Tannins of Euphorbiaceous Plants. X.[1] Antidesmin A, a New Dimeric Hydrolyzable Tannin from *Antidesma pentandrum* var. *barbatum*

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A new hydrolyzable tannin, antidesmin A (4), was isolated along with carpinusin (1) and geraniin (2) from dried leaves of *Antidesma pentandrum* MERR. var. *barbatum* MERR., and its dimeric structure, composed of davidiin (3) and geraniin (2), has been elucidated by spectral and chemical methods.

Keywords *Antidesma pentandrum* var. *barbatum*; Euphorbiaceae; tannin; dimeric hydrolyzable tannin; antidesmin A

Some *Antidesma* species of plants (Euphorbiaceae) are used as folk medicines in Southeast Asia for the treatment of diarrhea, skin complaints, hemorrhage and abdominal disorders.[2] Although their medicinal value is ascribable to tannins, few of the polyphenols in the plants of this genus have been studied. During a chromatographic survey on tannin constituents of the Euphorbiaceous plants, we have found that *A. pentandrum* MERR. var. *barbatum* MERR. is rich in tannins. As for the chemical consituents of this plant, only a triterpene (lupeolactone) exhibiting an anti-cholesteremic activity has been reported.[3] We have now isolated three hydrolyzable tannins including a new dimer, named antidesmin A (**4**), from the leaf extract of this plant.

The concentrated filtrate from the aqueous acetone homogenate of the dried leaves of *A. pentandrum* var. *barbatum* was extracted successively with ether, ethyl acetate and *n*-butanol. Column chromatography over Toyopearl HW-40 of the butanol extract yielded carpinusin (**1**)[4] and antidesmin A (**4**). Geraniin (**2**)[5] was isolated from the ethyl acetate extract by repeated chromatography on an MCI Gel CHP 20P column.

Antidesmin A (**4**), a pale yellow amorphous powder, showed positive colorations of ellagitannin with the $FeCl_3$ and $NaNO_2$–AcOH reagents.[6] Its molecular formula, $C_{82}H_{56}O_{53}$, which is consistent with a dimeric ellagitannin, was determined based on the fast-atom bombardment mass spectrum (FAB-MS) (*m/z* 1911 $[M+Na]^+$) and elemental analysis. Acid hydrolysis of **4** gave glucose, gallic acid (**10**), ellagic acid (**11**) and valoneic acid dilactone (**12**). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **4** showed the presence of a dehydrohexahydroxydiphenoyl group equilibrating between five- and six-membered hemiacetal forms, as revealed by the characteristic set of methine proton signals [δ 5.21 (s) and 4.95 (d, $J=1.5$ Hz), H-1″] and vinyl proton signals [δ 6.24 (s) and 6.05 (d, $J=1.5$ Hz), H-3″], and duplication of the other signals.[5] The presence of three galloyl groups, a hexahydroxydiphenoyl group and a valoneoyl group was also indicated by three 2H singlets and five 1H singlets appearing as duplicated signals in the aromatic region. The coupling patterns of the sugar proton signals assigned by the ^{1}H–^{1}H shift correlation spectrum (COSY) (Table I), indicated that the glucose cores I and II adopt the skew boat and $^1C_4$ conformations, respectively, which are indicative of the presence of a hexahydroxydiphenoyl (or valoneoyl) group bridged at *O*-1/*O*-6 and *O*-3′/*O*-6′.[5,7] This assumption was supported by the ^{1}H-NMR and ^{13}C-NMR signals due to the glucose cores of **4**, which are in agreement with sum of those of davidiin (**3**)[7] and geraniin (**2**)[5] (Tables I and II). Therefore, antidesmin A is biogenetically regarded as a product of intermolecular C–O oxidative coupling[8,9] between **3** and **2**.

Condensation of **4** with *o*-phenylenediamine in an acidic medium gave a phenazine derivative (**5**) [FAB-MS, *m/z*: 1943 $(M+Na)^+$]. The ^{1}H-NMR spectrum of **5** indicated conformational change ($^1C_4\rightarrow$skew boat) of one of the glucose cores, which is accompanied by a significant upfield shift ($\Delta\delta$ 0.46 ppm) of the anomeric proton signal and downfield shift ($\Delta\delta$ 0.19 ppm) of H-5′ from those of **4**. These spectral changes are similar to those observed upon formation of the phenazine derivative of geraniin,[5] substantiating the presence of a geraniin moiety in **4**.

Partial hydrolysis of **5** in hot water afforded a hydrolyzate (**6**), which exhibited the $[M+Na]^+$ ion peak at *m/z* 1593 in FAB-MS. The ^{1}H-NMR spectrum of **6** showed disappearance of the signals due to the phenylphenazine moiety and remarkable upfield shifts of H-2′ and H-4′ from those of **5** (Table I), indicating that the hydrolysis occurred only at *O*-2′/*O*-4′. The ^{1}H–^{13}C long-range COSY ($J_{CH}=7$ Hz) of **6** revealed the connectivity between glucose H-6′ and valoneoyl H_B signals through three-bond couplings with the ester carbonyl carbon signal at δ 168.5. The assignment of the valoneoyl H_B signal was confirmed by its two- and three-bond couplings with the valoneoyl C-4′ and C-1′ signals. Similarly, the connectivities of H-1′ with the galloyl proton, and of H-3′ with H_A of the valoneoyl group, verified the substitution pattern on glucose II in **4**. The H-6 of glucose-I was correlated with the carbonyl carbon at δ 168.4, which showed three-bond long-range coupling with one (δ 6.85) of the HHDP protons.

Enzymatic hydrolysis with tannase of **6** yielded gallic acid (**10**), ellagic acid (**11**), valoneic acid dilactone (**12**) and three hydrolyzates (**7**—**9**), which are monomeric tannins derived from the glucose I part of **6**, as indicated by the low field signals characteristic of the valoneoyl dilactone group (δ 7.0—7.5) in their ^{1}H-NMR spectra. The most polar partial hydrolyzate (**7**) was identified as oenothein C.[10] The ^{1}H-NMR spectrum of **8** indicated the presence of an HHDP group, in addition to a galloyl group and a valoneoyl dilactone group. The sugar proton signals of **8** are similar to those of the glucose-I in **4** and **5**, except for a remarkable upfield shift of the H-4 signal ($\Delta\delta$ 1 ppm) in the former, indicating that the hydroxyl group at *O*-4 in **8** is free. The HHDP group in **8** should thus be located at *O*-1/*O*-6. The

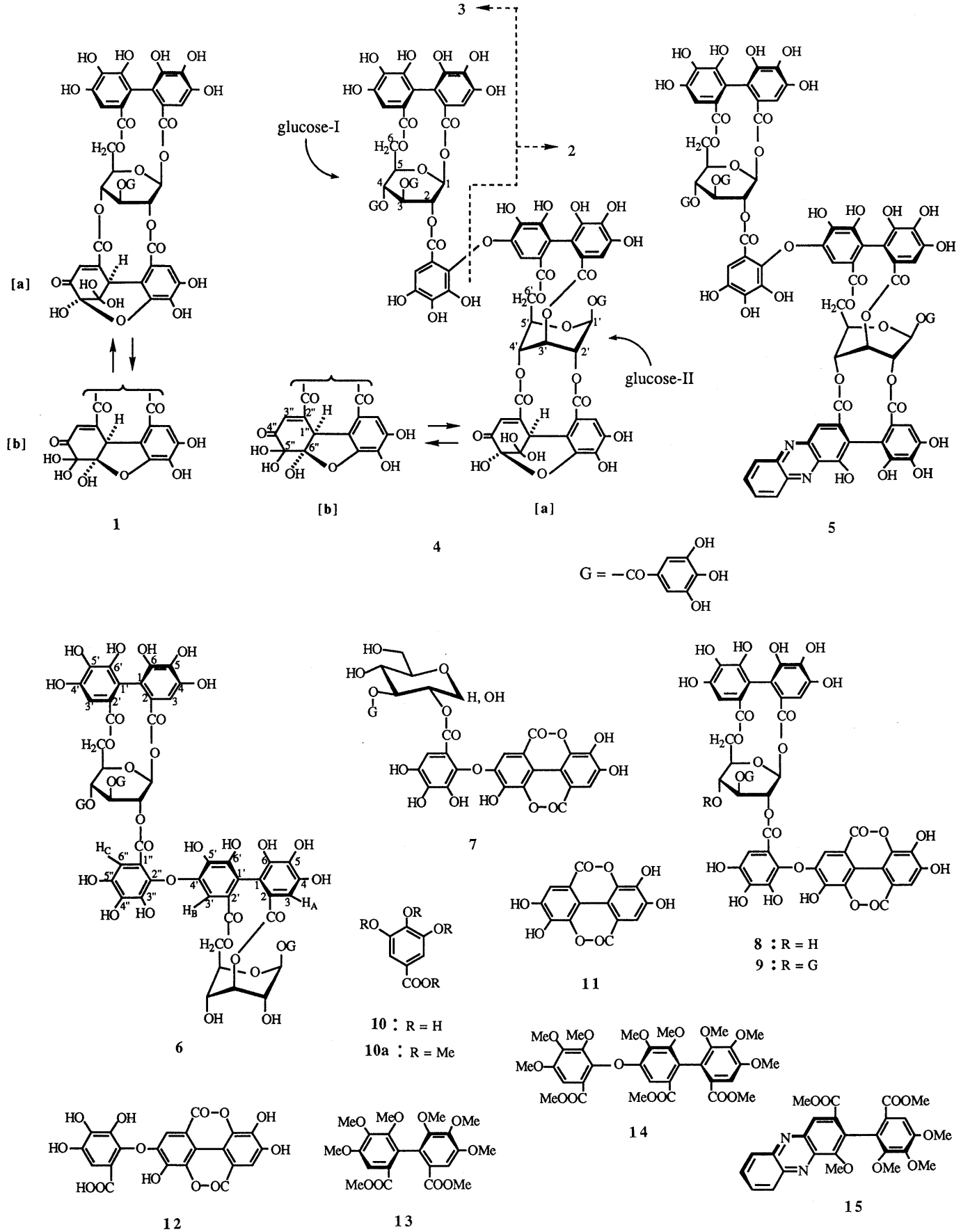

Chart 1

TABLE I. ^{1}H-NMR Chemical Shifts for the Glucose Moieties of **2**, **3**, **4** and **5** (500 MHz, Acetone-d_6–D_2O, J Values in Hz)

H-Atom		**2a**[a]	**2b**[a]	**3**[b]	**4a**	**4b**	**5**
Glucose-I	1			6.11 (d, J=3)	6.23 (d, J=3)	6.25	6.21 (d, J=3.5)
	2			5.52 (dd, J=3, 7)	5.61 (dd, J=3, 8.5)	5.59	5.58 (dd, J=3.5, 8.5)
	3			5.78 (t, J=7)	5.63 (dd, J=7, 8.5)		5.63 (dd, J=7.5, 8.5)
	4			5.20 (dd, J=3, 7)	5.12 (dd, J=3, 7)		5.10 (dd, J=2.5, 7.5)
	5			4.55 (ddd, J=3, 5.5, 12)	4.48[c]		4.46 (ddd, J=2.5, 5.5, 11.5)
	6			4.81 (t, J=12) 4.41 (dd, J=5.5, 12)	4.74 (t, J=12) 4.45[c]		4.72 (t, J=11.5) 4.43 (dd, J=5.5, 11.5)
Glucose-II	1′		6.60 (br s)		6.55 (br s)	6.54	6.09 (d, J=6)
	2′		5.60 (br s)		5.57 (br s)		5.64 (d, J=6)
	3′	5.50 (br s)	5.60		5.49 (br s)	5.57	5.30 (d, J=4)
	4′	5.56 (br s)	5.46		5.42 (br s)	5.33	5.49 (d, J=4)
	5′		4.81 (m)		4.70 (dd, J=8, 10.5)		4.89 (dd, J=4, 8.5)
	6′	4.93 (t, J=11) 4.33 (dd, J=8, 11)	4.78 (m) 4.45 (dd, J=6, 9)		4.82 (t, J=10.5)	4.66	4.64 (dd, J=8.5, 12)
					4.23 (dd, J=8, 10.5)	4.37	3.98 (dd, J=4, 12)

a) At 400 MHz. b) In acetone-d_6. c) Overlapped by each other.

TABLE II. ^{13}C-NMR Chemical Shifts for the Glucose Moieties of **2**, **3**, **4** and **5** (126 MHz, Acetone-d_6–D_2O)

C-Atom		**2a**[a]	**2b**[a]	**3**[b]	**4a**	**4b**	**5**
Glucose-I	1			94.2	94.6	94.7	94.9
	2			70.2	71.1	71.2	71.3
	3			68.8	69.2	69.3	69.3
	4			71.0	71.2	71.5	71.6
	5			75.0	75.4	75.6	75.6
	6			64.8	64.87	64.91	64.9
Glucose-II	1′	90.8	91.8		90.8	91.8	91.5
	2′	69.9	70.4		69.9	70.6	76.4
	3′	63.3	62.3		63.2	62.4	68.6
	4′	65.9	66.8		65.9	66.9	67.7
	5′	72.6	73.1		72.4	73.1	76.8
	6′	63.6	63.8		63.7	64.0	65.3

a) At 100 MHz. b) In acetone-d_6.

structure of the remaining hydrolyzate was readily assigned as **9** based on its ^{1}H-NMR spectrum, which showed the presence of two galloyl groups and an HHDP group besides a valoneoyl dilactone group, and a fully acylated glucose core with skew boat conformation.

The absolute configurations of the hexahydroxydiphenoyl, valoneoyl and phenylphenazine moieties in **5** were determined from the chiroptical properties of their methylated derivatives obtained along with methyl tri-*O*-methylgallate (**10a**), upon methanolysis after methylation of **5**. The specific optical rotations of dimethyl hexamethoxydiphenate (**13**), trimethyl octa-*O*-methylvaloneate (**14**) and the hexamethyl derivative (**15**) were $[\alpha]_D$ $-32°$ (acetone),[5] $+18°$ (acetone),[11] and $+13°$ (acetone),[5] indicating that they have *S*, *R* and *R* configurations, respectively. Since the (*R*)-phenylphenazine group is known to be produced from the (1′*R*)-dehydrohexahydroxydiphenoyl group,[5] the stereostructure of antidesmin A has been established to be **4**.

Antidesmin A is the first dimeric hydrolyzable tannin in which geraniin and the 1,6-*O*-(*S*)-hexahydroxydiphenoylglucose unit are linked with each other, forming a valoneoyl group.

Experimental

General ^{1}H-NMR (500 MHz) and ^{13}C-NMR (126 MHz) spectra were recorded on a Varian VXR 500 instrument, and chemical shifts are given in δ values (ppm) relative to tetramethylsilane. Normal phase high-performance liquid chromatography (HPLC) was conducted on a Superspher Si 60 (4 mm × 119 mm) column with *n*-hexane–MeOH–THF–HCOOH (60:45:15:1) and oxalic acid 500 mg/l, and reversed-phase HPLC on a LiChrospher RP-18 (4 × 250 mm) column using the following solvent systems: (1) 0.05 M H_3PO_4–0.05 M KH_2PO_4–EtOH–EtOAc (42.5:42.5:10:5), (2) 0.05 M H_3PO_4–0.05 M KH_2PO_4–CH_3CN (42.5:42.5:15). Column chromatography was carried out on Toyopearl HW-40 (fine and superfine grades) (Tosoh), Diaion HP-20 and MCI Gel CHP 20P (Mitsubishi Chemical Industry Co., Ltd.). TLC was performed on silica gel [Kieselgel PF_{254} (Merck)] with benzene–acetone (15:1).

Plant Materials The leaves of *Antidesma pentandrum* MERR. var. *barbatum* MERR. were collected in Taiwan. A voucher specimen was deposited at the Herbarium of the Faculty of Pharmaceutical Sciences, Okayama University.

Isolation of Tannins The dried leaves (1 kg) were homogenized three times in acetone–H_2O (7:3) and the combined homogenates were filtered. After removal of acetone by evaporation, the aqueous concentrate was extracted with ether, EtOAc, and *n*-BuOH saturated with H_2O, successively, to yield the ether extract (0.79 g), EtOAc extract (8.4 g), BuOH extract (34 g), and residue (85 g) from the aqueous layer. Geraniin (**2**, 137 mg) was isolated from the EtOAc extract by a combination of column chromatographies over Diaion HP-20 and MCI Gel CHP 20P with aqueous MeOH. A part (10 g) of the BuOH extract was chromatographed over

Toyopearl HW-40 (fine) (2.2 i.d. × 30 cm) developing with EtOH–H_2O (7:3)→EtOH–H_2O–acetone (7:2:1)→EtOH–H_2O–acetone (6:2:2)→acetone–H_2O (7:3) in a stepwise gradient mode. The eluate with EtOH–H_2O (7:3) gave carpinusin (**1**) (616 mg). The eluates with EtOH–H_2O–acetone (7:2:1) and EtOH–H_2O–acetone (6:2:2) gave antidesmin A (**4**) (1123 mg). The contents of these components in dried leaves were determined to be 1.1% (**1**), 0.09% (**2**) and 1.3% (**4**) by quantitative HPLC analysis (reversed-phase; system 2; flow rate, 1.3 ml/min) of the acetone–H_2O (7:3) extract of the dried leaves. This HPLC analysis also revealed davidiin (**3**)[7] existing in the dried leaves in a trace amount (t_R 6.5 min).

Carpinusin (1) A pale yellow amorphous powder, $[\alpha]_D$ +15° (c=1.0, MeOH). UV λ_{max}^{MeOH} nm (log ε): 220 (4.88), 278 (4.52). ^{1}H-NMR (acetone-d_6–D_2O) showed the presence of **1a** and **1b** in a ratio of *ca.* 7:3. **1a**: δ 7.12 (s, galloyl), 7.25, 6.86, 6.77, 6.55 (each s, HHDP and DHHDP), 5.20 (s, DHHDP H-1″), 6.19 (br s, H-1), 5.13 (br d, J=2.5 Hz, H-2), 5.83 (br s, H-3), 5.39 (br s, H-4), 4.66 (dd, J=5.5, 13 Hz, H-5), 5.37 (dd, J=12, 13 Hz, H-6), 4.24 (dd, J=5.5, 12 Hz, H-6) (glucose). **1b**: δ 7.15 (s, galloyl), 7.26, 6.88, 6.85 (each s, HHDP and DHHDP), 6.24 (d, J=1.5 Hz, DHHDP H-3″), 4.96 (d, J=1.5 Hz, DHHDP H-1″), 6.25 (br s, H-1), 5.04 (br d, J=3 Hz, H-2), 6.03 (br s, H-3), 5.45 (br s, H-4), 4.68 (dd, J=5.5, 12 Hz, H-5), 5.40 (t, J=12 Hz, H-6), 4.16 (dd, J=5.5, 12 Hz, H-6) (glucose). These data are consistent with the proposed structure.[4]

Antidesmin A (4) A pale yellow amorphous powder, $[\alpha]_D$ −76° (c=1.0, MeOH). *Anal.* Calcd for $C_{82}H_{56}O_{53}\cdot 12H_2O$: C, 46.78; H, 3.83. Found: C, 46.82; H, 3.72. UV λ_{max}^{MeOH} nm (log ε): 218 (5.20), 276 (4.85). FAB-MS m/z: 1911 $(M+Na)^+$. ^{1}H-NMR (acetone-d_6–D_2O) δ: 7.26, 7.20 (each s, 1H in total), 7.18, 7.17 (each s, 2H in total), 7.15 (1H, s), 7.14, 7.09 (each s, 1H in total), 7.13, 7.12 (each s, 2H in total), 7.03, 7.02 (each s, 2H in total), 6.860, 6.857 (each s, 1H in total), 6.84, 6.27 (each s, 1H in total) (aromatic), 6.56 (s), 6.25 (d, J=1.5 Hz, 1H in total, DHHDP H-3″), 5.14 (s), 4.93 (d, J=1.5 Hz, 1H in total, DHHDP H-1″), glucose protons, see Table I. ^{13}C-NMR (acetone-d_6–D_2O) δ: 46.0, 51.8 (C-1″), 147.6, 154.3 (C-2″), 125.0, 128.7 (C-3″), 191.8, 194.6 (C-4″), 92.8, 96.1 (C-5″), 92.3, 108.8 (C-6″) (DHHDP), 105.1, 105.4, 109.2, 109.3, 110.3, 110.4, 110.5, 110.7, 113.2, 113.3, 113.5, 113.6, 115.6, 115.8, 116.3, 116.58, 116.64, 116.77, 116.81, 116.9, 119.2, 119.6, 119.7, 119.9, 120.0, 120.1, 123.8, 123.9, 124.60, 124.62, 125.0, 125.3, 125.8, 136.7, 136.91, 136.97, 137.07, 137.15, 137.4, 137.7, 137.8, 138.9, 139.4, 139.8, 139.9, 140.36, 140.39, 140.5, 143.21, 143.25, 144.4, 144.5, 144.6, 144.9, 145.5, 145.6, 145.75, 145.83, 146.5, 146.6, 147.0, 149.0 (aromatic), 164.3, 164.4, 164.6, 164.9, 165.0, 165.3, 165.6, 165.8, 165.97, 165.99, 166.32, 166.34, 166.4, 168.2, 168.3 (ester carbonyl), glucose carbons, see Table II.

Acid Hydrolysis of Antidesmin A (4) A solution of **4** (5 mg) in 5% H_2SO_4 (2 ml) was heated in a boiling-water bath for 6 h. After cooling, the reaction mixture was extracted with EtOAc. The EtOAc extract was analyzed by HPLC [reversed-phase; system 1; flow rate, 1.3 ml/min] to show three peaks identical with those of authentic valoneic acid dilactone (**12**, t_R 2.3 min), gallic acid (**10**, t_R 4.6 min) and ellagic acid (**11**, t_R 6.4 min). The sugar component in the aqueous layer remaining after EtOAc extraction was identified as glucose by gas liquid chromatography (GLC) (G-250; column temperature, 180 °C) of the trimethylsilyl derivative.

Preparation of the Phenazine Derivative (5) from Antidesmin A (4) A solution of *o*-phenylenediamine (20 mg) in 15% AcOH (6 ml) was added to a solution of **4** (100 mg) in MeOH (2 ml) and the reaction mixture was left standing overnight at room temperature. The residue obtained after evaporation of the solvent and drying *in vacuo* was dissolved in a minimum amount of tetrahydrofuran (THF). The solution was added dropwise to an excess of ether under stirring, and the orange precipitate was collected by filtration. Reprecipitation from MeOH–$CHCl_3$ gave the phenazine derivative (**5**) (95 mg) as an orange amorphous powder, $[\alpha]_D$ −29° (c=0.3, THF). *Anal.* Calcd for $C_{88}H_{58}O_{50}N_2\cdot 9H_2O$: C, 50.20; H, 3.64; N, 1.33. Found: C, 50.37; H, 3.66; N, 1.02. UV λ_{max}^{MeOH} nm (log ε): 217 (5.08), 278 (4.88). FAB-MS m/z: 1943 $(M+H)^+$. ^{1}H-NMR (acetone-d_6–D_2O) δ: 8.31, 8.22 (each 1H, dd, J=1.5, 8.5 Hz), 8.29 (1H, s), 7.98 (2H, m), 7.47 (1H, s) (phenylphenazine), 7.09, 7.03, 6.94 (each 2H, s, galloyl), 7.16, 6.97, 6.84, 6.82, 6.30 (each 1H, s, HHDP and valoneoyl), glucose protons, see Table I. ^{13}C-NMR (acetone-d_6–D_2O) δ: 105.7, 109.2, 109.3, 109.6, 109.9, 110.2, 110.4, 110.5, 113.1, 113.5, 116.0, 116.30, 116.31, 116.35, 116.6, 117.0, 119.6, 119.7, 119.8, 120.0, 120.1, 123.8, 124.6, 124.9, 125.7, 130.1, 130.2, 132.29, 132.33, 135.9, 136.70, 136.74, 137.00, 137.04, 137.3, 138.9, 139.3, 139.4, 139.5, 139.6, 140.4, 140,8, 142.8, 143.4, 144.5, 144.6, 144.80, 144.84, 145.0, 145.1, 145.2, 145.6, 145.76, 145.82, 145.92, 146.6, 152.1 (aromatic), 164.3, 164.8, 166.2, 166.47, 166.51, 166.61, 166.67, 167.8, 168.1, 168.3 (ester carbonyl), glucose carbons, see Table II.

Partial Hydrolysis of 5 An aqueous suspension (10 ml) of **5** (150 mg) was heated in a water bath (80 °C) for 1 h. After cooling and filtration, the filtrate was passed through a column of Diaion HP-20. Elution with aqueous MeOH gave a partial hydrolyzate (**6**) (107 mg) as a tan amorphous powder, $[\alpha]_D$ −49° (c=1.0, MeOH). *Anal.* Calcd for $C_{68}H_{50}O_{44}\cdot 5H_2O$: C, 49.17; H, 3.64. Found: C, 49.10; H, 4.01. UV λ_{max}^{MeOH} nm (log ε): 218 (5.09), 274 (4.78). FAB-MS m/z: 1593 $(M+Na)^+$. ^{1}H-NMR (acetone-d_6–D_2O) δ: 7.12, 7.09, 7.03 (each 2H, s, galloyl), 7.14 (1H, s), 6.85 (2H, s), 6.82, 6.28 (each 1H, s) (HHDP, valoneoyl), 6.33 (br s, H-1′), 6.18 (d, J=3 Hz, H-1), 5.61 (t, J=8 Hz, H-3), 5.55 (dd, J=3, 8 Hz, H-2), 5.14 (dd, J=3, 8 Hz, H-4), 4.83 (t, J=11 Hz, H-6′), 4.80 (br s, H-3′), 4.73 (t, J=12 Hz, H-6), 4.47 (ddd, J=3, 5.5, 12 Hz, H-5), 4.41 (dd, J=5.5, 12 Hz, H-6), 4.39 (H-5′, overlapped with H-6 and H-4′ signals), 4.38 (br s, H-4′), 4.03 (br s, H-2′), 4.00 (dd, J=8, 11 Hz, H-6′) (glucose). ^{13}C-NMR (acetone-d_6–D_2O) δ: 62.0 (C-4′), 64.4 (C-6′), 64.9 (C-6), 68.8 (C-2′), 69.4 (C-3), 70.6 (C-3′), 71.3 (C-2, 4), 75.3, 75.4 (C-5, 5′), 94.3 (C-1′), 94.7 (C-1) (glucose), 105.2 [valoneoyl (Val) C-3′], 109.2, 109.4 (HHDP C-3, 3′), 109.9 (Val C-3), 110.1 (Val C-6″), 110.2 110.4, 110.5 [each galloyl (Gall) C-2, 6], 113.6 (Val C-1″), 115.9, 116.4 (HHDP C-1, 1′), 116.4 (Val C-1), 117.2 (Val C-1′), 119.5, 120.0, 120.5 (Gall C-1), 124.6, 124.9, 125.1, 125.6 (HHDP C-2, 2′, Val C-2, 2′), 136.7, 136.8 (HHDP C-5, 5′), 136.9 (Val C-2″), 137.1 (Val C-5′), 137.2 (Val C-5), 139.41, 139.43, 139.5 (Gall C-4), 140.4 (Val C-3″), 140.7 (Val C-4″), 143.3 (Val C-5″), 144.5 (Val C-6), 144.5, 144.6 (HHDP C-4, 4′, 6, 6′), 145.0 (Val C-4), 145.5 (Val C-6′), 145.7, 145.8 (Gall C-3, 5), 146.6 (Val C-4′) (aromatic), 164.6, 165.5, 166.2, 166.4, 166.5, 167.4, 168.4, 168.5 (ester carbonyl).

Methylation of 5 Followed by Methanolysis A mixture of **5** (50 mg), dimethyl sulfate (250 μl) and anhydrous potassium carbonate (250 mg) in dry acetone (10 ml) was stirred overnight at room temperature and then refluxed for 7 h. After removal of potassium carbonate by filtration followed by evaporation of the solvent, the residue was directly subjected to methanolysis with 1% NaOMe in MeOH (5 ml) at room temperature overnight. After acidification with AcOH and evaporation, the residue was submitted to preparative TLC to give methyl tri-*O*-methylgallate (**10a**, 9.3 mg), dimethyl (*S*)-4,4′,5,5′,6,6′-hexamethoxydiphenate [13, 6.1 mg, $[\alpha]_D$ −32° (c=1.0, acetone)], methyl (*R*)-4-methoxy-3-(4,5,6-trimethoxy-2-methoxycarbonylphenyl)phenazine-2-carboxylate [**15**, 2.3 mg, $[\alpha]_D$ +13° (c=1.0, acetone)] and trimethyl (*R*)-octa-*O*-methylvaloneate [**14**, 5.0 mg, $[\alpha]_D$ +18° (c=1.0, acetone)].

Enzymic Hydrolysis of 6 An aqueous solution of **6** (70 mg/10 ml) was incubated at 37°C with tannase, which was prepared from *Aspergillus niger*,[12] and the progress of the reaction was monitored by HPLC. After disappearance of the starting material, the reaction mixture was evaporated and the residue was dissolved in EtOH. Insoluble material was removed by centrifugation and the supernatant was chromatographed over Toyopearl HW-40 (superfine) using EtOH–H_2O (6:4)→EtOH–H_2O (7:3) as eluants to give two partial hydrolyzates, **8** (13.3 mg) and **9** (5.1 mg) together with gallic acid (**10**, 9.2 mg), valoneic acid dilactone (**12**, 1.7 mg), and a mixture (5.9 mg) of ellagic acid (**11**) and oenothein C (**7**). Oenothein C (**7**) (2.5 mg) was separated from **11** (precipitate, 3.3 mg) by centrifugation of an aqueous suspension of the mixture. Hydrolyzate **8** was obtained as a tan amorphous powder, $[\alpha]_D$ +70° [c=1.0, MeOH–THF (1:1)]. UV λ_{max}^{MeOH} nm (log ε): 217 (4.66), 263 (4.59), 358 (3.81). ^{1}H-NMR (acetone-d_6–D_2O) δ: 7.58, 7.23, 7.10 (each 1H, s, Val), 7.01 (2H, s, Gall), 6.81, 6.77 (each 1H, s, HHDP), 5.80 (d, J=2.5 Hz, H-1), 5.17 (dd, J=2.5, 5 Hz, H-2), 5.10 (dd, J=5, 7 Hz, H-3), 4.52 (dd, J=8, 11 Hz, H-6), 4.10—4.00 (H-4, 5, 6) (glucose). Hydrolyzate **9** was obtained as a tan amorphous powder, $[\alpha]_D$ −11° (c=1.0, MeOH). UV λ_{max}^{MeOH} nm (log ε): 217 (4.89), 265 (4.74), 360 (sh) (3.88). FAB-MS m/z: 1261 $(M+Na)^+$. ^{1}H-NMR (acetone-d_6–D_2O) δ: 7.58, 7.21 (each 1H, s, Val), 7.06 (3H, s, galloyl and Val), 6.93 (2H, s, Gall), 6.77, 6.62 (each 1H, s, HHDP), 5.90 (d, J=3 Hz, H-1), 5.63 (dd, J=7, 8 Hz, H-3), 5.49 (dd, J=3, 8 Hz, H-2), 5.11 (dd, J=3, 7 Hz, H-4), 4.66 (t, J=12 Hz, H-6), 4.43 (ddd, J=3, 5, 12 Hz, H-5), 4.34 (dd, J=5, 12 Hz, H-6) (glucose).

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