Tannins and Related Polyphenols of Theaceous Plants. IV.[1] Monomeric and Dimeric Hydrolyzable Tannins Having a Dilactonized Valoneoyl Group from *Schima wallichii* KORTH.

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Two new hydrolyzable tannins, schimawalins A (10) and B (17), have been isolated from the dried flowers of *Schima wallichii* (DC) KORTH. (Theaceae), and their structures, having a dilactonized valoneoyl group in the molecule, were established based on spectral and chemical evidence. Eight known hydrolyzable tannins, including camelliin B (8), the main constituent of the flower, with a macrocyclic dimer structure, were also isolated. The orientation of the valoneoyl groups in camelliin B was completely determined.

Keywords *Schima wallichii*; Theaceae; tannin; schimawalin A; schimawalin B; camelliin B; hydrolyzable tannin dimer; dilactonized valoneoyl group

Schima wallichii (DC) KORTH. (Theaceae) is widely grown in Southeast Asia, and its astringent corollas are used for the treatment of uterine disorders and hysteria, and also as an ointment to treat smallpox, in Indonesia and Malaysia.[2,3] Although this plant is known to be rich in saponins and tannins,[3] little chemical work has been reported. In a continuing study of tannins of the family Theaceae, we have examined a crude drug called "Buah cangkok" in Indonesia,[3] (dried flowers of *S. wallichii*) and isolated ten polyphenolics including camelliin B (**8**), a dimeric hydrolyzable tannin, and two new hydrolyzable tannins named schimawalins A and B.

The concentrate of 70% aqueous acetone homogenate of the flowers was rich in saponins, which cause difficulty in subsequent extraction with ether and ethyl acetate. It was treated with 20% MeOH–BuOH, and the organic layer was evaporated to dryness. The residue was passed through a column of Diaion HP-20, with water containing increasing amounts of MeOH. The eluates with 30% MeOH and 60% MeOH were further chromatographed separately to yield schimawalins A (**10**) and B (**17**), along with known tannins which were identified as 2,3-di-*O*-galloyl-D-glucose (**1**),[4] 1,2,3,6-tetra-*O*-galloyl-*β*-D-glucose (**2**),[5] gemin D (**3**),[6] tellimagrandin I (**4**) and II (**5**),[7] heterophyllin A (**6**),[8] pedunculagin (**7**)[7] and camelliin B (**8**).[9]

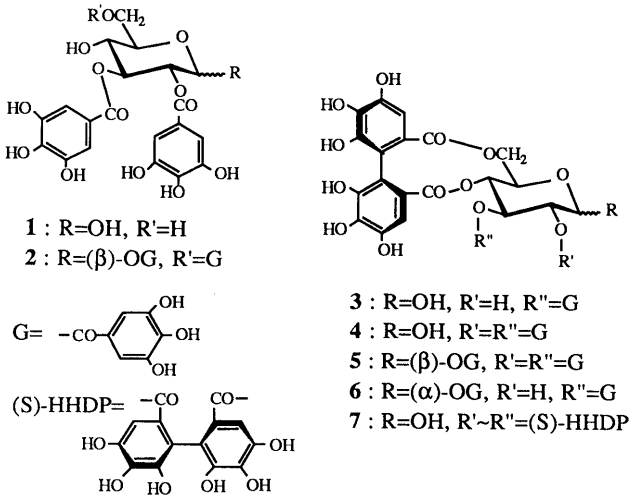
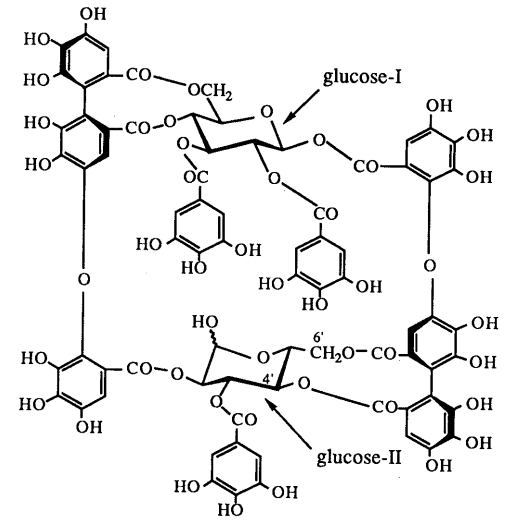
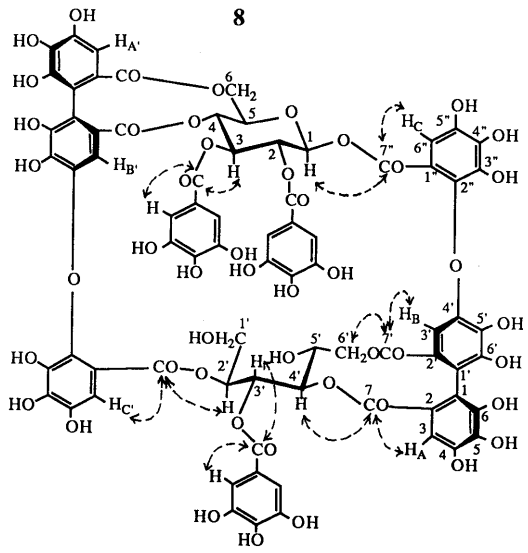


Chart 1

Camelliin B (**8**), which is the main tannin of this crude drug, was previously isolated from the flower buds of *Camellia japonica* L. and *C. sasanqua* THUNB., and its unique macrocyclic structure, except for the orientation of the valoneoyl group at O-4′/O-6′, was established as **8**.[9] The orientation of the valoneoyl group has been



8



9

Chart 2

determined in the present study as follows. Reduction of **8** with $NaBH_4$ furnished a dihydro derivative (**9**), which shows an $(M+Na)^+$ ion peak at m/z 1745 in the fast-atom bombardment mass spectrum (FAB-MS). Its proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed a fairly well-resolved sharp peak for each proton, unlike the complex spectrum of **8**, which forms an equilibrium mixture of α- and β-anomers. The ^{1}H–^{1}H shift correlation spectrum (COSY) of **9** indicated that the glucose-II of **8** was reduced to a glucitol (see Experimental).

Among the valoneoyl proton signals (δ 6.18, 6.32, 6.64, 6.79, 6.83, 7.19) in the ^{1}H-NMR spectrum of **9**, the H_A ($H_{A'}$) and H_B ($H_{B'}$) signals (δ 6.18—6.79) of each valoneoyl group were distinguished from the H_C ($H_{C'}$) signal [δ 7.19 (6.83)], by the correlations of the former two signals with C-1 and C-1′ at δ 115.7—117.3 through three-bond couplings in the ^{1}H–^{13}C long-range COSY. The signals at δ 6.18 and 6.32 were assigned to H_B ($H_{B'}$), based on the correlation through two-bond coupling with the signals at δ 146.2 and 146.3, which are attributable to the phenyl ether carbons (C-4′). The remaining two singlets at δ 6.79 and 6.64 were thus attributed to H_A ($H_{A'}$). A connectivity between H-4′ [δ 5.33 (dd, J=3.0, 9.0 Hz)] of the glucitol core and valoneoyl H_A (δ 6.79) was indicated by the three-bond correlations with the carbonyl carbon signal at δ 168.8 (Fig. 1). Similarly, the glucitol H-6′ signal [δ 4.55 (dd, J=5.0, 12.5 Hz)] was correlated with the carbonyl signal at δ 169.4, which showed a cross peak with the valoneoyl H_B at δ 6.18. The orientation of the valoneoyl group at O-4′/O-6′ in **9**, and consequently in camellin B (**8**), was thus established. The other long-range correlations through three-bond couplings illustrated in the formula **9**, also provided further evidence for the proposed structure (**8**) of camelliin B.

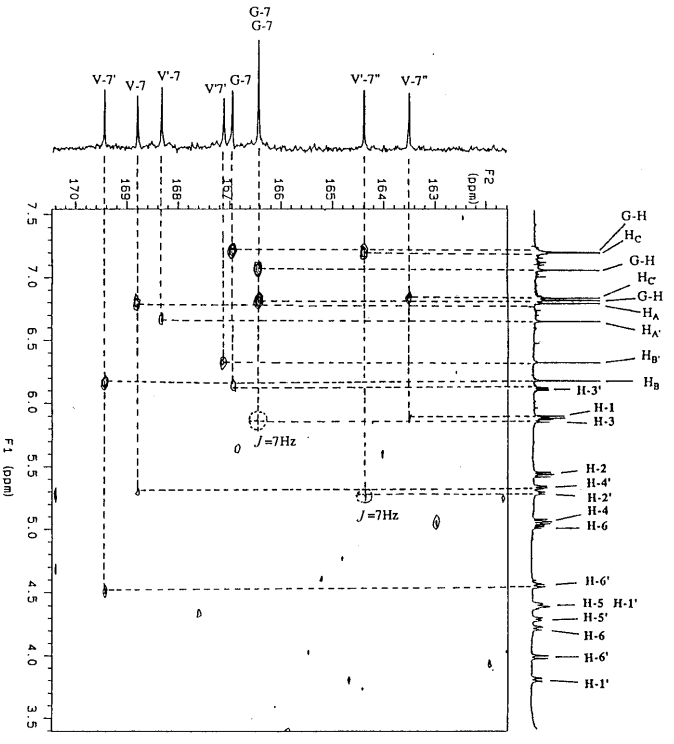


Fig. 1. A Part of ^{1}H–^{13}C Long Range Shift Correlation Spectrum of Dihydrocamelliin B (**9**) (Acetone-d_6 + D_2O, J_{CH} = 8 Hz)

Cross peaks in dotted circles were observed in a separate experiment with an average J_{CH} value of 7 Hz.

A new tannin, schimawalin A (**10**), was obtained as a light brown amorphous powder, $[\alpha]_D$ +74.3° (MeOH). Its FAB-MS exhibited the $(M+Na)^+$ ion peak at m/z 1277, which is consistent with the molecular formula $C_{55}H_{34}O_{35}$. Schimawalin A (**10**) forms an equilibrium mixture of α- and β-anomers as revealed by duplication of each signal in the ^{1}H-NMR spectrum. The presence of a dilactonized valoneoyl group in **10** was indicated by the characteristic low field aromatic signals[10] [δ 7.60, 7.59 (1H in total), 7.12, 7.11 (1H in total), 7.09, 7.08 (1H in total)], and by the ultraviolet (UV) absorption at 360 nm.[11]

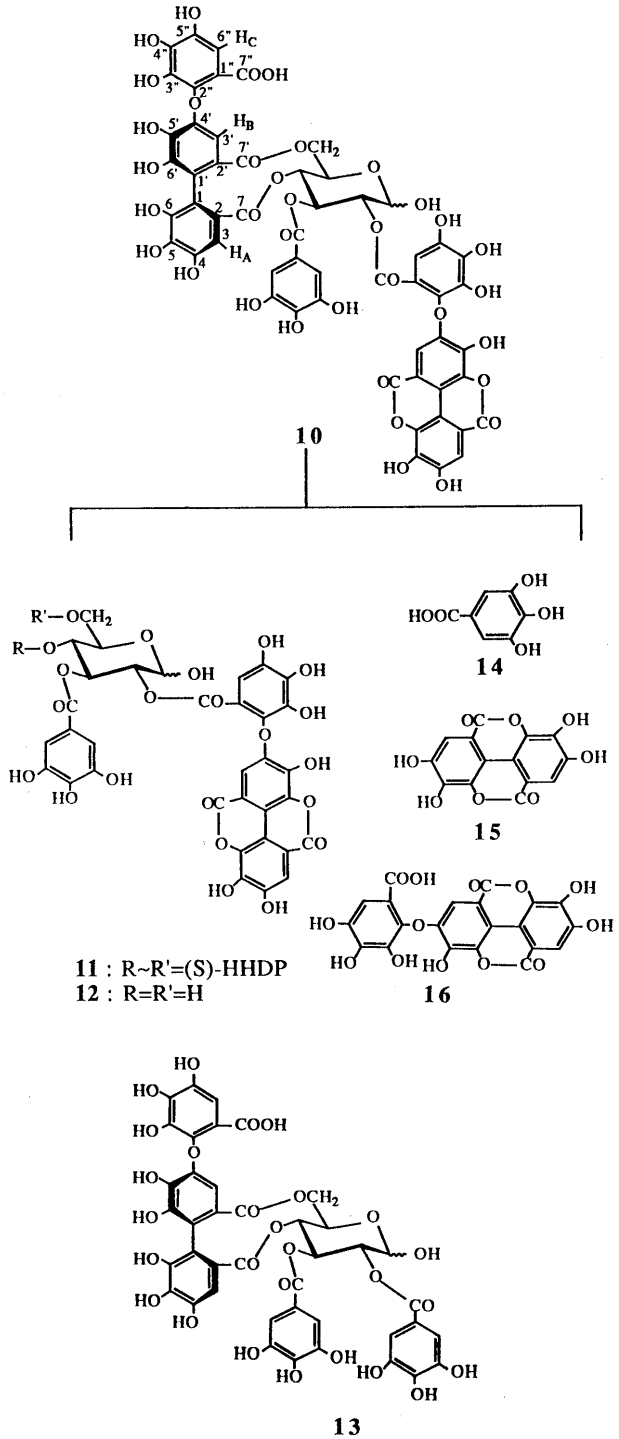


Chart 3

The paired signals were also exhibited for a galloyl group and a valoneoyl group (see Experimental). The coupling patterns of the aliphatic proton signals which were assigned by ^1H–^1H COSY are typical of the $^4C_1$ glucopyranose residue with a free anomeric hydroxyl group. The *S*-configuration of the valoneoyl group in **10** was indicated by a positive Cotton effect at 223 nm[12] in the circular dichroism (CD) spectrum. Schimawalin A is therefore regarded as an ellagitannin composed of a galloyl, and (*S*)-valoneoyl, a dilactonized valoneoyl group and glucose. These structural characteristics are similar to those of cornusiin B (**11**),[13] and the sugar proton signals of **10** are virtually identical with those of **11**, as shown in Table I. A feature distinguishing **10** and **11** is the difference of the chemical shifts of the H-6 signals, which indicates that the valoneoyl group of **10** is at O-4/O-6, and that the other acyl groups on the glucose residue are located similarly to those of **11**. The orientation of the valoneoyl group at O-4/O-6, as in the structure **10**, was determined based on the analogy of the chemical shifts of the valoneoyl H_A signal (δ 6.46, 6.42) to those (δ 6.46, 6.44) of rugosin B (**13**),[14] whose structure was already established by ^1H–^{13}C long-range COSY.

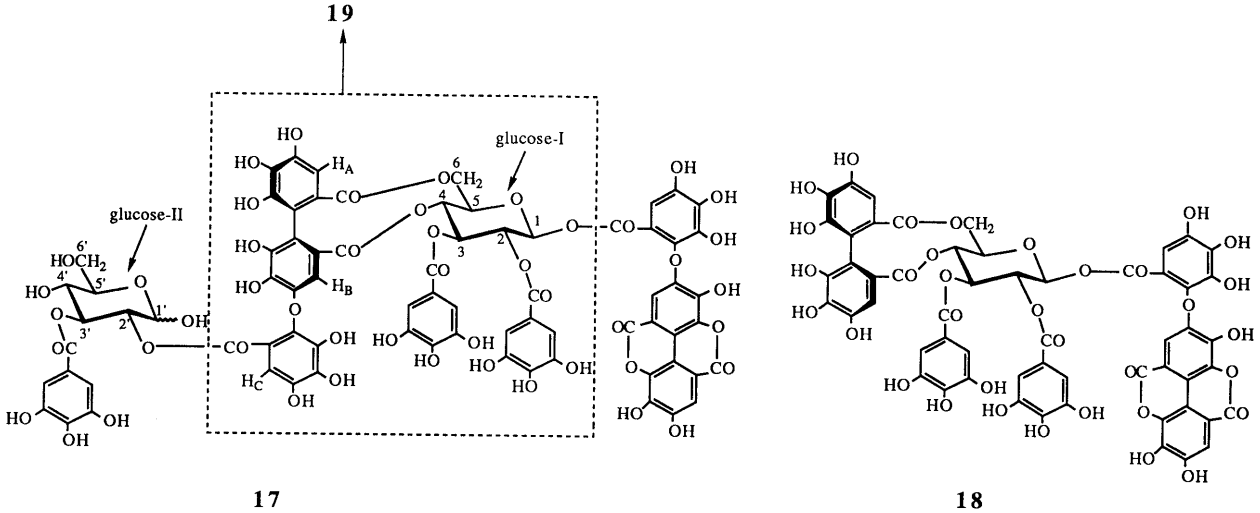
TABLE I. ^1H-NMR Data for the Glucose Moieties of **10** and **11** (500 MHz, Acetone-d_6 + D_2O, *J* in Hz)

	10		**11**[a]	
	α-Anomer	β-Anomer	α-Anomer	β-Anomer
H-1	5.32 d (J=3.8)	4.70 d (J=8.0)	5.32 d (J=3.5)	4.70 d (J=8.0)
H-2	5.04 dd (J=3.8, 10.0)	5.15 dd (J=8.0, 10.0)	5.05 dd (J=3.5, 10.0)	5.15 dd (J=8.0, 10.0)
H-3	5.70 t (J=10.0)	5.30 t (J=10.0)	5.76 t (J=10.0)	5.38 t (J=10.0)
H-4	4.95 t (J=10.0)	4.89 t (J=10.0)	5.01 t (J=10.0)	4.97 t (J=10.0)
H-5	4.52 m	4.00 m	4.56 br dd (J=6.5, 10.0)	4.06 br dd (J=6.5, 10.0)
H-6	5.09 dd (J=6.0, 13.0) 3.57 d (J=13.0)	5.09 dd (J=6.0, 13.0) 3.57 d (J=13.0)	5.21 dd (J=6.5, 12.5) 3.66 dd (J=1.0, 12.5)	5.22 dd (J=6.5, 13.0) 3.71 dd (J=0.5, 13.0)

a) Data are taken from ref. 13.

The chemical evidence for the structure (**10**) of schimawalin A was obtained as follows. Upon treatment with hot water containing a small amount of trifluoroacetic acid, **10** gave gallic acid (**14**), ellagic acid (**15**), valoneic acid dilactone (**16**) and oenothein C (**12**).[13] A milder partial hydrolysis of **10** with hot water furnished **14** and cornusiin B (**11**). Among these products, ellagic acid (**15**) and cornusiin B (**11**) are regarded as having been formed by the cleavage of an ether bond of the valoneoyl group of **10**, in an analogous way to the partial hydrolysis of a variety of tannins possessing a valoneoyl group in the molecule.[15] Based on these findings, the structure **10** was assigned to schimawalin A.

Shimawalin B (**17**) is a dimeric hydrolyzable tannin as indicated by the $(M+Na)^+$ ion peak at *m/z* 1743 in FAB-MS. The duplication of each signal in the ^1H-NMR spectrum implied that **17** forms an equilibrium mixture of two anomers, like **10**. The presence of three galloyl groups in **17** was indicated by three pairs of signals [δ 7.03, 7.06 (2H in total), 6.89, 6.89 (2H in total) and 6.73, 6.75 (2H in total)] in the aromatic region. The presence of two valoneoyl groups, one of which is dilactonized, was also shown by six aromatic 1H singlets appearing as paired signals similar to those of **10**. The anomeric proton signals [δ 6.08 (1H, d, J=8.0 Hz, H-1), 5.18 (1/4H, J=3.0 Hz, H-1′) and 4.22 (3/4H, d, J=8.0 Hz, H-1′)] and other sugar proton signals, of large coupling constants (J=8—13.5 Hz), indicate the presence of two $^4C_1$ glucopyranose residues, one of which has a free hydroxyl group at the anomeric center. The chemical shift of H-1′ (δ 4.23) of the β-anomer, which is shifted to higher field than that (δ 5.13) of **4** and is comparable to those (δ 4.70—4.22) of **8** and **10**—**12**, indicates that the galloyl part of the valoneoyl group is located at O-2′. The presence of free hydroxyl groups at O-4′ and O-6′ of the glucose-II was also indicated by the H-4′—H-6′ signals in the upfield region (δ 3.6—3.9). The chemical shifts and coupling pattern of the glucose-I residue are virtually identical with those of prostratin A (**18**), which was recently isolated from *Euphorbia prostrata*,[10] suggesting an analogy of the substitution pattern on the



17 18

Chart 4

glucose core to that in **18**. The valoneoyl group in **17** is thus located at O-4/O-6 of the glucose-I, and its orientation is indicated to be the same as that of isorugosin B (**19**)[16] by the chemical shift of the H_A signal (δ 6.62), which is similar to that (δ 6.65) of **19**. In fact, **19** and 2,3-di-*O*-galloylglucose (**1**) were formed upon partial hydrolysis of **17** with hot water. Schimawalin B is, therefore, assigned the structure **17**. Although this dimer (**17**) is one of the degradation products obtained from camelliin B,[9] this is the first report of its isolation from a natural source.[17]

Experimental

General Instruments ($[\alpha]_D$, UV, NMR, MS) used in this work were the same as those described in the preceding paper.[1] Reversed-phase high-performance liquid chromatography (HPLC) was conducted on a column of LiChrospher RP-18 (5 μm) (4 × 250 mm) using 0.01 M H_3PO_4–0.01 M KH_2PO_4–EtOH–EtOAc (42.5 : 42.5 : 10 : 5), in an oven at 40 °C. Normal-phase HPLC was carried out on a column of Superspher Si 60 (4 × 119 mm) developed with hexane–MeOH–tetrahydrofuran–HCOOH (60 : 45 : 15 : 1) containing oxalic acid (500 mg/l). Toyopearl HW-40 (Tosoh, Corp.), Diaion HP-20 and MCl-Gel CHP-20P (Mitsubishi Kasei Co., Ltd.) were used for column chromatography.

Plant Material The dried flowers of *S. wallichii* (DC) KORTH. (Indonesian trivial name, "buah cangkok") were purchased at a market in Bogor, Indonesia, in September 1989, and a voucher specimen (AN-BJ No. 84) has been deposited at the Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Kyoto University.

Isolation of Tannins The dried flowers (940 g) were homogenized in 70% acetone (10 l) and filtered. The filtrate was concentrated to *ca.* 1.5 l. The sticky precipitate was filtered off, and the filtrate was extracted with *n*-BuOH–MeOH (8 : 2). The organic layer was evaporated to give a dark brown residue (63 g), and a part (30 g) of this residue was suspended in H_2O. After removal of insoluble materials (15 g) by filtration, the water-soluble portion was subjected to column chromatography over Diaion HP-20 (3.5 cm i.d. × 30 cm) with H_2O→20% MeOH→30% MeOH→40% MeOH→60% MeOH→MeOH. The 30% MeOH and 40% MeOH eluates were combined and rechromatographed over Toyopearl HW-40 (fine grade) [50% MeOH→60% MeOH→70% MeOH→MeOH→acetone–H_2O (7 : 2 : 1)] to yield 2,3-di-*O*-galloylglucose (**1**) (13 mg), gemin D (**3**) (8 mg), pedunculagin (**7**) (7 mg), tellimagrandin I (**4**) (24 mg) and camelliin B (**8**) (2 mg). The 60% MeOH eluate (880 mg) was also chromatographed on Toyopearl HW-40 (fine grade) using the same solvent system to give 1,2,3,6-tetra-*O*-galloyl-β-D-glucose (**2**) (14 mg), crude schimawalin A (30 mg), tellimagrandin I (4) (33 mg), heterophyllin A (**6**) (7 mg), tellimagrandin II (**5**) (29 mg), crude schimawalin B (25 mg) and camelliin B (66 mg). Crude schimawalins A (**10**) and B (**17**) were separately purified by column chromatography over MCl-gel CHP-20P (H_2O→20% MeOH→30% MeOH to give **10** (1.5 mg) and **17** (4.5 mg).

Reduction of Camelliin B A mixture of **8** (100 mg) and $NaBH_4$ (100 mg) in H_2O (20 ml) was left standing at room temperature for 30 min. After acidification with diluted HCl (pH 3), the reaction mixture was directly applied on a column of MCl-Gel CHP-20P (1.1 cm i.d. × 25 cm) and eluted with H_2O containing increasing amounts of MeOH in a stepwise gradient mode. The 30% MeOH eluate gave dihydrocamelliin B (**9**) (27 mg) as a light yellow amorphous powder, $[\alpha]_D$ +52.5° (c = 1.0, MeOH). FAB-MS m/z: 1745 $(M+Na)^+$. *Anal.* Calcd for $C_{75}H_{54}O_{48}\cdot 10H_2O$: C, 47.32; H, 3.89. Found: C, 47.26; H, 4.18. UV λ_{max} (MeOH) nm ($\log\varepsilon$): 217 (5.01), 272 (4.61). ^{1}H-NMR (acetone-d_6 + D_2O) δ: 7.20, 7.06, 6.81 [each 2H, s, galloyl (G)], 5.89 (1H, d, J = 8.0 Hz, H-1), 5.44 (1H, dd, J = 8.0, 10.0 Hz, H-2), 5.87 (1H, t, J = 10.0 Hz, H-3), 5.06 (1H, t, J = 10.0 Hz, H-4), 4.39 (1H, m, H-5), 5.02 (1H, dd, J = 8.6, 12.5 Hz, H-6), 4.20 (1H, dd, J = 2.5, 12.5 Hz, H-6), 3.80 (1H, dd, J = 4.0, 13 Hz, H-1′), 4.40 (2H, m, H-1′ and H-5′), 5.28 (1H, m, H-2′), 6.11 (1H, dd, J = 3.0, 9.0 Hz, H-3′), 5.33 (1H, dd, J = 3.0, 9.0 Hz, H-4′), 4.28 (1H, dd, J = 3.0, 9.0 Hz, H-5′), 4.55 (1H, dd, J = 5.0, 12.5 Hz, H-6′), 3.98 (1H, d, J = 12.5 Hz, H-6′), valoneoyl and dilactonized valoneoyl protons, see text. ^{13}C-NMR (acetone-d_6 + D_2O) δ: 94.1 (C-1), 71.1 (C-2), 74.2 (C-3), 71.7 (C-4), 72.3 (C-5), 63.8 (C-6), 61.5 (C-1′), 75.3 (C-2′), 71.1 (C-3′), 73.7 (C-4′), 68.6 (C-5′), 68.9 (C-6′), 104.8, 106.1 [valoneoyl (Val) C-3′], 108.3, 108.5 (Val C-3), 108.9, 109.4 (Val C-6″), 110.0, 110.1, 110.4 [each 2C, galloyl (G) C-2, 6], 113.2, 115.9 (Val C-1″), 115.7, 116.3, 117.0, 117.3 (Val C-1, C-1′), 120.0, 120.2, 120.5 (G C-1), 125.0, 125.1, 125.7, 126.6 (Val C-2, C-2′), 136.2, 136.9 (Val C-5′), 136.6, 136.5 (Val C-5), 137.3, 137.8 (Val C-2″), 139.0, 139.3, 139.4 (G C-4), 139.4, 139.6 (Val C-3″), 140.4, 140.6 (Val C-4″), 142.0, 143.0 (Val C-5″), 144.5, 144.6, 144.7, 145.0, 145.1 (Val C-6, C-6′, C-4), 145.6, 145.7, 145.9 (G C-3, C-5), 146.2, 146.3 (Val C-4′), 163.5, 164.4 (Val C-7″), 166.5 (2C) (G C-7), 167.0 (G C-7), 167.1, 168.4, 168.8, 169.4 (Val C-7, 7′).

Schimawalin A (10) An off-white amorphous powder, $[\alpha]_D$ +74.3° (c = 0.4, MeOH). FAB-MS m/z: 1277 $(M+Na)^+$. UV λ_{max} (MeOH) nm ($\log\varepsilon$): 206 (4.95), 258 (4.56), 360 (3.70). CD (MeOH) [θ] (nm): $+5.6\times10^4$ (223), -1.3×10^4 (261), $+2.0\times10^4$ (287). ^{1}H-NMR (acetone-d_6 + D_2O) δ: 6.82, 6.73 [each s, 2H in total, galloyl (G)], 7.60, 7.59 (each s, 1H in total), 7.12, 7.11 (each s, 1H in total), 7.09, 7.08 (each s, 1H in total) [dilactonized valoneoyl (DLV)], 7.07, 7.00 (each s, 1H in total), 6.46, 6.42 (each 1H in total), 6.19, 6.18 (each s, 1H in total) (Val), glucose protons, see Table I.

Partial Hydrolysis of Schimawalin A (10) a) A solution of **10** (0.5 mg) in H_2O containing CF_3COOH (1 drop) was heated in a boiling-water bath for 30 min, and the reaction mixture was extracted with AcOEt. HPLC (reversed-phase) analysis of the AcOEt extract indicated the formation of gallic acid (**14**) (t_R 2.92 min), valoneic acid dilactone (**16**) (t_R 7.65 min) and oenothein C (**12**) (t_R 3.39 min). The identities of these products were confirmed by co-chromatography with authentic samples.

b) An aqueous solution (0.5 ml) of **10** (0.5 mg) was heated in a boiling-water bath for 30 min. The reaction mixture was directly analyzed by HPLC (reversed-phase) to detect gallic acid and cornusiin B (**11**) (t_R 4.65 and 5.70 min).

Schimawalin B (17) An off-white amorphous powder, $[\alpha]_D$ +75° (c = 1.0, MeOH). FAB-MS: m/z 1743 $(M+Na)^+$. *Anal.* Calcd for $C_{75}H_{52}O_{48}\cdot 4H_2O$: C, 50.28; H, 3.35. Found: C, 50.26; H, 3.63. UV λ_{max} (MeOH) nm ($\log\varepsilon$): 208 (4.66), 270 (4.57), 358 (3.61). CD (MeOH) [θ] (nm): $+13.8\times10^4$ (220), $+6.8\times10^4$ (237), -3.1×10^4 (257), $+4.0\times10^4$ (283). ^{1}H-NMR (acetone-d_6 + D_2O) δ: 7.03, 7.06 (each s, 2H in total), 6.89 (2H, s), 6.73, 6.75 (each s, 2H in total) (G), 7.59 (1H, s), 7.18 (1H, s), 7.10 (1H, s) (DLV), 7.00 (1H, s), 6.61, 6.62 (each s, 1H in total), 6.10, 6.13 (each s, 1H in total) (Val), 6.08 [d, J = 8.0 Hz, H-1 of α-anomer and β-anomer (α and β)], 5.49 [dd, J = 8.0, 10.0 Hz, H-2 (α)], 5.45 [d, J = 8.0, 10.0 Hz, H-2 (β)], 5.53 [t, J = 10.0 Hz, H-3 (α)], 5.50 [t, J = 10.0 Hz, H-3 (β)], 4.95 (t, J = 10.0 Hz, H-4 (α)], 5.00 [t, J = 10.0 Hz, H-4 (β)], 4.34, 4.36 [m, H-5 (α and β)], 5.14 [dd, J = 6.0, 13.5 Hz, H-6 (α)], 5.20 [dd, J = 6.0, 13.5 Hz, H-6 (β)], 3.70 [d, J = 13.5 Hz, H-6 (α and β)], 5.18 [d, J = 3.0 Hz, H-1′ (α)], 4.87 [dd, J = 3.0, 10.0 Hz, H-2′ (α)], 5.29 [t, J = 10.0 Hz, H-3′ (α)], 3.81 [t, J = 10.0 Hz, H-4′ (α)], 4.22 [d, J = 8.0 Hz, H-1′ (β)], 4.89 [dd, J = 8.0, 10.0 Hz, H-'2 (β)], 5.27 [t, J = 10.0 Hz, H-3′ (β)], 3.59 [t, J = 10.0 Hz, H-4′ (β)], 3.9—3.7 (H-5′, 6′ (α and β)].

Partial Hydrolysis of Schimawalin B (17) An aqueous solution (1 ml) of **17** (1 mg) was heated in a boiling-water bath for 3 h. The HPLC (reversed-phase) analysis of the reaction mixture showed the production of **19** (t_R 3.57 and 4.87 min), 2,3-di-*O*-galloylglucose (**1**) (t_R 2.55 and 2.76 min) and valoneic acid dilactone (**16**) (t_R 7.65 min).

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