Tannins and Related Polyphenols of Rosaceous Medicinal Plants. XII.[1] Roshenins A—E, Dimeric Hydrolyzable Tannins from *Rosa henryi* Boul.

Takashi Yoshida,[a] Wei-Sheng Feng,[b] and Takuo Okuda*,[a]

Faculty of Pharmaceutical Sciences, Okayama University,[a] Tsushima, Okayama 700, Japan and Henan College of Traditional Chinese Medicine,[b] Zhengzhou 450003, China. *Received January 16, 1992*

Five new hydrolyzable tannin dimers, roshenins A—E, and eight known tannins and related polyphenols [(+)-catechin, (−)-epicatechin, procyanidins B-3 and B-4, sanguisorbic acid dilactone, sanguiins H-2, H-6 and lambertianin A], have been isolated from the root of *Rosa henryi* Boul. The structures of roshenins A—E (9—12, 19), which have a sanguisorboyl group as a linking unit between monomeric components, were established on the basis of spectral and chemical evidence.

Keywords *Rosa henryi*; Rosaceae; ellagitannin; tannin; roshenin A; roshenin B; roshenin C; roshenin D; roshenin E

Rosa henryi Boul. (Rosaceae) is a shrub widely grown in China, and its dried root and fruit have been used as a Chinese traditional medicine for treatment of diarrhea and enuresis, for example, as diurnal enuresis for children and old persons.[2] In our continuing study on the polyphenols of Rosaceous medicinal plants, we have isolated, along with catechin derivatives, five new ellagitannins named roshenins A—E, and three known hydrolyzable tannins, all having a sanguisorboyl group[3] in the molecule.

The aqueous acetone homogenate of the dried root of *R. henryi*, collected in Henan Province, China, was concentrated and extracted with ether, ethyl acetate and 1-butanol, successively. Chromatographic separation of the ethyl acetate extract afforded (+)-catechin (**1**), (−)-epicatechin (**2**), procyanidins B-3 (**3**) and B-4 (**4**),[4] sanguisorbic acid dilactone (**5**)[3] and sanguiin H-2 (**6**).[3,5] The butanol extract was chromatographed over a Diaion HP-20 column, and subsequently purified by column chromatographies over Toyopearl HW-40 and MCI-gel CHP 20P, to yield sanguiins H-2 (**6**) (monomer), H-6 (**8**) (dimer)[5] and lambertianin A (**7**) (trimer),[6] and five new tannins, roshenins A (**9**), B (**10**), C (**11**), D (**12**) and E (**19**).

All of the new polyphenols have been shown to be ellagitannin dimers composed of gallic acid, hexahydroxydiphenic acid, sanguisorbic acid and glucose, by acid hydrolysis, which commonly yielded gallic acid (**13**), ellagic acid (**14**), sanguisorbic acid dilactone (**5**), and glucose, and also by their retention times, which were similar to that of **8** in high-performance liquid chromatography (HPLC; normal phase).[7]

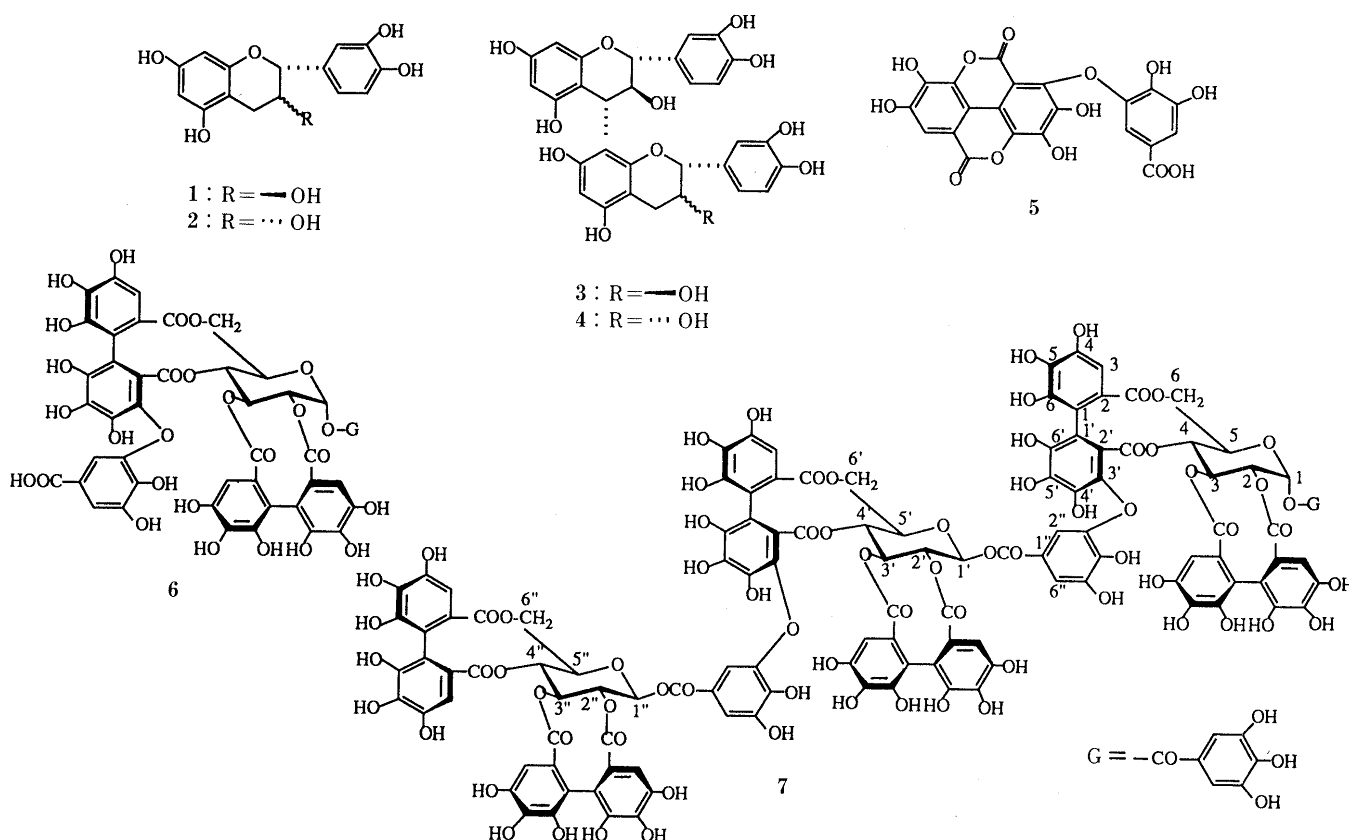

Chart 1

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The ^{1}H–^{1}H shift correlation (COSY) spectra (500 MHz, acetone-d_6 + D_2O) of roshenins A, B, C and E revealed that these tannins commonly have two glucose cores with *C1* conformation, each of which has the hexahydroxydiphenoyl (HHDP) or HHDP part of the sanguisorboyl group at O-4/O-6, as indicated by a large difference ($\Delta\delta > 1.5$ ppm)[8,9] between the chemical shifts of geminal protons of the C-6 methylene group (Table I). These tannins were therefore regarded as dimers structurally related to sanguiin H-6 (**8**).

Roshenin A (**9**), $[\alpha]_D -39°$ (MeOH), showed in the fast-atom bombardment mass spectrum (FAB-MS), the $(M+Na)^+$ ion peak at *m/z* 2061, corresponding to the molecular formula $C_{89}H_{58}O_{57}$. Its proton nuclear magnetic resonance (^{1}H-NMR) spectrum exhibited a 2H singlet (δ 7.09), six 1H singlets (δ 6.79, 6.77, 6.37, 6.33, 6.29, 6.21) and four *meta*-coupled doublets (J = 2 Hz) (δ 7.20, 7.16, 7.11, 7.04). These signals can be accounted for by the presence of a galloyl group and two HHDP and two sanguisorboyl groups in the molecule of **9**. The chemical shifts of the glucose proton signals implied that both glucose cores are fully acylated (Table I). The presence of both α- and β-glycosidic linkages in **9** was indicated by the coupling constants (J = 3.5 and 8.5 Hz) of the anomeric proton signals. Based on these spectral data, taking the co-occurrence of **7** and **8** in the same plant into consideration, roshenin A was presumed to be formulated as **9**. This assumption was substantiated by the finding that roshenin A is identical with the hydrolyzate **9**[6] produced by partial hydrolysis of lambertianin A (**7**) in boiling water. The structure (**9**) of roshenin A, including the orientation of the sanguisorboyl groups and the absolute configuration of all the chiral HHDP and sanguisorboyl groups, was thus established.

Roshenin B (**10**), $[\alpha]_D -43°$ (MeOH), was obtained as

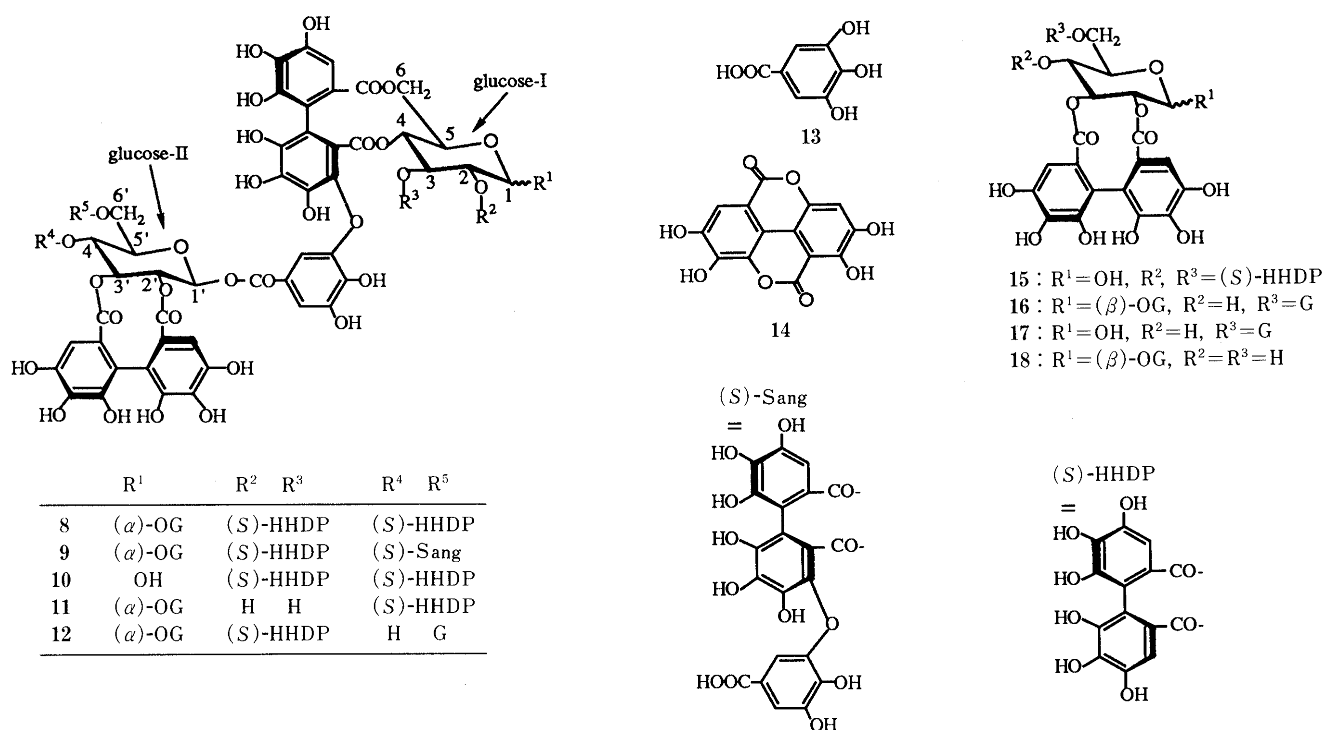

Chart 2

Table I. ^{1}H-NMR Data for the Glucose Moieties of Sanguiin H-6 (**8**) and Roshenins A—E (**9**—**12** and **19**) (500 MHz, Acetone-d_6 + D_2O, J in Hz)

	8	9	10 α-Anomer	10 β-Anomer	11	12	19 α-Anomer	19 β-Anomer
H-1	6.51 d (4)	6.49 d (3.5)	5.25 d (3.5)	4.83 d (8.5)	6.21 d (3.5)	6.42 d (4)	6.20 d (8.5)	6.23 d (8.5)
H-2	5.28 dd (4, 9.5)	5.27 dd (3.5, 9)	5.22 dd (3.5, 9.5)	5.21 dd (8.5, 9.5)	3.75 dd (3.5, 9.5)	5.20 dd (4, 10)	5.18 br t (9.5)	5.20 br t (9.5)
H-3	5.11 br t (10)	5.14 br t (9)	5.41 t (9.5)	5.40 t (9.5)	3.73 t (9.5)	5.11 t (10)	5.40 t (9.5)	
H-4	5.01 t (10)	5.01 t (9)	5.13 t (9.5)	5.12 t (9.5)	4.64 t (9.5)	4.88 t (10)	5.10 t (9.5)	5.11 t (9.5)
H-5	4.30 m	4.31 m	4.44 m	4.31 m	3.95 m	4.11 m	4.44 m	
H-6	3.88 d (13)	3.81 d (13)	3.88 d (13)	3.85 d (13)	3.68 d (13)	3.71 d (13)	3.87 d (13)	3.84 d (13)
	5.55 dd (6.5, 13)	5.49 dd (6.5, 13)	5.64 dd (6.5, 13)	5.70 dd (6.5, 13)	5.20 dd (6.5, 13)	5.36 dd (6.5, 13)	5.28 dd (6.5, 13)	
H-1'	6.15 d (8.5)	5.81 d (8.5)	6.21 d (8.5)	6.25 d (8.5)	6.10 d (8.5)	6.15 d (8.5)	5.33 d (4)	4.59 d (8)
H-2'	5.17 t (8.5)	5.03 dd (8.5, 9.5)	4.96 dd (8.5, 9.5)	4.74 t (8.5)	5.12 dd (8.5, 9.5)	5.04 dd (8.5, 9.5)	4.75 dd (4, 10)	4.89 dd (8, 10)
H-3'	5.35 dd (8.5, 10)	4.76 t (9.5)	4.96 m	4.69 br t (9)	5.06 t (9.5)	5.19 t (9.5)	3.75 t (10)	
H-4'	5.09 t (10)	4.85 t (9.5)	4.89[a] t (9.5)	4.88[a] t (9)	5.34 t (9.5)	4.00 t (9.5)	4.68 t (10)	4.71 t (10)
H-5'	4.34 m	3.79 m	4.34 m		4.34 m	3.98 m	4.08 m	
H-6'	3.81 d (13)	3.88 d (13)	3.85[b] d (13)	3.88[b] d (13)	3.76 d (13)	4.47 s	3.74 d (13)	3.79 d (13)
	5.22 dd (6.5, 13)	5.52 dd (6.5, 13)	5.31[c] dd (6.5, 13)	5.33[c] dd (6.5, 13)	5.24 dd (6.5, 13)	4.47 s	5.34 dd (6.5, 13)	

a—*c*) Assignments of the signals with the same superscript letter may be interchangeable.

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an off-white amorphous powder. Its ^{1}H-NMR spectrum showed dual signals attributable to anomerization in the sugar moiety for most of the protons, among which were two pairs of *meta*-coupled doublets ($J=2$ Hz) and seven pairs of 1H signlets assignable to a sanguisorboyl group and three HHDP groups (see Experimental). The absolute configuration of all the chiral HHDP and sanguisorboyl groups in **10** was determined to be *S* from the circular dichroism (CD) spectrum, which exhibits a strong positive Cotton effect at 236 nm and a negative one at 261 nm.[10] In the ^{1}H-NMR spectrum of **10**, the anomeric proton signals were observed at δ 6.21, 6.25 (each d, $J=8.5$ Hz, 1H in total) and at δ 5.44 (d, $J=3.5$ Hz), 5.03 (d, $J=8.5$ Hz), implying acylation at only one of the anomeric centers with a β-oriented group. Based on these spectral data and the FAB-MS data [*m/z* 1741 $(M+Na)^+$] consistent with the molecular formula $C_{75}H_{50}O_{48}$, the most plausible structure (**10**) was deduced for roshenin B. This structure was confirmed by degalloylation of sanguiin H-6 (**8**) with tannase,[11] yielding roshenin B.

Roshenin C (**11**), $[\alpha]_D$ $-55°$ (MeOH), showed the $(M+Na)^+$ ion peak at *m/z* 1591 in the FAB-MS. It is a dimer composed of a galloyl, a sanguisorboyl and two HHDP groups, as revealed by a 2H singlet (δ 7.10), five 1H singlets (δ 6.66, 6.65, 6.49, 6.41, 6.30) and two meta-coupled doublets [δ 7.33, 7.00 (each $J=2$ Hz)], in the aromatic region of the ^{1}H-NMR spectrum. The (*S*)-configuration of the HHDP and sanguisorboyl groups was evidenced by the similarity of the CD spectrum to that of **10**. The H-2 and H-3 signals of a glucose core, which has an α-oriented acyl group at the anomeric center, are shifted remarkably upfield [δ 3.75 (dd, $J=3.5$, 9.5 Hz), 3.73 (t, $J=9.5$ Hz)] from those of the other glucose core (Table I), indicating that the C-2 and C-3 hydroxyl groups are free. Upon partial hydrolysis in a boiling-water both, roshenin C yielded ellagic acid (**14**), sanguisorbic acid dilactone (**5**) and pedunculagin (**15**).[12] The orientation of the sanguisorboyl group in **11** was presumed to be the same as that in **6** and **7**, by analogy based on the pattern of aromatic proton signals. Roshenin C was thus formulated as **11**.

Roshenin D (**12**), $[\alpha]_D+12°$ (MeOH), showed the $(M+Na)^+$ ion peak at *m/z* 1743 in the FAB-MS, corresponding to the molecular formula $C_{75}H_{52}O_{48}$. The ^{1}H-NMR spectrum exhibited two 2H singlets (δ 7.12, 7.11), five 1H singlets (δ 6.65, 6.60, 6.40, 6.35, 6.15) and two doublets [δ 7.21, 7.02 (each 1H, $J=2$ Hz)], indicating the presence of a sanguisorboyl, two galloyl and two HHDP groups in the molecule. One (glucose-I) of the glucose cores of **12**, which has an α-glycosidic linkage [δ 6.42 (d, $J=4$ Hz, H-1)], was shown to be fully acylated by the chemical shifts of its proton signals (Table I). The other glucose core (glucose-II) having a β-glycosidic linkage [δ 6.15 (d, $J=8.5$ Hz, H-1′)] has a free hydroxyl group at C-4′, as indicated by an upfield shift of the H-4′ signal [δ 4.00 (t, $J=9.5$ Hz)] relative to the corresponding signal [δ 4.88 (t, $J=10$ Hz)] of glucose-I. The presence of the biphenyl moiety at O-4/O-6 was evidenced by a large difference ($\Delta\delta$ 1.65 ppm) between the chemical shifts of geminal protons at C-6, while the H-6′ signal appears at δ 4.47 as a 2H singlet, indicating the presence of a galloyl group at O-6′. The glucose carbon resonances in the ^{13}C-NMR spectrum of **12** are in agreement with those of nobotanin D (**16**) (1,6-di-*O*-galloyl-2,3-*O*-(*S*)-

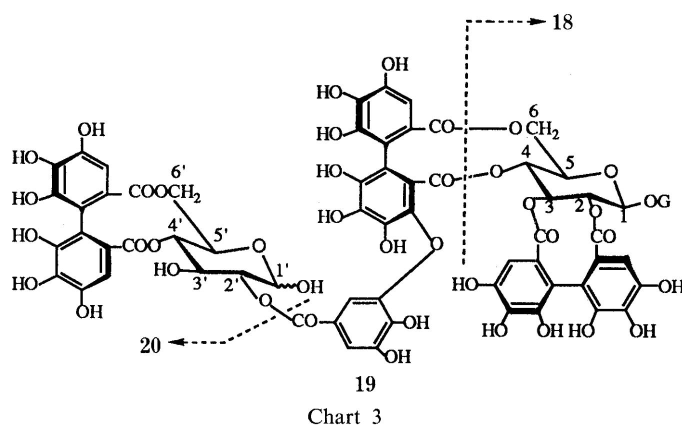

Chart 3

hexahydroxydiphenolyl-β-D-glucose)[13,14] and sanguiin H-2 (**6**).[5,14] These allocations of the acyl groups of **12** were substantiated by partial hydrolysis of **12** in boiling water to give sanguiin H-2 (**6**) and 6-*O*-galloyl-2,3-*O*-(*S*)-hexahydroxydiphenoyl-D-glucose (**17**). Consequently, the structure of roshenin D was established to be **12**.

The structure (**19**) of roshenin E was determined as follows. The molecular formula of **19** was determined to be $C_{68}H_{48}O_{44}$ from the FAB-MS [*m/z* 1591 $(M+Na)^+$] and NMR spectral data (*vide infra*). The presence of a galloyl, a sanguisorboyl and two HHDP groups was indicated in the ^{1}H-NMR spectrum (see Experimental) by a 2H singlet, five 1H singlets and two *meta*-coupled doublets, appearing as dual peaks due to formation of an equilibrium mixture of α- and β-anomers. The anomeric proton signals are observed at δ 6.20, 6.23 (each d, $J=8.5$ Hz), 5.33 (d, $J=4$ Hz), 4.59 (d, $J=8$ Hz). The H-3 signal of a glucose core, which has a free anomeric hydroxyl group, appears at δ 3.75 (t, $J=10$ Hz), indicating that the C-3 position of this glucose core is also unacylated. A significant upfield shift of the anomeric proton signal (δ 4.59) of the β-anomer is analogous to that of ellagitannin oligomers such as camelliin A,[15] cornusiin A[16] and others,[9] having the galloyl part of a valoneoyl group at O-2 of *C1* glucopyranose. Partial hydrolysis of **19** in boiling water gave isostrictinin (**18**)[12] and 4,6-*O*-hexahydroxydiphenoyl-D-glucose (**20**).[17] The (*S*)-configuration of the sanguisorboyl group and of HHDP groups in **19** was determined by CD spectral analogy to **10**—**12**. Based on these data, the structure of roshenin E was concluded to be represented by the formula **19**, in which the orientation of the sanguisorboyl group may be reversed.

The oligomeric hydrolyzable tannins (sanguiin-type) possessing the sanguisorboyl group as a linking unit between monomeric constituents have hitherto been found only in the *Sanguisorba* and *Rubus* species.[1] This paper is the first report of the isolation of oligomers of this type from a *Rosa* species.

Experimental

General ^{1}H-(500 MHz) and ^{13}C-NMR (126 MHz) spectra were measured on a Varian VXR 500 instrument and chemical shifts are given in δ (ppm) values relative to acetone-d_6 (2.04 ppm for ^{1}H and 29.8 ppm for ^{13}C). HPLC was conducted on Superspher Si 60 (4 mm × 119 mm) and LiChrosphere RP-18 (4 mm × 250 mm) columns, using the following solvent systems: (A) hexane–MeOH–THF–HCOOH (60 : 45 : 15 : 1) and oxalic acid (500 mg/1.2 l), (B) 0.05 M phosphate buffer–EtOH–EtOAc (85 : 10 : 5), (C) 0.05 M phosphate buffer–CH_3CN (85 : 15), (D) 0.05 M phosphate buffer–EtOH–EtOAc (87 : 8 : 5), (E) 0.05 M phosphate buffer–CH_3CN (87 : 13), (F) 0.05 M phosphate buffer–EtOH–EtOAc (83 : 12 : 5).

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Column chromatography was carried out on Toyopeal HW-40 (coarse and fine grades) (Toso), Diaion HP-20 and MCI-gel CHP-20P (Mitsubishi Chemical Industry Co., Ltd.).

Isolation of Tannins The dried roots (700 g) of *R. henryi*, collected in XiXia county, Henan Province, China, in June 1991, were chipped and homogenized in 70% aqueous acetone (1 l × 3). The filtrate was concentrated to *ca.* 0.5 l, and extracted with Et_2O, EtOAc and 1-butanol, successively. A part (5 g) of the EtOAc extract (10.7 g) was chromatographed over Toyopeal HW-40 (coarse) (2.2 × 42 cm) developing with aqueous MeOH (30% MeOH→40%→50%→60%→70%) and MeOH–H_2O–acetone (7 : 2 : 1) to yield (+)-catechin (**1**) (113 mg), (−)-epicatechin (**2**) (142 mg), procyanidins B-3 (**3**) (63 mg), B-4 (**4**) (382 mg), sanguisorbic acid dilactone (**5**) (113 mg), and sanguiin H-2 (**6**) (117 mg). A part (11 g) of the butanol extract (12.7 g) was first fractionated by column chromatography over Diaion HP-20 (6.5 × 40 cm) with water and aqueous MeOH (10% MeOH→60%). The 60% MeOH eluate (3.9 g) was further chromatographed over Toyopearl HW-40 (coarse) (2.2 × 42 cm) developing with 30% MeOH→40%→50%→60%→70% MeOH→MeOH–H_2O–acetone (7 : 2 : 1)→MeOH–H_2O–acetone (6 : 2 : 2) to afford sanguiin H-2 (**6**) (100 mg), roshenins A (**9**) (48 mg), B (**10**) (54 mg), C (**11**) (90 mg), D (**12**) (60 mg), E (**19**) (65 mg), sanguiin H-6 (**8**) (150 mg) and lambertianin A (**7**) (347 mg).

Lambertianin A (7) An off-white amorphous powder, $[\alpha]_D$ −5° (c = 1.0, MeOH). UV λ_{max}^{MeOH} nm (log ε): 223 (4.41), 263 (4.17). ^{1}H-NMR (acetone-d_6 + D_2O) δ: 7.12 [2H, s, galloyl (Gal)], 6.19, 6.21 (each 1H, br s), 6.33, 6.34, 6.37, 6.52, 6.53, 6.67, 6.75, 6.84 (each 1H, s), 7.03, 7.10, 7.11, 7.21 (each 1H, d, J = 2 Hz) [HHDP and sanguisorboyl (Sang)], 6.51 [d, J = 4 Hz, glucose (Glc) H-1], 5.28 (dd, J = 4, 9.5 Hz, Glc H-2), 5.18 (br d, J = 9.5 Hz, Glc H-3), 4.97 (t, J = 9.5 Hz, Glc H-4), 4.28 (m, Glc H-5), 3.86 (d, J = 13 Hz, H-6), 5.57 (dd, J = 6.5, 13 Hz, H-6), 6.00 (d, J = 8 Hz, Glc H-1′), 5.08 (dd, J = 8, 9.5 Hz, H-2′), 5.00 (br t, J = 10 Hz, Glc H-3′), 4.93 (t, J = 10 Hz, Glc H-4′), 4.07 (m, Glc H-5′), 3.89 (d, J = 13 Hz, Glc H-6′), 5.41 (dd, J = 6.5, 13 Hz, Glc H-6′), 6.15 (d, J = 8 Hz, Glc H-1″), 5.15 (t, J = 8 Hz, Glc H-2″), 5.41 (dd, J = 8, 9.5 Hz, Glc H-3″), 5.10 (t, J = 9.5 Hz, H-4″), 4.43 (dd, J = 6.5, 9.5 Hz, Glc H-5″), 3.90 (d, J = 13 Hz, Glc H-6″), 5.31 (dd, J = 6.5, 13 Hz, Glc H-6″), ^{13}C-NMR (acetone-d_6 + D_2O) δ: 90.61 (Glc C-1), 92.39 (Glc C-1′), 92.31 (Glc C-1″), 73.85 (Glc C-2), 75.67 (Glc C-2′), 75.90 (Glc C-2″), 75.24 (Glc C-3), 76.79 (Glc C-3′), 77.26 (Glc C-3″), 69.08, 69.24, 69.31 (Glc C-4, C-4′, C-4″), 71.21 (Glc C-5), 73.85 (Glc C-5′), 73.26 (Glc C-5″), 62.79, 62.97, 63.08 (Glc C-6, C-6′, C-6″) 107.09, 107.33, 107 99, 108.35 (each 2C), 107.48, 108.25 (HHDP C-3, C-3′, Sang C-3), 110.21 (2C, Gal C-2, C-6), 109.96, 110.80, 112.18, 112.51 (Sang C-2″, C-6″), 165.02, 165.19, 165.39, 165.91, 166.02, 167.80, 167.89, 167.93, 168.07, 168.13 (2C), 168.20, 168.39, 168.49, 169.36 (ester carbonyl).

Sanguiin H-6 (8) An off-white amorphous powder, $[\alpha]_D$ +66° (c = 1.0, acetone). ^{1}H-NMR (acetone-d_6 + D_2O) δ: 6.23 (1H, br s), 6.29, 6.37, 6.45, 6.49, 6.75, 6.76 (each 1H, s), 7.24 (1H, d, J = 2 Hz), 7.09 (1H, overlaped with Gal-H) (HHDP and Sang), 7.09 (2H, s, Gal), glucose protons, see Table I. ^{13}C-NMR (acetone-d_6 + D_2O) δ: 90.63 (Glc C-1), 73.77 (Glc C-2), 75.16 (Glc C-3), 69.17 (Glc G-4), 71.11 (Glc C-5), 63.00 (Glc C-6), 92.44 (Glc C-1′), 75.80 (Glc C-2′), 77.23 (Glc C-3′), 68.91 (Glc C-4′), 73.39 (Glc C-5′), 62.73 (Glc C-6′), 107.09, 107.13, 107.39, 107.44, 108.00, 108.23, 108.26 (HHDP C-3, C-3′, Sang C-3), 110.12 (2C, Gal C-2, C-6), 110.12, 112,62 (Sand C-2″, C-6″), 165.06, 165.37, 165.86, 167.85, 167.98, 168.15. 168.38, 169.30 (ester carbonyl).

Roshenin A (9) An off-white amorphous powder, $[\alpha]_D$ −39° (c = 1.0, MeOH). *Anal.* Calcd for $C_{89}H_{58}O_{57} \cdot 14H_2O$: C, 46.64; H, 3.76%. Found: C, 46.94; H, 4.06. FAB-MS m/z: 2061 $(M+Na)^+$. UV λ_{max}^{MeOH} nm (log ε): 220 (4.56), 265 (4.20). ^{13}C-NMR (acetone-d_6 + D_2O) δ: 90.64 (Glc C-1), 73.96 (Glc C-2), 75.17 (Glc C-3), 69.31 (Glc C-4), 71.00 (Glc C-5), 63.06 (Glc C-6), 92.36 (Glc C-1′), 75.63 (Glc C-2′), 76.68 (Glc C-3′), 69.19 (Glc C-4′), 73.77 (Glc C-5′), 62.70 (Glc C-6′), 107.07, 107.30, 108.13, 108.26, 107.95 (2C) (HHDP C-3, C-3′, Sang C-3), 110.10 (2C, Gal C-2, C-6), 109.90, 110.42, 111.93, 112.64 (Sang C-2″, C-6″), 165.10, 165.26, 166.03 (2C), 167.92, 167.99, 168.19, 168.23 (2C), 168.47, 168.79 (ester carbonyl). ^{1}H-NMR, see Table I.

Acid Hydrolysis of Roshenins A—E A solution of roshenin A (**9**) (1 mg) in 1% H_2SO_4 (1 ml) was heated in a boiling-water bath for 5 h. The reaction mixture was extracted with EtOAc. A sirupy residue obtained from the aqueous layer after neutralization with Amberlite IR-120 (OH form) was trimethylsilylated and subjected to gas-liquid chromatography to detect glucose. The EtOAc extract was analyzed by HPLC (reversed-phase; solvent B) to detect peaks identical with those of anthentic gallic acid (**13**) (t_R 3.0 min), sanguisorbic acid dilactone (**5**) (t_R 7.0 min) and ellagic acid (**14**) (t_R 10.2 min). Roshenins B (**10**), C (**11**), D (**12**) and E (**19**) were similarly hydrolyzed, with the same results.

Partial Hydrolysis of Lambertianin A (7) to Roshenin A (9) A solution of **7** (30 mg) in H_2O (30 ml) was heated in a boilling-water bath for 6 h, and the reaction mixture was concentrated and chromatographed over an MCI-gel CHP-20P column developing with aqueous EtOH. The 20% EtOH eluate gave a hydrolyzate (9.4 mg), which was shown to be identical with roshenin A (**9**) by reversed-phase HPLC (solvent B) (t_R 5.5 min) and ^{1}H-NMR. The formation of sanguiin H-2 (**6**) was also confirmed by HPLC (t_R 6.9 min).

Roshenin B (10) An off-white amorphous powder, $[\alpha]_D$ −43° (c = 1.0, MeOH). *Anal.* Calcd for $C_{75}H_{50}O_{48} \cdot 13.5H_2O$: C, 45.89; H, 3.92. Found: C, 45.71; H, 3.62. FAB-MS m/z: 1741 $(M+Na)^+$. UV λ_{max}^{MeOH} nm (log ε): 223 (4.68), 261 (4.47), CD (MeOH) [θ] (nm): 2.32×10^5 (236), -8.33×10^4 (261), $+3.67 \times 10^3$ (282), -3.37×10^4 (307). ^{1}H-NMR, see text and Table I. ^{13}C-NMR (acetone-d_6 + D_2O), glucose carbons (α-anomer) δ: 92.16 (C-1), 73.42 (C-2), 75.47 (C-3), 69.09 (C-4), 69.68 (C-5), 63.37 (C-6), 91.36 (C-1′), 75.24 (C-2′), 77.31 (C-3′), 69.68 (C-4′), 72.70 (C-5′), 63.42 (C-6′); (β-anomer) δ: 95.09 (C-1), 75.74 (C-2), 75.82 (C-3), 69.05 (C-4), 73.36 (C-5), 62.91 (C-6), 92.21 (C-1′), 77.05 (C-2′), 77.80 (C-3′), 70.10 (C-4′), 73.81 (C-5′), 62.91 (C-6′).

Partial Hydrolysis of Sanguiin H-6 (8) to Roshenin B (10) A solution of **8** (20 mg) in H_2O (30 ml) was incubated with tannase prepared according to ref. 11 at 37 °C for 36 h. The reaction mixture after concentration, was applied to a BondElut C18 column, which was washed with water. The MeOH eluate gave a hydrolyzate (8 mg), which was identical with roshenin B (**10**) by HPLC (reversed-phase; solvent B, t_R 3.2 min) and ^{1}H-NMR. Gallic acid (**13**) was detected on HPLC (t_R 3.0 min) of the water washings.

Roshenin C (11) An off-white amorphous powder, $[\alpha]_D$ −55° (c = 1.0, MeOH). *Anal.* Calcd for $C_{68}H_{48}O_{44} \cdot 12H_2O$: C, 45.74; H, 4.03. Found: C, 45.91; H, 3.78. FAB-MS m/z: 1591 $(M+Na)^+$. UV λ_{max}^{MeOH} nm (log ε): 222 (4.56), 260 (4.31), CD (MeOH) [θ] (nm): 2.37×10^5 (236), -9.67×10^4 (261), $+3.30 \times 10^3$ (282), -4.33×10^3 (307). ^{1}H-NMR, see text and Table I.

Partial Hydrolysis of Roshenin C (11) An aqueous solution of **11** (1 mg) was heated in a boiling-water bath for 6 h, and the reaction mixture was analyzed by reversed-phase HPLC (solvent B), which showed peaks identical with those of authentic pedunuclagin (**15**) (t_R 2.8, 3.1 min), ellagic acid (**14**) and sanguisorbic acid dilactone (**5**) (t_R 7.0 min).

Roshenin D (12) An off-white amorphous powder, $[\alpha]_D$ + 12° (c = 1.0, MeOH). *Anal.* Calcd for $C_{75}H_{52}O_{48} \cdot 11H_2O$: C, 46.92; H, 3.86. Found C, 46.74; H, 3.74. FAB-MS m/z: 1743 $(M+Na)^+$. UV λ_{max}^{MeOH} nm (log ε): 201 (4.65), 243 (4.41), ^{1}H-NMR, see Table I. ^{13}C-NMR (acetone-d_6 + D_2O) δ: 90.55 (Glc C-1), 73.90 (Glc C-2), 75.15 (Glc C-3), 69.13 (Glc C-4), 71.27 (Glc C-5), 63.10 (Glc C-6), 92.53 (Glc C-1′), 75.41 (Glc C-2′), 80.03 (Glc C-3′), 67.40 (Glc C-4′), 76.31 (Glc C-5′), 63.67 (Glc C-6′), 107.93, 107.36, 107.46, 108.02, 108.12 (HHDP C-3, C-3′, Sang C-3), 109.62, 112.31 (Sang C-2″, C-6″), 109.87, 110.16 (each 2C, Gal C-2, C-6), 164.96, 165.42, 165.82, 166.88, 167.92, 168.28, 168.38, 168.61, 169.51 (ester carbonyl).

Roshenin E (19) An off-white amorphous powder, $[\alpha]_D$ −30° (c = 1.0, MeOH). *Anal.* Calcd for $C_{68}H_{48}O_{44} \cdot 10H_2O$: C, 46.68; H, 3.89. Found: C, 46.60; H, 3.61. FAB-MS m/z: 1591 $(M+Na)^+$. UV λ_{max}^{MeOH} nm (log ε): 221 (4.58), 263 (4.34), CD (MeOH) [θ] (nm): 2.91×10^5 (236), -1.03×10^5 (261), $+3.03 \times 10^4$ (281), -4.24×10^4 (307). ^{1}H-NMR, see Table I. ^{13}C-NMR (acetone-d_6 + D_2O) δ: 92.16 [Glc α-anomer (α) C-1], 75.87 [Glc (α) C-2], 77.29 [Glc (α and β) C-3], 69.07 [Glc (α) C-4], 73.36 [Glc (α and β) C-5], 62.93 [Glc (α and β) C-6], 92.24 [Glc (β) C-1], 75.97 [Glc (β) C-2)], 69.05 [Glc (β) C-4], 90.94 [Glc (α) C-1′], 75.42 [Glc (α) C-2′], 70.69 [Glc (α and β) C-3′], 74.00 [Glu (α) C-4′], 67.25 [Glc (α and β) C-5′], 63.91 [Glc (α) C-6′], 96.51 [Glc (β) C-1′], 76.30 [Glc (β) C-2′], 73.60 [Glc (β) C-4′], 63.78 [Glc (β) C-6′], 107.14, 107.41 (1C in total), 107.41 (2C), 107.97, 108.10 (1C in total), 108.10 (1C) (HHDP C-3, C-3′, Sang C-3), 109.94 (2C, Gal C-2, C-6), 110.35, 110.44 (1C in total), 111.84, 111.96 (1C in total) (Sang C-2″, C-6″), 164.98 164.95 (1C in total), 166.46, 166.04 (1C in total), 166.87, 166.58 (1C in total), 167.89 (1C), 168.04 (1C), 168.25, 168.10 (1C in total), 168.44 (1C), 169.29 (1C) (ester carbonyl).

Partial Hydrolysis of Roshenin D (12) and Roshenin E (19) Roshenin D (**12**) and roshenin E (**19**) were partially hydrolyzed in a way similar to that described for **9—11**, and the HPLC of their reaction mixtures showed the formation of the following products: from **12**; 6-*O*-galloyl-2,3-*O*-hexahydroxydiphenoyl-D-glucose (**17**) (t_R 4.3, 5.1 min) and sanguiin H-2 (**6**) (t_R 5.6 min); from **19**, isostrictinin (**18**) (t_R 2.93 min) and 4,6-*O*-hexahydroxydiphenyl-D-glucose (**20**) (t_R 3.5, 4.3 min).

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References and Notes

1) Part XI: T. Okuda, T. Yoshida, T. Hatano, M. Iwasaki, M. Kubo, T. Orime, N. Naruhashi, and M. Yoshizaki, *Phytochemistry*, in press.
2) "Flora Henan," Vol. 2, ed. by B.-ZH Ding, Henan Sci. and Tech. Pub. House, Zhengzhou, 1988, p. 209.
3) G. Nonaka, T. Tanaka, and I. Nishioka, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 1067.
4) R. S. Thompson, D. Jacques, E. Haslam, and R. N. J. Tanner, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 1387.
5) T. Tanaka, G. Nonaka, and I. Nishioka, *J. Chem. Res. (M)*, **1985**, 2001.
6) H. Tachibana, T. Tanaka, G. Nonaka, I. Nishioka, and F.-L. Xu, Abstracts of Papers, 36th Annual Meeting of the Japanese Society of Pharmacognosy, Kumamoto, 1989, p. 171.
7) T. Okuda, T. Yoshida, and T. Hatano, *J. Nat. Prod.*, **52**, 1 (1989).
8) C. K. Wilkins and B. A. Bohm, *Phytochemistry*, **15**, 211 (1976).
9) T. Yoshida, T. Hatano, T. Kuwajima, and T. Okuda, *Heterocycles*, **33**, 463 (1992).
10) T. Okuda, T. Yoshida, T. Hatano, T. Koga, N. Toh, and K. Kuriyama, *Tetrahedron Lett.*, **23**, 3937 (1982).
11) T. Yoshida, K. Tanaka, X.-M. Chen, and T. Okuda, *Chem. Pharm. Bull.*, **37**, 920 (1989).
12) T. Okuda, T. Yoshida, M. Ashida, and K. Yazaki, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1865.
13) T. Yoshida, H. Ohbayashi, K. Ishihara, K. Haba, Y. Okano, T. Shingu, and T. Okuda, *Chem. Pharm. Bull.*, **39**, 2233 (1991).
14) ^{13}C-NMR data for the glucose moiety of **6** and **16** (126 MHz, acetone-d_6 + D_2O). **6**, δ: 90.51 (C-1), 73.88 (C-2), 75.01 (C-3), 69.18 (C-4), 71.56 (C-5), 62.77 (C-6); **16**, δ: 92.1 (C-1), 75.3 (C-2), 79.9 (C-3), 67.8 (C-4), 76.2 (C-5), 63.6 (C-6).
15) T. Yoshida, T. Chou, Y. Maruyama, and T. Okuda, *Chem. Pharm. Bull.*, **38**, 2681 (1990).
16) T. Hatano, N. Ogawa, R. Kira, T. Yasuhara, and T. Okuda, *Chem. Pharm. Bull.*, **37**, 2083 (1989).
17) M. K. Seikel and W. E. Hillis, *Phytochemistry*, **9**, 1115 (1970).

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