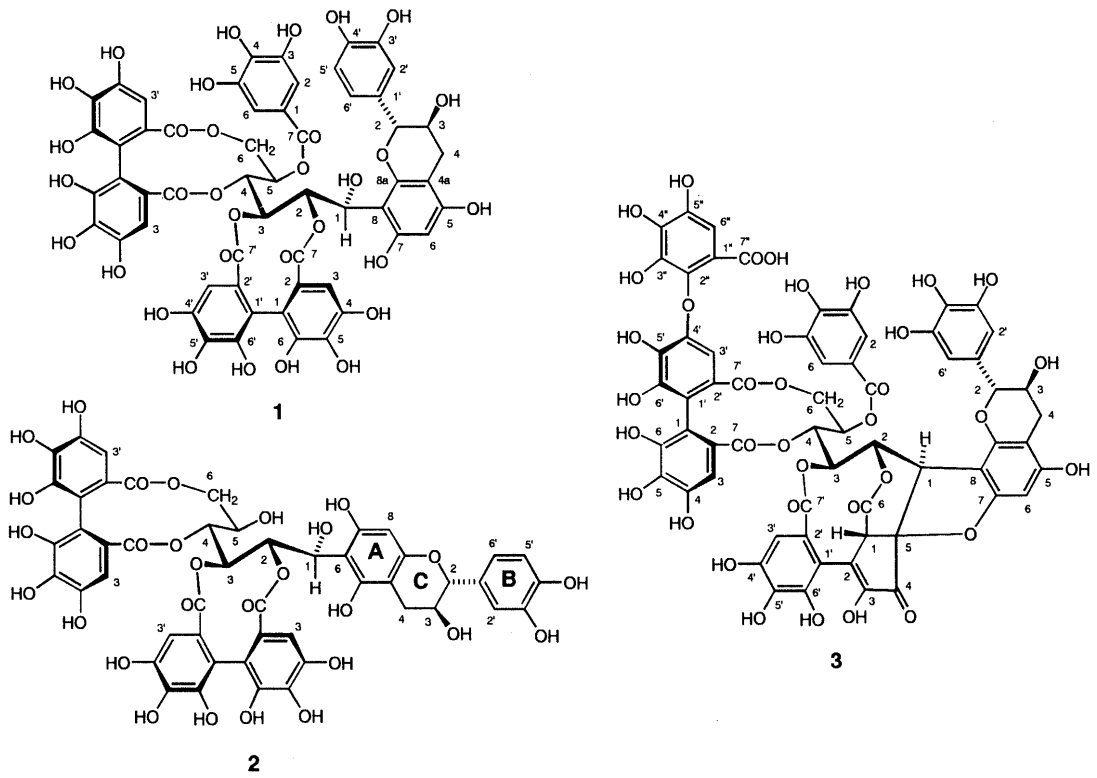

Chart 1

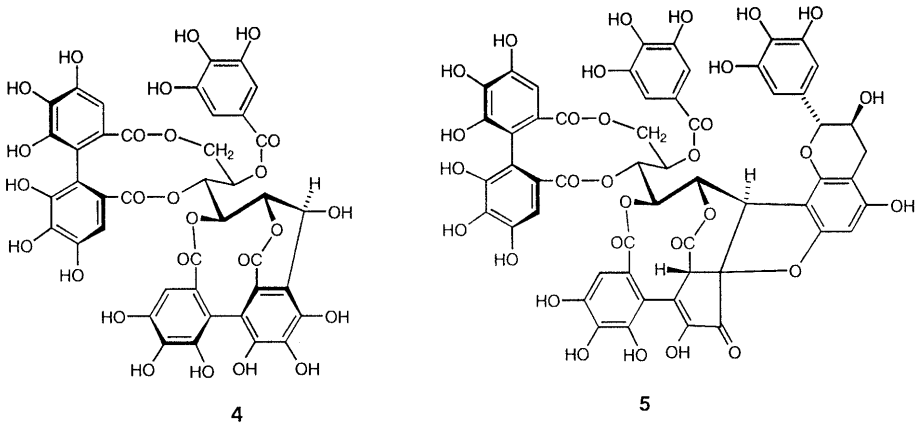

Chart 2

is indicated by the above-mentioned transformation into **6**, which contains (+)-catechin (**9**) in the molecule.[8]

The *S*-configuration of the two HHDP groups in **1** was also shown by the transformation of **1** into **6**, which has two (*S*)-HHDP groups. The circular dichroism (CD) spectrum of **1** showed a positive Cotton effect with a large amplitude in the short-wavelength region ($[\theta]_{234}+1.4\times 10^5$), substantiating the *S*-configuration[9] of the HHDP groups.

Structure **1** was assigned for stachyuranin A based on these data, and the transformation of **1** into **6** at room temperature strongly suggested that **6** is produced from **1** non-enzymatically in plants.

Structure of Stachyuranin B Stachyuranin B (**2**) was also obtained as an off-white powder. The $[M+Na]^+$ ion peak at *m/z* 1097 in the FAB-MS indicated that the molecular weight of **2** is the same as those of **7** and **8** ($C_{49}H_{38}O_{28}=1074$).

The ^{1}H-NMR spectrum of **2** (in acetone-d_6+D_2O) showed signals assignable to protons of the B-ring [δ 6.83 (1H, d, $J=2$ Hz, H-2′), 6.74 (1H, d, $J=8$ Hz, H-5′), 6.69 (1H, dd, $J=2$, 8 Hz, H-6′)], A-ring [δ 5.78 (1H, s)], and C-ring [δ 4.50 (1H, d, $J=8$ Hz, H-2), 3.98 (1H, m, H-3), 2.87 (1H, dd, $J=5.5$, 16.5 Hz, H-4), 2.62 (1H, dd, $J=8.5$, 16.5 Hz, H-4)] of a flavan residue. Four 1H singlets at δ 6.53—6.70 due to protons of two HHDP groups, and seven protons of a glucose residue (Table 1) were also observed in the spectrum.

The ^{13}C-NMR spectrum of **2** also showed the signals of these constituent units in the molecule (see Experimental). The ^{13}C chemical shift of glucose C-1 (δ 68.7) indicated that this tannin also belongs to a type of complex tannin which lacks the C–C linkage between glucose C-1 and the aroyl group at glucose O-2, but has a hydroxyl

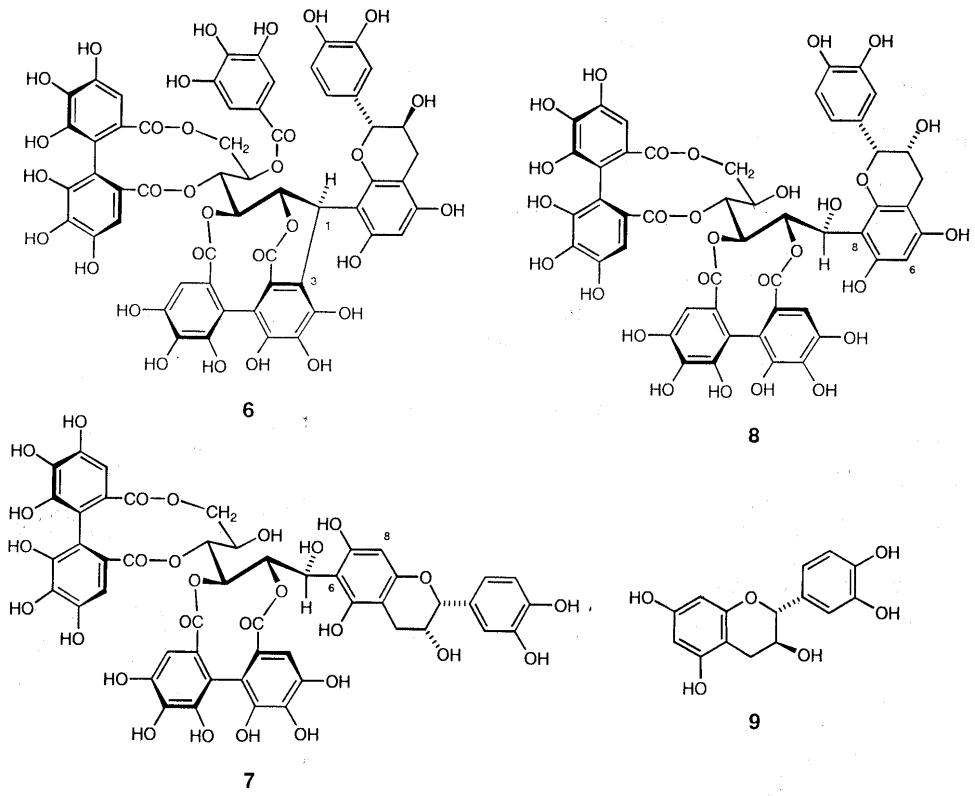

Chart 3

group at glucose C-1.

Although these data suggest that the structure is closely similar to **7** and **8**, the coupling constant (8 Hz) between H-2 and H-3 of the flavan residue in the ^{1}H-NMR spectrum of **2** is larger than that ($\leq$2 Hz) for **7** and **8**, indicating the 2,3-*trans* (catechin) structure of the flavan residue in **2**, instead of the 2,3-*cis* (epicatechin) structure for **7** and **8**. The ^{13}C chemical shift of flavan C-2 (δ 82.3) of **2** also substantiates the 2,3-*trans* structure.[10]

The chemical shift of the A-ring proton of the catechin residue of **2** (δ 5.78) is similar to that for **7** (δ 5.84), rather than those for complex tannins with an 8-substituted flavan residue [**1** (δ 6.01) and **8** (δ 6.03)[4]], indicating the 6-substitution of the catechin residue in **2**. The 6-substitution for **2** is substantiated by the similarity in the ^{13}C chemical shifts of the A-ring carbons of **2** [δ 94.5 (C-8) and 103.9 (C-6)] and **7** [δ 94.9 (C-8) and 103.8 (C-6)], since those for **7** with its 6-substituted flavan are distinguishable from those for **8** with its 8-substituted flavan [δ 96.6 (C-6) and 104.2 (C-8)].

As shown in Table 1, the chemical shifts and the coupling constants of the glucose protons of **2** are practically the same as those of the corresponding protons of **7**, and therefore the locations of the two HHDP groups on the glucose residue (O-2/O-3 and O-4/O-6) and the configuration at glucose C-1 (*S*) in **2** should be the same as those for **7**. The *S*-configuration at glucose C-1 was also substantiated by the rotating-frame Overhauser enhancement data for **2**, which showed correlations of H-1—H-4 and H-3—H-5, in a way analogous to those for **7**.[4]

The CD curve of **2** is almost superimposable on that of **1**, indicating the *S*-configuration of the two HHDP groups[9] and the 2*R*,3*S*-configuration of the catechin residue.[11] Structure **2** was thus assigned for stachyuranin B.

Table 1. ^{1}H-NMR Spectral Data for Glucose Protons of Stachyuranin B (**2**) and Camelliatannin C (**7**)[4]

	Stachyuranin B (**2**) δ	Camelliatannin C (**7**) δ
H-1	5.77 (d, J=2 Hz)	5.75 (d, J=2 Hz)
H-2	5.42 (dd, J=2, 9 Hz)	5.42 (dd, J=2, 9 Hz)
H-3	5.91 (dd, J=2, 9 Hz)	5.89 (dd, J=2, 9 Hz)
H-4	5.51 (dd, J=2, 8 Hz)	5.53 (dd, J=2, 8 Hz)
H-5	4.33 (br d, J=8 Hz)	4.32 (br d, J=8 Hz)
H-6	4.61 (dd, J=2.5, 12 Hz)	4.60 (dd, J=2.5, 12.5 Hz)
H-6	3.96 (br d, J=12 Hz)	3.98 (br d, J=12.5 Hz)

500 MHz, in acetone-d_6 + D_2O.

Structure of Stachyuranin C Stachyuranin C (**3**) was obtained as an off-white powder. The FAB-MS showed the $[M+Na]^+$ ion peak at m/z 1385, corresponding to the molecular formula $C_{62}H_{42}O_{36}$.

The ^{1}H-NMR spectrum of **3** (in acetone-d_6 + D_2O) showed signals of twelve aliphatic and nine aromatic protons. Signals at δ 5.24 (1H, d, J=5 Hz, H-2), 4.36 (1H, m, H-3), 2.68 (1H, dd, J=5, 16 Hz, H-4) and 2.61 (1H, dd, J=5, 16 Hz, H-4) in the aliphatic region and signals at δ 6.04 (1H, s, A-ring H) and 6.39 (2H, s, H-2′ and H-6′) in the aromatic region are attributable to protons of a flavan residue. The 2H singlet in the aromatic region indicated the 3,4,5-trihydroxyphenyl structure for the B-ring of the flavan residue. A 2H singlet at δ 6.98 is ascribable to H-2 and H-6 of a galloyl group, and three 1H singlets at δ 6.12, 6.58 and 7.06 are due to protons of a valoneoyl group. Two 1H singlets at δ 4.31 (H-1) and

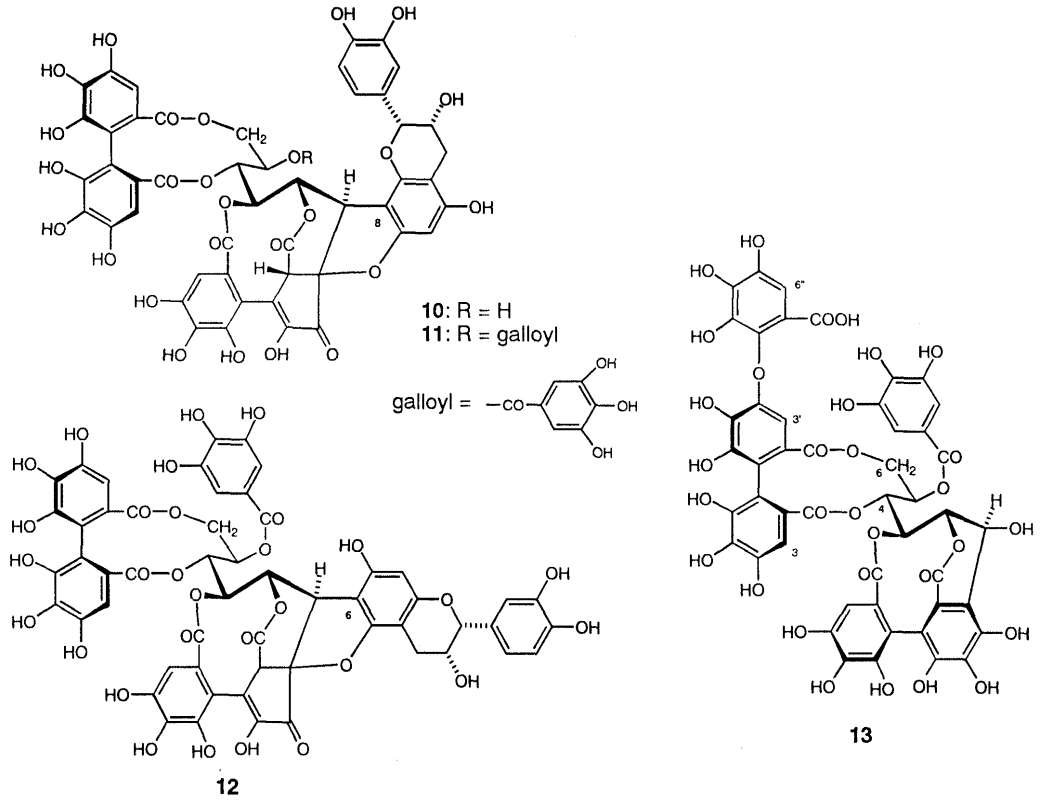

Chart 4

6.97 (H-3′) suggested the presence of a phenylcyclopentenone (PCP) structure in an oxidative type of complex tannin, such as camelliatannin F (**10**)[7] or malabathrin E (**11**).[12] The remaining seven aliphatic proton signals at δ 4.03 (1H, s), 5.25 (1H, br s), 5.14 (1H, d, J=6 Hz), 5.72 (1H, dd, J=6, 8 Hz), 5.61 (1H, br d, J=8 Hz), 4.03 (1H, d, J=13 Hz) and 4.46 (1H, dd, J=2.5, 13 Hz) are respectively assigned to glucose protons H-1—H-6, based on the similarity of these coupling constants in **3** to the corresponding ones in **10** and **11**. The chemical shifts and the coupling constants of the glucose protons indicate that all of the hydroxyl groups at glucose C-2—C-6 are acylated and the locations of the acyl groups are the same as those for **11** (except for the presence of a valoneoyl group in **3** instead of the HHDP group in **11**).

The ^{13}C-NMR spectrum of **3** showed signals of thirty aromatic carbons in five benzene rings, in addition to the signals of twelve aromatic carbons of the flavan residue. The former signals are attributable to a galloyl group, a valoneoyl group and a phenyl ring of the PCP moiety (see Experimental). The spectrum also showed signals at δ 49.4 (C-1), 138.0 (C-2), 149.2 (C-3), 196.9 (C-4) and 90.4 (C-5), substantiating the presence of the cyclopentenone structure[7,12] of the PCP moiety in **3**. The chemical shift of C-5 suggested the presence of an ether linkage between this carbon and a hydroxyl group of the A-ring of the flavan, and a C–C linkage between the carbon and glucose C-1. The presence of the latter (the C–C linkage) was also shown by the chemical shift of glucose C-1 (δ 46.0), which is similar to those of complex tannins with two C–C linkages at glucose C-1.[5,7,8,12]

The presence of the trihydroxyphenyl structure of the B-ring in the flavan residue was substantiated by carbon signals at δ 130.8 (C-1′), 105.8 (2C) (C-2′, C-6′), 146.4 (2C) (C-3′, C-5′) and 133.0 (C-4′), and the 2,3-*trans* structure of its C-ring was indicated by a signal at δ 81.3 of flavan C-2.[10] Therefore, the flavan residue in **3** is gallocatechin. Chemical shifts of the A-ring carbon signals of the gallocatechin residue [δ 90.7 (C-6), 101.5 (C-4a), 104.7 (C-8), 151.7 (C-8a), 158.4 (C-5) and 160.1 (C-7)] are almost the same as the shifts of the corresponding carbon signals of **10**[7] and **11**.[12] On the other hand, the chemical shifts of C-4a, C-6 and C-8 among the A-ring carbons of malabathrin F (**12**) [δ 95.8 (C-4a), 97.4 (C-8), 104.9 (C-6), 153.1 (C-8a), 157.9 (C-5) and 160.0 (C-7)], which has a 6-substituted flavan residue,[12] are distinctively different from those of **3**. Therefore, the structure in which C-8 and the hydroxyl group at C-7 of the gallocatechin residue are respectively linked to glucose C-1 and PCP C-5 can be assigned for stachyuranin C.

The orientation[13] of the valoneoyl group at glucose O-4/O-6 was assigned to be the same as that for hippophaenin B (**13**),[14] based on the similarity of the ^{1}H chemical shifts of valoneoyl protons of **3** to those of the corresponding protons of **13** [δ 6.50 (H-3) , 6.25 (H-3′) and 7.09 (H-6″) (**13**); δ 6.58 (H-3), 6.12 (H-3′) and 7.06 (H-6″) (**3**)].

The CD spectrum of **3** showed a positive Cotton effect with a large amplitude in the short-wavelength region ($[\theta]_{225}+9.1\times10^4$), indicating the *S*-configuration[9] of the biphenyl moiety of the valoneoyl group in **3**. The spectrum also showed a positive Cotton effect at 280 nm ($[\theta]_{280}+3.2\times10^4$), reflecting the 2*R* configuration[11] of the gallocatechin residue. The configuration at gallocatechin C-3 is therefore assigned as *S*, based on the 2,3-*trans* structure.

The orientation of the proton at glucose C-1 is assigned as α, based on the coupling constant $J_{1,2}$ (<2 Hz) of the glucose protons.[5,7,12,15]

Based on these data, structure **3** was assigned for stachyuranin C.

Experimental

Optical rotations were measured on a JASCO DIP-4 polarimeter. Ultraviolet (UV) spectra were recorded on a Hitachi 200-10 spectrophotometer. ^{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) at ambient temperature. Chemical shifts are given in δ values (ppm), based on those of the ^{1}H and ^{13}C signals of solvents [acetone-d_6 (δ_H 2.04; δ_C 29.8)]. FAB-MS were recorded on a VG 70-SE mass spectrometer using 3-nitrobenzyl alcohol as the matrix agent. CD spectra were recorded on a JASCO J-500A spectrometer, equipped with a DP-501N data processor. HPLC was performed on a LiChrospher RP-18 (5 μm) column (4×250 mm) with 10 mM H_3PO_4–10 mM KH_2PO_4–MeCN (11:11:3) as the eluant. The flow rate was set at 1.0 ml/min, and the column was kept at 40 °C in an oven. Detection was effected with a Shimadzu SPD-6A spectrophotometric detector at 280 nm. A YMC Pack A324 (ODS) column (10×300 mm) connected with a YMC Pack A312 (ODS) column (6×150 mm) was used for preparative HPLC.

Isolation of Tannins from Leaves of *Stachyurus praecox* Fresh leaves (5 kg) of *Stachyurus praecox*, collected at the Herbal Garden of Okayama University in June, were homogenized in 70% acetone (24.5 l), and the concentrated filtrate (1.5 l) from the homogenate was extracted with EtOAc (6 l). The aqueous mother liquor was concentrated, and subjected to column chromatography over Dia-ion HP-20 (6.5×50 cm) with increasing concentrations of MeOH in H_2O (0%→20%→40%→60%→80%→100%). The eluate with 40% MeOH (29.1 g) was chromatographed on Toyopearl HW-40 (2.2×100 cm) (fine grade) with MeOH–H_2O (7:3), and 15-g fractions were collected. Combined fractions 216—265 (1360 mg) were chromatographed on MCI-gel CHP-20P with increasing concentrations of MeOH in H_2O (0%→5%→10%→15%→25%). The eluate with 10% MeOH (204 mg) was further purified by preparative HPLC to give stachyuranin B (**2**) (9 mg) and casuarinin (**4**)[5] (22 mg). The eluate with 25% MeOH (333 mg) was purified in a similar way to give stachyuranin A (**1**) (45 mg), stachyuranin C (**3**) (7 mg) and guavin C (**5**)[6] (25 mg).

Stachyuranin A (1) An off-white amorphous powder, $[\alpha]_D$ −15° (c=1, MeOH). *Anal.* Calcd for $C_{56}H_{42}O_{32}\cdot 7H_2O$: C, 49.71; H, 4.17. Found: C, 49.68; H, 4.30. FAB-MS (positive-ion mode) m/z: 1249 ($[M+Na]^+$). UV λ_{max}^{MeOH} nm (log ε): 209 (5.04), 231 (sh, 4.86), 265 (sh, 4.56). CD (MeOH): $[\theta]_{310}$ -1.1×10^4, $[\theta]_{284}+2.0\times10^4$, $[\theta]_{262}$ -5.5×10^4, $[\theta]_{234}+1.4\times10^5$. ^{1}H-NMR (500 MHz, acetone-d_6+D_2O) δ: 2.50 [1H, dd, J=5, 16.5 Hz, catechin (Cat) H-4], 2.59 (1H, dd, J=5, 16.5 Hz, Cat H-4), 3.94 (1H, m, Cat H-3), 4.26 [1H, d, J=12.5 Hz, glucose (Glc) H-6], 4.63 (1H, dd, J=2.5, 12.5 Hz, Glc H-6), 4.66 (1H, d, J=5 Hz, Cat H-2), 5.40 (1H, dd, J=2.5, 9 Hz, Glc H-2), 5.51 (1H, br d, J=7 Hz, Glc H-5), 5.75 (1H, dd, J=2, 7 Hz, Glc H-4), 5.78 (1H, dd, J=2, 9 Hz, Glc H-3), 5.79 (1H, d, J=2.5 Hz, Glc H-1), 6.01 (1H, s, Cat H-6), 6.46 (1H, dd, J=2, 8 Hz, Cat H-6′), 6.55, 6.60, 6.69, 6.74 (1H each, s, HHDP H-3, H-3′), 6.57 (1H, d, J=2 Hz, Cat H-2′), 6.59 (1H, d, J=8 Hz, Cat H-5′), 7.10 (2H, s, galloyl H-2, H-6). ^{13}C-NMR (125.7 MHz, acetone-d_6+D_2O) δ: 25.7 (Cat C-4), 64.2 (Glc C-6), 67.0 (Cat C-3), 68.3 (Glc C-1), 70.0 (Glc C-4), 71.7 (Glc C-5), 76.1 (Glc C-3), 78.4 (Glc C-2), 81.0 (Cat C-2), 96.4 (Cat C-6), 99.5 (Cat C-4a), 103.0 (Cat C-8), 107.5, 107.6, 107.8, 109.0 (HHDP C-3, C-3′), 110.2 (2C, galloyl C-2, C-6), 113.8, 114.2, 115.1, 115.5 (HHDP C-1, C-1′), 114.0 (Cat C-2′), 115.8 (Cat C-5′), 118.8 (Cat C-6′), 120.6 (galloyl C-1), 124.9, 126.2, 127.0, 127.2 (HHDP C-2, C-2′), 131.6 (Cat C-1′), 135.8, 135.9, 136.0, 136.8 (HHDP C-5, C-5′), 139.2 (galloyl C-4), 143.9, 144.2, 144.3, 144.6, 144.9, 145.0 (3C), 145.1, 145.2 (HHDP C-4, C-4′, C-6, C-6′, Cat C-3′, C-4′), 145.9 (2C, galloyl C-3, C-5), 151.7 (Cat C-8a), 156.7, 157.3 (Cat C-5, C-7), 166.1 (galloyl C-7), 167.1, 168.8, 169.1, 169.2 (HHDP C-7, C-7′).

Stachyuranin B (2) An off-white amorphous powder, $[\alpha]_D$+120° (c=1, MeOH). *Anal.* Calcd for $C_{49}H_{38}O_{28}\cdot 8H_2O$: C, 48.28; H, 4.13. Found: C, 48.23; H, 4.39. FAB-MS (positive-ion mode) m/z: 1097 ($[M+Na]^+$). UV λ_{max}^{MeOH} nm (log ε): 207 (4.97), 230 (sh, 4.82), 260 (sh, 4.53). CD (MeOH): $[\theta]_{312}$ -1.1×10^4, $[\theta]_{282}+2.7\times10^4$, $[\theta]_{261}$ -4.3×10^4, $[\theta]_{235}+1.6\times10^5$. ^{1}H-NMR (500 MHz, in acetone-d_6+D_2O) δ: 2.62 (1H, dd, J=8.5, 16.5 Hz, Cat H-4), 2.87 (1H, dd, J=5.5, 16.5 Hz, Cat H-4), 3.98 (1H, m, Cat H-3), 4.50 (1H, d, J=8 Hz, Cat H-2), 5.78 (1H, s, Cat H-8), 6.53, 6.59, 6.64, 6.70 (1H each, s, HHDP H-3, H-3′), 6.69 (1H, dd, J=2, 8 Hz, Cat H-6′), 6.74 (1H, d, J=8 Hz, Cat H-5′), 6.83 (1H, d, J=2 Hz, Cat H-2′). Glucose protons: See Table 1. ^{13}C-NMR (125.7 MHz, acetone-d_6+D_2O) δ: 28.4 (Cat C-4), 67.8 (Glc C-6), 68.2 (Cat-3), 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), 82.3 (Cat C-2), 94.5 (Cat C-8), 100.6 (Cat C-4a), 103.9 (Cat C-6), 106.7, 107.6, 107.8, 109.0 (HHDP C-3, C-3′), 113.7, 114.4, 115.0, 116.8 (HHDP C-1, C-1′), 115.1 (Cat C-2′), 115.5 (Cat C-5′), 119.9 (Cat C-6′), 125.0, 127.3, 127.6, 127.8 (HHDP C-2, C-2′), 131.8 (Cat C-1′), 135.4, 135.7, 136.0, 136.8 (HHDP C-5, C-5′), 143.9, 144.2, 144.4 (2C), 144.7, 145.1 (2C), 145.2, 145.5, 145.6 (HHDP C-4, C-4′, C-6, C-6′, Cat C-3′, C-4′), 153.9 (Cat C-8a), 155.4, 156.9 (Cat C-5, C-7), 167.3, 168.8, 169.3, 169.7 (HHDP C-7, C-7′).

Stachyuranin C (3) An off-white amorphous powder, $[\alpha]_D$+39° (c=1, MeOH). *Anal.* Calcd for $C_{62}H_{42}O_{36}\cdot 11H_2O$: C, 47.70; H, 4.13. Found: C, 47.56; H, 4.03. FAB-MS (positive-ion mode) m/z: 1385 ($[M+Na]^+$). UV λ_{max}^{MeOH} nm (log ε): 212 (5.09), 231 (sh, 4.90), 264 (sh, 4.61). CD (MeOH): $[\theta]_{305}$ -1.5×10^3, $[\theta]_{280}+3.2\times10^4$, $[\theta]_{260}$ -3.8×10^4, $[\theta]_{225}+9.1\times10^4$. ^{1}H-NMR (500 MHz, in acetone-d_6+D_2O): δ 2.61 [1H, dd, J=5, 16 Hz, gallocatechin (GC) H-4], 2.68 (1H, dd, J=5, 16 Hz, GC H-4), 4.03 (1H, s, Glc H-1), 4.03 (1H, br d, J=13 Hz, Glc H-6), 4.31 [1H, s, phenylcyclopentenone (PCP) H-1], 4.36 (1H, m, GC H-3), 4.46 (1H, dd, J=2.5, 13 Hz, Glc H-6), 5.14 (1H, d, J=6 Hz, Glc H-3), 5.24 (1H, d, J=5 Hz, GC H-2), 5.25 (1H, br s, Glc H-2), 5.61 (1H, br d, J=8 Hz, Glc H-5), 5.72 (1H, dd, J=6, 8 Hz, Glc H-4), 6.04 (1H, s, GC H-6), 6.12 [1H, s, valoneoyl (Val) H-3′], 6.39 (s, 2H, GC H-2′, H-6′), 6.58 (1H, s, Val H-3), 6.97 (1H, s, PCP H-3′), 6.98 (2H, s, galloyl H-2, H-6), 7.06 (1H, s, Val H-6″). ^{13}C-NMR (125.7 MHz, acetone-d_6+D_2O) δ: 25.2 (GC C-4), 46.0 (Glc C-1), 49.4 (PCP C-1), 64.6 (Glc C-6), 67.3 (GC-3), 70.4 (Glc C-4), 71.8 (Glc C-5), 76.5 (Glc C-3), 80.9 (Glc C-2), 81.3 (GC C-2), 90.4 (PC C-5), 90.7 (GC C-6), 101.5 (GC C-4a), 104.5, 108.1, 109.1, 109.9 (Val C-3, C-3′, C-6″, PCP C-3′), 104.7 (GC C-8), 105.8 (2C, GC C-2′, C-6′), 110.2 (2C, galloyl C-2, C-6), 111.7, 114.9, 116.2, 117.0 (Val C-1, C-1′, C-1″, PCP C-1′), 120.6 (galloyl C-1), 123.3, 124.6, 126.7 (Val C-2, C-2′, PCP C-2′), 130.8 (GC C-1′), 133.0 (GC C-4′), 136.5, 136.8, 137.4, 137.6 (Val C-5, C-5′, C-2″, PC C-5′), 138.0 (PCP C-2), 139.3 (galloyl C-4), 139.8, 140.2 (Val C-3″, C-4″), 143.1, 144.5, 144.9, 145.1, 145.2, 146.1 (Val C-4, C-6, C-6′, C-5″, PCP C-4′, C-6′), 145.7 (2C, galloyl C-3, C-5), 146.4 (2C, GC C-3′, C-5′), 147.0 (Val C-4′), 149.2 (PCP C-3), 151.7 (GC C-8a), 158.4, 160.1 (GC C-5, C-7), 165.6 (2C), 167.1, 167.2, 168.2, 168.9 (galloyl C-7, Val C-7, C-7′, C-7″, PCP C-6, C-7′), 196.9 (PCP C-4).

Transformation of Stachyuranin A (1) into Stenophyllanin A (6) 1) Stachyuranin A (**1**) (40 mg) was dissolved in 50% MeOH (5 ml), and the solution was left to stand for 7 d at room temperature. After evaporation of the solvent, the residue was subjected to preparative HPLC, to give stenophyllanin A (**6**) (16 mg), which was identified by ^{1}H-NMR spectroscopy and HPLC (t_R 4.78 min).

2) A solution of **1** (0.5 mg) in dioxane (1 ml) containing polyphosphoric acid[4] (7 mg) in a sealed tube was heated in a boiling-water bath for 10 min. The HPLC analysis of the reaction mixture also showed formation of **6**.

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References and Notes

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