Tannins and Related Compounds. CII.[1] Structures of Terchebulin, an Ellagitannin Having a Novel Tetraphenylcarboxylic Acid (Terchebulic Acid) Moiety, and Biogenetically Related Tannins from *Terminalia chebula* RETZ.

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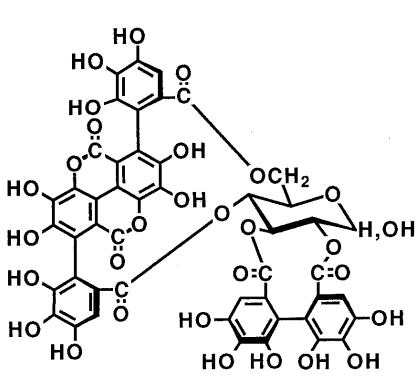
A chemical examination of mylobalans (the fruits of *Terminalia chebula* RETZ., Combretaceae) has led to the isolation and characterization of punicalagin (1), terflavin A (2) and a new ellagitannin named terchebulin (3), which possesses a novel tetraphenylcarboxylic acid (terchebulic acid) moiety. Furthermore, from the leaves of *T. chebula*, a series of biogenetically related hydrolyzable tannins, terflavins B (7), C (9) and D (10), punicalagin (1) and punicalin (8), have been isolated and structurally elucidated. The concomitant isolation of terflavins A (2) and B (7) provides biogenetic evidence that the terchebulic acid moiety is derived by an oxidative carbon-oxygen coupling of adjacent flavogallonic acid and gallic acid esters.

Keywords mylobalan; *Terminalia chebula*; Combretaceae; terchebulin; terchebulic acid; flavogallonic acid; terflavin C; terflavin D; tannin; oxidative phenol coupling

Recent chemical work has shown that one of the major metabolic patterns of gallic acid esters is oxidative carbon–carbon and/or carbon–oxygen coupling(s) of vicinal aromatic rings leading to esters of higher-molecular-weight phenolcarboxylic acids,[2] and that as well as hexahydroxydiphenic acid esters (ellagitannins), esters of so-called gallic acid trimers, such as valoneaic acid, flavogallonic acid, *etc.*, occur widely in the plant kingdom.[3] To date, however, only one gallic acid tetramer, gallagic acid, has been found as a constituent of pomegranate (*Punica granatum* L.)[4] and Indian almond (*Terminalia catappa* L.)[5] tannins. In the course of our chemical work on tannins in mylobalans, the fruits of *Terminalia chebula* RETZ. (Combretaceae), which are important not only for medicinal use but also as a commercial source of vegetable tannins, we have isolated a hydrolyzable tannin [terchebulin (**3**)] having a new gallic acid tetramer (terchebulic acid) and biogenetically related tannins [punicalagin (**1**)[4] and terflavin A (**2**)[5]], besides the tannins [chebulagic acid,[6] chebulinic acid[6,7] and corilagin[6]] which were isolated previously from this material. Furthermore, examination of the leaf extract has resulted in the isolation of a series of related tannins, terflavins B (**7**),[5] C (**9**) and D (**10**), punicalagin (**1**) and punicalin (**8**).[4] This paper deals with the isolation and structure elucidation of these compounds.

Initial fractionation of the aqueous acetone extract of commercial mylobalans was achieved by Sephadex LH-20 chromatography with water containing increasing proportions of methanol.[8] Each fraction was repeatedly chromatographed over a variety of reversed-phase gels to yield compounds **1**—**3**, among which two compounds were found to be identical with punicalagin (**1**)[4] and terflavin A (**2**)[5] by comparisons of their physical and proton-nuclear magnetic resonance (^{1}H-NMR) spectral data with those of samples isolated from *T. catappa*.

The new tannin, terchebulin (**3**) was obtained as tan crystals, but the ^{1}H-NMR spectrum was duplicated, showing that in solution **3** exists as an equilibrium mixture of α- and β-forms [δ 5.32 (2/3H), d, J=4 Hz, α-anomeric H; δ 5.01 (1/3H), d, J=8 Hz, β-anomeric H]. The fact that all the aromatic signals corresponding to five protons in total appear as sharp singlets (see Experimental) indicated the presence of five penta-substituted aromatic rings. Furthermore, lowfield shift (δ 7.58) of one of the aromatic signals implied the occurrence of a depside-like linkage.[5] The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum more clearly indicated the presence of α- and β-anomers (δ 90.8, α-anomeric C; δ 94.1, β-anomeric C) and two aromatic δ-lactone rings (δ 157.9, 160.3).[4,5] The observation of four carboxyl carbon signals with normal



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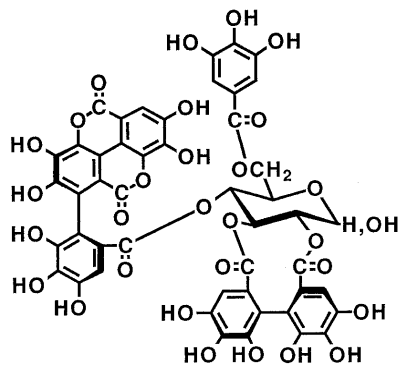

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Chart 1

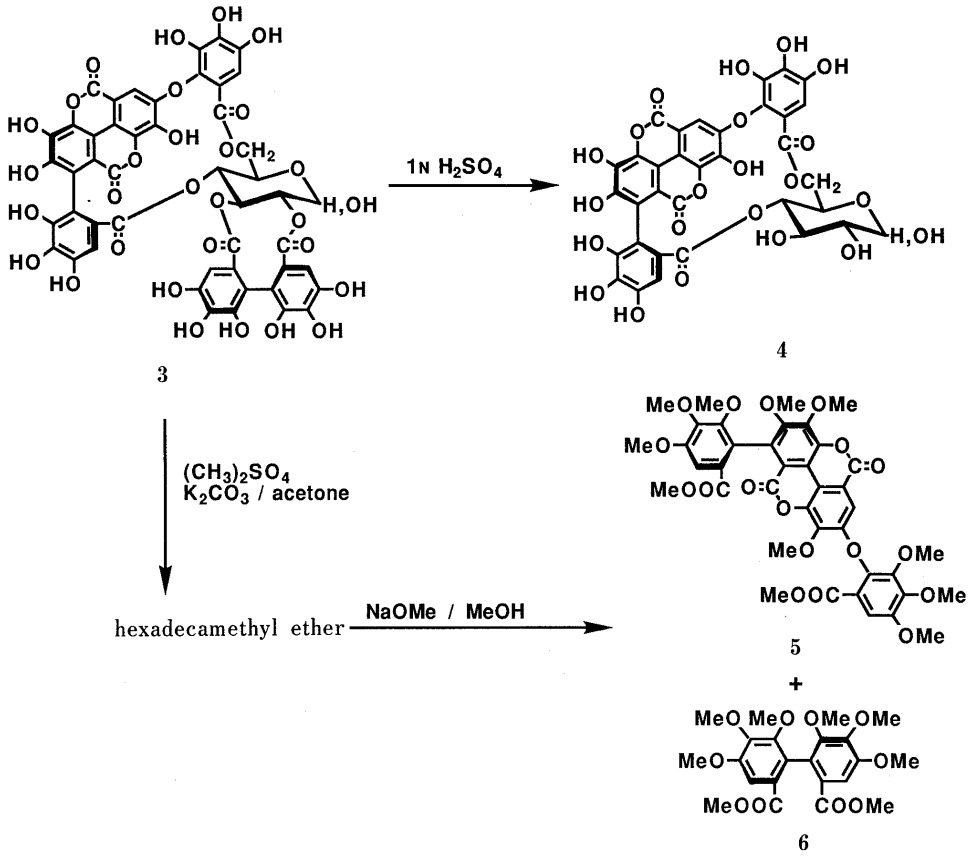


Chart 2

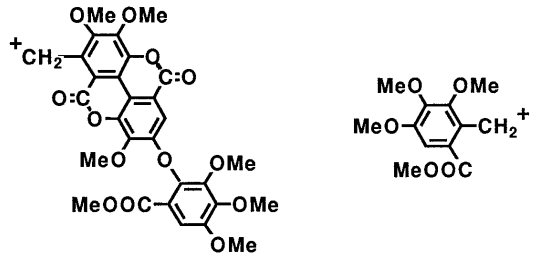


Chart 3

chemical shifts (δ 166.8, 167.6, 169.1 and 169.9) is consistent with the 2,3,4,6-tetra-acylation pattern of the hexopyranose moiety.

Partial acid hydrolysis of **3** yielded a hydrolysate (**4**), together with ellagic acid. The negative fast atom bombardment mass spectrum (FAB-MS)[9] of **4** exhibited a prominent $(M-H)^-$ peak at *m/z* 781, which was 302 mass units less than that of **3**, in agreement with the deshexahydroxydiphenoyl structure. In the ^{1}H-NMR spectrum of **4**, the aliphatic signal pattern, although complicated, was similar to that of punicalin (**8**),[4] suggesting the 4,6-substitution of the glucopyranose ring.

Ordinary phenol methylation of **3** afforded the hexadecamethyl ether [field-desorption mass spectrum (FD-MS): *m/z* 1308 (M^+)], which was methanolyzed with sodium methoxide in methanol to give dimethyl-(*S*)-hexamethoxydiphenoate (**6**)[10] ($[\alpha]_D$ $-29.4°$ ($CHCl_3$)) and a new phenolcarboxylic acid (terchebulic acid) methylate (**5**). The electron-impact mass spectrum (EI-MS) of **5** exhibited,

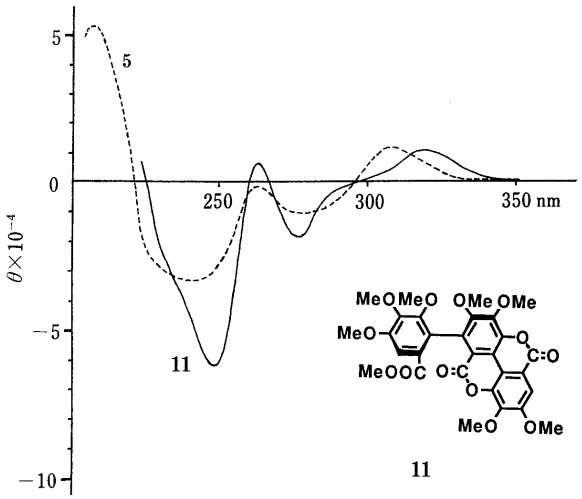
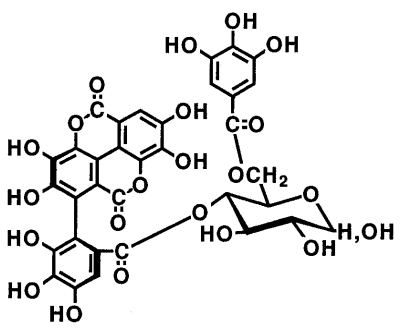


Fig. 1. CD Spectra of **5** and **11** (in MeOH)

together with a prominent M^+ peak at *m/z* 792, characteristic fragment peaks at *m/z* 581 and 239 (Chart 3) resulting from the cleavage of the phenyl–phenyl bond.[4,11] The ^{1}H-NMR spectrum showed signals due to eleven methoxyl groups and three aromatic one-proton singlets (δ 7.21, 7.45 and 7.74). The presence of two δ-lactone rings in **5** was confirmed by ^{13}C-NMR spectroscopy, which showed relatively upfield carboxyl carbon signals at δ 156.6 and 159.0. Furthermore, the two-dimensional nuclear Overhauser effect (NOESY) spectrum of **5** displayed cross peaks between two (δ 7.21, 7.45) of the above three aromatic signals and methoxyl signals, whereas there was no cross



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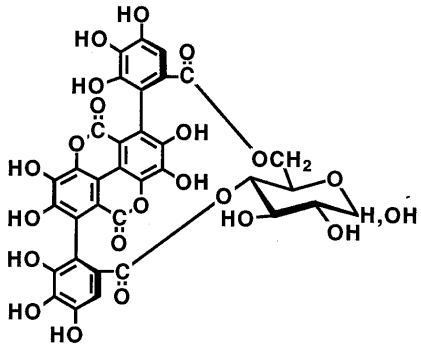

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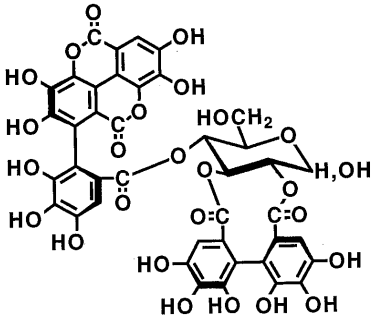
Chart 4



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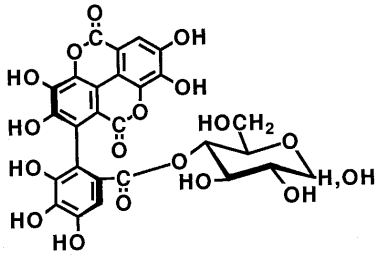

10

Chart 5

peak between the aromatic singlet at δ 7.74 and the methoxyl signals, thus indicating clearly that the aromatic proton and the methoxyl group are not located adjacently. As for the atropisomerism of the phenyl–phenyl bond, the circular dichroism (CD) spectral comparison of **5** with the *S*-flavogallonic acid methylate (**11**)[5] (Fig. 1) established it to be in the *S*-series.

Although there is no unequivocal evidence for the orientation of the 4,6-substituted terchebulic acid ester in terchebulin, the fact that terchebulin co-occurs with terflavin A (**2**) led us to conclude its structure to be as shown by the formula **3**.

Our previous work demonstrated that the compositions of tannins almost invariably differ quite remarkably in each plant material, particularly in leaf and bark.[3a,4a] Thus, we examined the leaves of *T. chebula* to isolate biogenetically related compounds.

The aqueous acetone extract of the leaves collected in Taiwan was separated in a similar manner to that used for the fruits to afford terflavins C (**9**) and D (**10**), together with the known tannins, terflavin B (**7**),[5] punicalagin (**1**)[4] and punicalin (**8**).[4] The ^{1}H- and ^{13}C-NMR spectra of **9** and **10** were also duplicated owing to the presence of α- and β-anomers. The relatively large coupling constants of the ^{1}H-NMR signals in **9** and **10** suggested the presence of a glucopyranose ring with a $^4C_1$ conformation. One of the characteristic features in the ^{13}C-NMR spectra of these compounds was the observation of two δ-lactone carbonyl carbon signals (δ 159.0, 161.0 in **9**; δ 159.7, 161.0 in **10**). The appearance of aromatic singlets at δ 6.39, 6.40 (1H in total) and 6.50 (1H) in the ^{1}H-NMR spectrum of **9** suggested the presence of a hexahydroxydiphenoyl ester group, whereas **10** showed no such peaks.

Complete acid hydrolysis of **9** yielded glucose, ellagic acid and flavogallonic acid.[5] On the other hand, partial acid hydrolysis of **9** gave **10**, together with ellagic acid. The location of each acyl group was unequivocally established by conversion of terflavin A (**2**) into **9** on partial enzymatic hydrolysis with tannase. Based on these chemical and spectroscopic findings, the structures of terflavins C and D were determined to be **9** and **10**, respectively.

The co-occurrence of 4-*O*-flavogallonyl-6-*O*-galloyl-D-glucose derivatives [terflavins A (**2**) and B (**7**)] with terchebulin (**3**) and punicalagin (**1**) provides support for an earlier scheme of biogenesis of component phenolcarboxylic acids.[2] Finally, it should be noted that the molecular weights of leaf tannins are, on the whole, less than those of the fruit tannins, that is, the leaf contains compounds of an earlier biosynthetic stage.

Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter. ^{1}H- and ^{13}C-NMR spectra were taken with a JEOL FX-100 spectrometer, with tetramethylsilane as an internal standard; chemical shifts are given on a δ (ppm) scale. FAB- and FD-MS were recorded on JEOL JMS DX-300 and D-300 spectrometers. Column chromatography was carried out with Sephadex LH-20 (25—100 μ, Pharmacia Fine Chemical Co., Ltd.), MCI-gel CHP 20P (75—150 μ, Mitsubishi Chemical Industries, Ltd.), Fuji-gel ODS G-3 (43—65 μ, Fuji Gel Hanbai Co., Ltd.), Bondapak C_{18}/Porasil B (37—75 mesh, Waters Associates, Inc.), Prep-pak 500/C_{18} (Waters Associates, Inc.), silica gel 60 (70—230 mesh, Merck) and Avicel cellulose (Funakoshi). Thin-layer chromatography (TLC) was performed on precoated Kieselgel 60 F_{254} plates (0.2 mm thick, Merck) with solvent systems of benzene–ethyl formate–formic acid (1 : 7 : 1, 2 : 10 : 3), and spots were located by ultraviolet

illumination (Manasul light, 2536 Å) and by spraying 1% ferric chloride reagent or 10% sulfuric acid, followed by heating.

Isolation of Tannins *a*) From Mylobalans: The commercial mylobalans (2.9 kg) were extracted four times with 60% aqueous acetone at room temperature. Concentration of the extracts under reduced pressure afforded dark brown precipitates, which were removed by filtration. The filtrate was applied to a Sephadex LH-20 column. Elution with H_2O containing increasing amounts of MeOH and finally with a mixture of H_2O–acetone (1 : 1) yielded four fractions: fr. 1 (550 g), fr. 2 (195 g), fr. 3 (178 g) and fr. 4 (117 g). Fraction 1 was rechromatographed over MCI-gel CHP 20P with H_2O–MeOH (1 : 0—1 : 1) and then over Sephadex LH-20 with H_2O–MeOH (1 : 0—0 : 1) to give gallic acid (12.5 g), ellagic acid (2 g), chebulic acid (25 g), corilagin (2.1 g), chebulagic acid (0.75 g) and chebulinic acid (32.6 g). Fraction 3 was repeatedly chromatographed over MCI-gel CHP 20P, Fuji-gel ODS G-3, Bondapak C_{18}/Porasil B and Prep-pak 500/C_{18} with H_2O–MeOH (1 : 0—1 : 1), and Sephadex LH-20 with EtOH to yield terflavin A (**2**) (48 mg) and punicalagin (**1**) (3.8 g). Repeated chromatography of fraction 4 as for fraction 3 gave terchebulin (**3**) (158 mg).

b) From Leaves: The dried leaves (2.1 kg) of *T. chebula*, collected at Ping-tung, Taiwan, R.O.C., were extracted with 70% aqueous acetone at room temperature. After concentration of the extract under reduced pressure, the resulting precipitates were removed by filtration. The aqueous solution was applied to a column of Sephadex LH-20, and elution with H_2O containing increasing amounts of MeOH yielded three fractions; fr. 1 (74.2 g), fr. 2 (42.9 g) and fr. 3 (244 g). Fraction 1 was rechromatographed over MCI-gel CHP 20P and Fuji-gel ODS-G3 with H_2O–MeOH (1 : 0—1 : 1) and Sephadex LH-20 with H_2O–MeOH (1 : 0—0 : 1) to give chebulic acid (631 mg) and 2,3-(*S*)-hexahydroxydiphenoyl-D-glucose (640 mg). Fraction 2 was repeatedly chromatographed over Sephadex LH-20 with EtOH and 60% aqueous MeOH and MCI-gel CHP 20P, Fuji-gel ODS G-3 and Pre-pak 500/C_{18} with H_2O–MeOH (1 : 0—1 : 1) to give gallic acid (112 mg), ellagic acid (795 mg), 2,3-di-*O*-galloyl-D-glucose (29 mg), corilagin (616 mg), terflavin C (**9**) (54 mg), punicalin (**8**) (246 mg), terflavin B (**7**) (180 mg) and terflavin D (**10**) (38 mg). Fraction 3 was chromatographed over MCI-gel CHP 20P and Fuji-gel ODS G-3 with H_2O–MeOH (1 : 0—1 : 1) and Sephadex LH-20 with EtOH and 80% aqueous MeOH to yield chebulagic acid (5.3 g) and punicalagin (**1**) (108 g).

Terchebulin (3) A tan crystalline powder (H_2O), mp 222—224 °C, $[\alpha]_D^{25}$ −136.2° (*c* = 1.5, MeOH). *Anal.* Calcd for $C_{48}H_{28}O_{30}\cdot 8H_2O$: C, 46.90; H, 3.58. Found: C, 47.08; H, 3.51. ^{1}H-NMR (acetone-d_6 + D_2O): 3.10 (1H, d, *J* = 12 Hz, glc. H-6), 4.88 (2/3 H, dd, *J* = 3, 9 Hz, glc. α-H-2), 5.01 (1/3 H, d, *J* = 8 Hz, glc. β-H-1), 5.32 (2/3 H, d, *J* = 4 Hz, glc. α-H-1), 5.32 (1/3 H, t, *J* = 8 Hz, glc β-H-3), 5.59 (2/3 H, t, *J* = 8 Hz, glc α-H-3), 6.37 (2/3 H, s, aromatic H), 6.39 (1/3 H, s, aromatic H), 6.44, 6.63 (each 1H, s, aromatic H), 6.77 (1/3 H, s, aromatic H), 6.80 (2/3 H, s, aromatic H), 7.58 (1H, s, aromatic H). ^{13}C-NMR (acetone-d_6 + D_2O): 64.4 (glc. C-6), 69.6, 70.1, 74.6, 75.1, 77.1, 77.5 (glc. C), 90.8 (glc. α-C-1), 94.1 (glc. β-C-1), 157.9, 160.3 (δ-lactone), 166.8, 167.6, 169.1, 169.9 (–COO–).

Partial Acid Hydrolysis of 3 A solution of **3** (55 mg) in 1 N H_2SO_4 (3 ml) was heated at 95°C for 4 h. After cooling, the reaction mixture was chromatographed over MCI-gel CHP 20P (H_2O–MeOH) and then over Sephadex LH-20 (EtOH) to yield ellagic acid (9 mg) and the hydrolysate (**4**) (13 mg) as a tan amorphous powder, $[\alpha]_D^{22}$ −195.0° (*c* = 1.0, MeOH). Negative FAB-MS *m/z*: 781 $(M-H)^-$. *Anal.* Calcd for $C_{34}H_{22}O_{22}\cdot 8H_2O$: C, 44.06; H, 4.10. Found: C, 44.41; H, 3.88. ^{1}H-NMR (acetone-d_6 + D_2O): 3.0—4.5 (glc. H), 5.02 (d, *J* = 4 Hz, glc. α-H-1), 6.54, 6.55 (1H in total, each s, terchebuloyl H), 7.12, 7.60 (each 1H, s, terchebuloyl H).

Methylation of 3 A mixture of **3** (230 mg), dimethyl sulfate (1.8 ml) and anhydrous K_2CO_3 (2.5 g) in dry acetone (20 ml) was heated under reflux for 3.5 h. After removal of the inorganic precipitates by filtration, the filtrate was concentrated to dryness under reduced pressure. The residue was chromatographed over silica gel, and elution with benzene–acetone (4 : 1) afforded the hexadecamethylate (**11**) (153 mg) as a pale yellow crystalline powder, mp 204—207 °C (dec.), $[\alpha]_D^{22}$ −239.5° (*c* = 1.0, $CHCl_3$). *Anal.* Calcd for $C_{64}H_{60}O_{30}$: C, 58.71; H, 4.58. Found: C, 58.47; H, 4.80. FD-MS *m/z*: 1308 (M^+). ^{1}H-NMR ($CDCl_3$): 6.53, 6.57 (1H in total, each s, aromatic H), 6.76, 6.78, 6.83 (2H in total, each s, aromatic H), 7.06, 7.07 (1H in total, each s, aromatic H), 7.66 (1H, s, aromatic H).

Alkaline Methanolysis of the Methylate (11) A solution of the hexadecamethylate (**11**) (94 mg) in 0.5% methanolic sodium methoxide (3 ml) was heated under reflux for 5 h. The reaction mixture was neutralized with Amberlite IR-120B (H^+ form), and the solvent was evaporated off under reduced pressure. The residue was chromatographed over silica gel. Elution with hexane–acetone (3 : 1) yielded dimethyl-(*S*)-hexamethoxydiphenoate (**6**) (30 mg) as a colorless syrup, $[\alpha]_D^{19}$ −29.4° (*c* = 1.3, $CHCl_3$). Further elution with the same solvent system afforded the terchebulic acid undecamethylate (**5**) (40 mg) as colorless needles (benzene), mp 77—80 °C (dec.), $[\alpha]_D^{25}$ −28.2° (*c* = 1.0, $CHCl_3$). *Anal.* Calcd for $C_{39}H_{36}O_{18}\cdot H_2O$: C, 57.78; H, 4.69. Found: C, 57.96; H, 4.52. EI-MS *m/z*: 792 (M^+, 100%), 581, 239. ^{1}H-NMR ($CDCl_3$): 3.61, 3.67 (each 6H, s, OMe), 3.77, 3.83, 3.88, 3.93, 3.96, 3.98, 4.25 (each 3H, s, OMe), 7.21, 7.45, 7.74 (each 1H, s, aromatic H). ^{13}C-NMR ($CDCl_3$): 51.8, 52.1, 56.0, 56.1, 56.9, 60.7, 61.0, 61.4, 61.7 (OMe), 107.7, 108.4, 109.5 (aromatic CH), 156.6, 159.0 (δ-lactone), 165.4, 166.1 (–COO–).

Methylation of 5 A mixture of **5** (10 mg), dimethyl sulfate (0.5 ml) and 10% NaOH (2 ml) in MeOH was heated at 90 °C for 2 h. The reaction mixture was acidified with 1 N HCl and extracted with ether. The organic layer was dried over Na_2SO_4 and concentrated to give a residue, which was treated with ethereal diazomethane for 30 min. Purification of the product over silica gel [benzene–acetone (5 : 1)] afforded the pentadecamethylate as a colorless syrup (2.1 mg), $[\alpha]_D^{22}$ +3.4° (*c* = 0.2, $CHCl_3$). *Anal.* Calcd for $C_{41}H_{42}O_{19}\cdot H_2O$: C, 57.47; H, 7.00. Found: C, 57.26; H, 7.18 EI-MS *m/z*: 884 (M^+).

Deuteromethylation of 5 A mixture of **5** (10 mg), hexadeuterodimethyl sulfate (0.5 ml) and 10% NaOH (2 ml) in MeOH (1 ml) was heated at 90 °C for 2 h. Work-up as above yielded the hexadeuteropentadecamethylate (3.7 mg) as a colorless syrup, $[\alpha]_D^{22}$ +1.1° (*c* = 0.3, $CHCl_3$). EI-MS *m/z*: 890 $(M)^+$.

Terflavin C (9) A pale yellow crystalline powder (H_2O–acetone), mp 225—227 °C, $[\alpha]_D^{22}$ +32.6° (*c* = 1.2, MeOH). *Anal.* Calcd for $C_{41}H_{26}O_{26}\cdot 2H_2O$: C, 50.73; H, 2.70. Found: C, 50.55; H, 2.87. Negative FAB-MS *m/z*: 933 $(M-H)^-$. ^{1}H-NMR (acetone-d_6 + D_2O): 3.56 (2H, br s, $W_{h/2}$ = 7 Hz, glc. H-6), 5.08 (t, *J* = 8 Hz, glc. α-H-3), 5.08 (d, *J* = 4 Hz, glc. α-H-1), 6.39, 6.40 (1H in total, each s, hexahydroxydiphenoyl H), 6.54 (1H, s, hexahydroxydiphenoyl H), 7.31, 7.32 (1H in total, each s, flavogallonyl H). ^{13}C-NMR (acetone-d_6 + D_2O): 61.4 (glc. C-6), 68.0, 68.3, 70.7, 75.1, 75.8, 77.4 (glc. C), 91.0 (glc. α-C-1), 94.5 (glc. β-C-1), 159.0, 161.0 (δ-lactone), 166.3, 169.2, 169.4, 169.6 (–COO–).

Complete Acid Hydrolysis of 9 A solution of **9** in 1 N H_2SO_4 (5 ml) was heated under reflux for 20 h. After cooling, the precipitates formed were collected by filtration and recrystallized from pyridine to give pale brown needles. This product was identified as ellagic acid by infrared (IR) and TLC comparisons. The filtrate was applied to a column of Sephadex LH-20. Elution with H_2O gave glucose (identifid by Avicel TLC), while 20% aqueous MeOH eluate gave ellagic acid (4 mg). Further elution with 60% aqueous MeOH furnished flavogallonic acid (9 mg) as a pale yellow crystalline powder, mp >290 °C. IR ν_{max}^{KBr} cm^{-1}: 1715 (–COO–), 1590 (aromatic ring). ^{1}H-NMR (CD_3OD): 7.29, 7.52 (each 1H, s, aromatic H). ^{13}C-NMR (DMSO-d_6): 106.6, 109.6 (×2) (aromatic CH), 157.4, 159.2 (δ-lactone), 167.5 (×2) (–COOH).

Partial Acid Hydrolysis of 9 A solution of **9** (40 mg) in 2% H_2SO_4 (10 ml) was heated at 95 °C for 15 h. After cooling, the resulting precipitates (7 mg) of ellagic acid were removed by filtration. The filtrate was concentrated under reduced pressure and the residue was applied to a column of Sephadex LH-20 with EtOH to give terflavin D (**10**) (13 mg).

Terflavin D (10) A pale yellow crystalline powder (H_2O–acetone), mp 215—228 °C (dec.), $[\alpha]_D^{22}$ +11.2° [*c* = 1.0, acetone–H_2O (1 : 1)]. *Anal.* Calcd for $C_{27}H_{20}O_{18}\cdot 5H_2O$: C, 44.88; H, 4.16. Found: C, 44.57; H, 3.50. Negative FAB-MS *m/z*: 631 $(M-H)^-$. ^{1}H-NMR (acetone-d_6 + D_2O): 3.0—4.2 (glc. H), 4.58 (t, *J* = 8 Hz, glc. H-4), 5.00 (d, *J* = 4 Hz, glc. α-H-1), 7.31, 7.50 (each 1H, s, flavogallonyl H). ^{13}C-NMR (acetone-d_6 + D_2O): 61.7 (glc. C-6), 92.8 (glc. α-C-1), 97.4 (glc. β-C-1), 159.7, 161.0 (δ-lactone), 167.1 (–COO–).

Acid Hydrolysis of 10 A solution of **10** (20 mg) in 1 N H_2SO_4 (3 ml) was heated at 90 °C for 20 h. After cooling, the reaction mixture was subjected to Sephadex LH-20 chromatography. Elution with H_2O gave a fraction containing a sugar and H_2SO_4. After neutralization with $BaCO_3$, the solution was analyzed by TLC on cellulose [*n*-BuOH–pyridine–H_2O (6 : 4 : 3)], which showed a spot (*Rf* 0.4) corresponding to glucose. Further elution with 60% aqueous MeOH gave flavogallonic acid (7 mg).

Tannase Hydrolysis of 2 A solution of **2** (30 mg) in H_2O was shaken with tannase (kindly provided by Dr. M. Kanaoka, Sankyo Co., Ltd.) at room temperature for 20 h. The reaction mixture was directly subjected to Sephadex LH-20 chromatography with EtOH to yield gallic acid and terflavin C (**9**) (10 mg).

Tannase Hydrolysis of 7 A solution of **7** (43 mg) in H_2O was shaken with tannase at room temperature for 20 h. Work-up as described above yielded gallic acid (5 mg) and terflavin D (**10**) (17 mg).

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