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Tannins of Hamamelidaceous Plants. III.¹⁾ Isorugosins A, B and D, New Ellagitannins from *Liquidambar formosana*

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A new dimeric hydrolyzable tannin named isorugosin D (**11**), and two new monomeric tannins of related structures, isorugosin A (**10**) and isorugosin B (**1**), were isolated from the leaf of *Liquidambar formosana* HANCE (Hamamelidaceae). The orientation of the valoneoyl group at O-4 and O-6 of the glucose core in isorugosins A, B and D was found to be different from that of rugosin A (**7**), rugosin B (**6**) and rugosin D (**18**), and the orientations of this group in the tannins of both type were confirmed on the basis of the two-dimensional nuclear magnetic resonance spectrum (long-range ¹H-¹³C correlation spectrum) of rugosin A (**7**).

Keywords—isorugosin A; isorugosin B; isorugosin D; rugosin A; tannin; ellagitannin; dimeric hydrolyzable tannin; *Liquidambar formosana*; Hamamelidaceae; centrifugal partition chromatography

The isolation and the structure elucidation of liquidambin, which could be a precursor of a C-glucosidic tannin, casuarinin,¹⁾ and the isolation of several co-existing hydrolyzable tannins,²⁾ from the leaf of *Liquidambar formosana* HANCE, were reported in our previous papers.^{1,2)} The remarkable seasonal change in the composition of the tannins, which is in accord with the biogenetic pathway from galloylglucoses to C-glucosidic tannins, was also reported.²⁾ Further investigation on the tannins of this plant has led to the isolation of three new tannins, which are described in this paper.

Results and Discussion

The *n*-butanol-soluble portion, obtained from the aqueous acetone homogenate of the autumn leaves of *Liquidambar formosana*, was chromatographed over Sephadex LH-20, and then on Toyopearl HW-40 to give a new compound, which was named isorugosin B on the basis of the following structural study. The ethyl acetate-soluble portion, obtained from the spring leaves of *L. formosana*, was subjected to centrifugal partition chromatography (CPC).³⁾ Subsequent column chromatography of a fraction from CPC over Toyopearl HW-40 and/or MCI-GEL CHP-20P, afforded another two new compounds, which were named isorugosin A and isorugosin D.

Isorugosin B (**1**), [α]_D + 28° (*c* = 1, methanol), was obtained as a light brown amorphous powder. The fast-atom bombardment mass spectrum (FAB-MS) shows the [M + Na]⁺ ion at 977. The proton nuclear magnetic resonance (¹H-NMR) spectrum of **1** (400 MHz, in acetone-*d*₆) indicates that this tannin forms an anomer mixture (α -anomer : β -anomer = 4 : 3), and that it possesses two galloyl groups [δ 7.04 (s) and 6.90 (s) (8/7H each, α -anomer); 7.05 (s) and 6.88 (s) (6/7H each, β -anomer)], a valoneoyl group [δ 7.27 (s), 6.65 (s) and 6.31 (s) (4/7H each, α -anomer); 7.28 (s), 6.66 (s) and 6.25 (s) (3/7H each, β -anomer)] and a glucopyranose core [δ 5.54 (d, *J* = 3.5 Hz, H-1), 5.10 (dd, *J* = 3.5, 10 Hz, H-2), 5.69 (t, *J* = 10 Hz, H-3), 5.03 (t, *J* =

10 Hz, H-4), 4.57 (ddd, $J=1, 7, 10$ Hz, H-5), 5.28 (dd, $J=7, 13$ Hz, H_a-6) and 3.75 (dd, $J=1, 13$ Hz, H_b-6) (4/7 H each, α -anomer); 5.05 (d, $J=8$ Hz, H-1), 5.22 (dd, $J=8, 10$ Hz, H-2), 5.39 (t, $J=10$ Hz, H-3), 5.02 (t, $J=10$ Hz, H-4), 4.20 (ddd, $J=1, 7, 10$ Hz, H-5), 5.29 (dd, $J=7, 13$ Hz, H_a-6) and 3.82 (dd, $J=1, 13$ Hz, H_b-6) (3/7 H each, β -anomer)]. The presence of valoneoyl and galloyl groups in isorugosin B was confirmed by methanolysis after methylation of **1**, which yielded methyl tri-*O*-methylgallate (**2**) and trimethyl octa-*O*-methylvaloneate (**3**).

The coupling constants of glucose protons in the ^1H -NMR spectrum of **1** indicate that the glucose core adopts the $^4\text{C}_1$ conformation, and the chemical shifts of H-4, H_a-6 and H_b-6 of the $^4\text{C}_1$ glucopyranose core indicate that the hexahydroxydiphenoyl (HHDP) part of the valoneoyl group is located at O-4 and O-6 of the glucopyranose core.^{4,5} As the anomeric center is not acylated, two galloyl groups should be at O-2 and O-3 of the glucose core. These locations of acyl groups on the glucose core were supported by treatment of isorugosin B with hot water, to afford 2,3-di-*O*-galloyl-D-glucose (**4**)⁶ and valoneic acid dilactone (**5**)⁷ (Chart 1). The circular dichroism (CD) spectrum of isorugosin B (**1**) (in methanol) shows a positive Cotton effect in the short wavelength region ($[\theta]_{222} +9.0 \times 10^4$), indicating the *S*-configuration^{8,9} of the HHDP part of the valoneoyl group. Therefore, isorugosin B is 2,3-di-*O*-galloyl-4,6-*O*-(*S*)-valoneoyl-D-glucose and is isomeric to rugosin B (**6**)¹⁰ (Chart 2), as it is not identical with the latter. It is considered that the orientation of the valoneoyl group in isorugosin B (**1**) is different from that of rugosin B (**6**).

The evidence concerning the orientations of the valoneoyl group in rugosin B (**6**), and in the co-existing tannins, rugosin A (**7**)¹⁰ and rugosin C (**8**)¹⁰ is as follows. The orientation of the valoneoyl group in rugosin B (**6**) is identical with that of rugosin A (**7**), as indicated by the chemical correlation of these tannins.¹⁰ The orientation of the valoneoyl group in rugosin C (**8**) should be as in structure **8** (Chart 3), which was correlated with praecoxin C (**9**)¹¹ by the selective hydrolysis of the depside linkage of **9**.¹¹ However, the identity of the orientation of

Chart 1

Chart 2

Chart 3

the valoneoyl group in **6** and in **7** with that of **8** was only based on the probable identity of their biogenetic routes. We have now confirmed the orientation of the valoneoyl group in **6** and in **7** as follows.

In the ^1H -NMR spectrum (90 MHz, in acetone- d_6 + D_2O) of rugosin A (**7**), the proton signals due to the valoneoyl group are at δ 7.14, 6.51 and 6.32. Obviously, the signal at δ 7.14 is assignable to the proton of the galloyl part of the valoneoyl group (H_A in formula **7**). Addition of pyridine- d_5 to a solution of rugosin A in acetone- d_6 + D_2O caused a large downfield shift of the proton at δ 6.32 to δ 6.58, while only small downfield shifts were observed for the other signals (δ 7.14 $\rightarrow$ 7.24, 6.51 $\rightarrow$ 6.61). The large downfield shift of the signal at δ 6.32 can be explained by association of a pyridine molecule with the carboxyl group of the valoneoyl group, which induced the large downfield shift of the neighboring proton (H_B in formula **7**). The remaining signal at δ 6.51 therefore should be H_C in formula **7**. In the long-range ^1H - ^{13}C correlation spectrum (Fig. 1), rugosin A (in acetone- d_6) showed a cross peak for an ester carbonyl carbon at δ 167.8 and the H_B proton of the valoneoyl group, and another cross peak for the same ester carbonyl carbon and the H-6 proton (δ 3.79) of the glucose core. The spectrum also showed a cross peak for the carbonyl carbon at δ 167.6 and the H_C proton

Fig. 1. The Long-Range ^1H - ^{13}C Correlation Spectrum of Rugosin A (7)

The region of the ester carbonyl carbons in the ^{13}C -NMR spectrum is shown. The average J_{CH} value for two- or three-bond couplings was set at 10 Hz.

of the valoneoyl group, and another cross peak for this carbonyl carbon and the H-4 proton (δ 5.16) of the glucose core. These data indicate that the orientation of the valoneoyl group in rugosin A should be as in structure 7 (Chart 2). Therefore, rugosin B should also be formulated as 6, and isorugosin B should have structure 1 as shown in Chart 1.

Isorugosin A (**10**), $[\alpha]_{\text{D}} + 30^\circ$ ($c=0.63$, acetone), was obtained as an off-white amorphous powder. The ^1H -NMR spectrum (500 MHz, in acetone- d_6) of **10** indicates the presence of three galloyl groups [δ 7.11 (2H, s), 6.99 (2H, s) and 6.90 (2H, s)], a valoneoyl group [δ 7.28 (1H, s, H_A), 6.65 (1H, s, H_C) and 6.29 (1H, s, H_B)] and a β -glucopyranose core adopting the $^4\text{C}_1$ conformation [δ 6.17 (d, $J=8$ Hz, H-1), 5.56 (dd, $J=8, 10$ Hz, H-2), 5.59 (t, $J=10$ Hz, H-3), 5.11 (t, $J=10$ Hz, H-4), 4.45 (dd, $J=6.5, 10$ Hz, H-5), 5.34 (dd, $J=6.5, 13$ Hz, $\text{H}_\text{a-6}$) and 3.84 (d, $J=13$ Hz, $\text{H}_\text{b-6}$) (1H each)]. The chemical shifts of the H-4, $\text{H}_\text{a-6}$ and $\text{H}_\text{b-6}$ protons on the $^4\text{C}_1$ glucopyranose core indicate that the HHDP part of the valoneoyl group in **10** is located at O-4 and O-6 of the glucose core. The three galloyl groups are therefore located at O-1, O-2 and O-3. Partial hydrolysis of isorugosin A (**10**) afforded isorugosin B (**1**). Therefore, the structure **10** (Chart 4), isomeric to rugosin A (**7**), was assigned for isorugosin A.

Isorugosin D (**11**), $[\alpha]_{\text{D}} + 75^\circ$ ($c=0.5$, methanol), was obtained as a light brown amorphous powder. The ^1H -NMR spectrum of **11** (500 MHz, in acetone- d_6) indicates the presence of five galloyl groups [δ 7.11 (2H, s), 7.04 (2H, s), 6.98 (2H, s), 6.96 (2H, s) and 6.91 (2H, s)], a valoneoyl group and an HHDP group [δ 7.23 (1H, s), 6.66 (1H, s), 6.65 (1H, s), 6.46 (1H, s) and 6.14 (1H, s)], and two β -glucopyranose cores both of which adopt the $^4\text{C}_1$ conformation [δ 6.11 (d, $J=8.5$ Hz, H-1), 5.58 (dd, $J=8.5, 10$ Hz, H-2), 5.80 (t, $J=10$ Hz, H-3), 5.19 (t, $J=10$ Hz, H-4), 4.49 (dd, $J=6, 10$ Hz, H-5), 5.29 (dd, $J=6, 13.5$ Hz, $\text{H}_\text{a-6}$) and 3.84 (d, $J=13.5$ Hz, $\text{H}_\text{b-6}$); 6.15 (d, $J=8$ Hz, H-1), 5.56–5.50 (2H, m, H-2 and H-3), 5.09 (t, $J=10$ Hz, H-4), 4.31 (dd, $J=6, 10$ Hz, H-5), 5.20 (dd, $J=6, 13.5$ Hz, $\text{H}_\text{a-6}$) and 3.84 (d, $J=13.5$ Hz, $\text{H}_\text{b-6}$)], in the molecule of **11**. The chemical shifts of the H-4, $\text{H}_\text{a-6}$ and $\text{H}_\text{b-6}$ protons

Chart 4

of the two 4C_1 glucose cores indicate that the HHDP part of the valoneoyl group and the HHDP group are located at O-4 and O-6 in the glucose cores. The galloyl part of the valoneoyl group and the five galloyl groups therefore should be at O-1, O-2 and O-3 on the two glucose cores. The CD spectrum of **11** (in methanol) shows a positive Cotton effect in the short-wavelength region ($[\theta]_{228} + 2.5 \times 10^5$), with an amplitude about twice as large as that of isorugosin B. The configuration of the valoneoyl group and the HHDP group in **11** therefore should be *S*.

Methylation of isorugosin D (**11**) afforded nonacosamethylate (**12**), $[\alpha]_D + 3.5^\circ$ ($c=0.23$, acetone). Methanolysis of **11** gave methyl tri-*O*-methylgallate (**2**), dimethyl hexamethoxybiphenylcarboxylate (**13**) and trimethyl octa-*O*-methylvaloneate (**3**) in a molar ratio of 5:1:1. Partial hydrolysis of isorugosin D (**11**) afforded isorugosin A (**10**) and tellimagrandin I (**14**), along with 1,2,3-tri-*O*-galloyl- β -D-glucose (**15**), **16** and tellimagrandin II (**17**)¹²⁾ (Chart 5). Therefore, the structure **11** (Chart 4), isomeric to rugosin D (**18**)¹³⁾ (Chart 6), was assigned for isorugosin D.

Rugosins A (**6**), B (**7**) and D (**18**) have not been found in the fractions obtained from *L. formosana*. It is biogenetically significant that the isomers of isorugosins A (**10**), B (**1**) and D (**11**) concerning the orientation of the valoneoyl group at O-4 and O-6 of the glucose cores, are absent in *L. formosana*, and that the latter type of tannins, **10**, **1** and **11**, have not been found in *Rosa rugosa* or in *Coriaria japonica*, which contain the former type of tannins, **6**, **7** and **18**.^{8,10,13,14)} As tellimagrandin I (**14**) and tellimagrandin II (**17**), which are presumed to be precursors of both types of tannins described above, are present in all of the three plants,^{2,10,14)} it is very probable that the C-O oxidative coupling¹⁵⁾ between the galloyl part and the HHDP part of the valoneoyl group in the biogenesis of isorugosins A, B and D (in *L.*

Chart 5

Chart 6

formosana) is effected by an enzyme different from that for rugosins A, B and D (in *R. rugosa* and *C. japonica*).

Experimental

Optical rotations were measured on a JASCO DIP-4 polarimeter. Ultraviolet (UV) and infrared (IR) spectra were recorded on a Hitachi 200-10 spectrophotometer and on a JASCO A-102 spectrometer, respectively. $^1\text{H-NMR}$ spectra were recorded on a Bruker AM-400 spectrometer (400 MHz) using tetramethylsilane as an internal standard;

chemical shifts are given in δ values (ppm). A Varian VXR-500 instrument (500 MHz) in the SC-NMR Laboratory of Okayama University, and a Hitachi R22-FTS spectrometer (90 MHz) were also used. FAB-MS spectra were measured on a JEOL JMS D-300 spectrometer and electron-impact mass spectra (EI-MS) on a Shimadzu LKB-9000 instrument. CD spectra were recorded on a JASCO J-500 machine equipped with a DP-501 data processor. CPC was performed on a Sanki L-90 machine equipped with twelve cartridges,³¹ developing with *n*-butanol-*n*-propanol-water (4:1:5) at 1000 rpm. Reversed-phase high-performance liquid chromatography (HPLC) was conducted on a YMC A312 (ODS) (6 $\times$ 150 mm) column at 40 °C in a column oven. A YMC A324 (ODS) (10 $\times$ 300 mm) column was also used for preparative HPLC. The solvent systems used were (R1) 0.01 M H₃PO₄-0.01 M KH₂PO₄-methanol (3:3:2, by volume), (R2) 0.1 M H₃PO₄-0.1 M KH₂PO₄-ethanol-ethyl acetate (10:10:2:1) and (R3) 0.1 M H₃PO₄-0.1 M KH₂PO₄-ethanol (10:10:1). Normal-phase HPLC was run on a column (4 $\times$ 150 mm) packed with Develosil 60-5, developing with a solvent system (N1) consisting of hexane-methanol-tetrahydrofuran-formic acid (55:33:11:1) containing oxalic acid (450 mg/ml), or (N2) hexane-ethyl acetate (2:1). Thin layer chromatography (TLC) was performed on Kieselgel 60PF₂₅₄ (Merck). Light petroleum refers to that fraction boiling in the range 75–125 °C.

Isolation of Isorugosin B (1)—Fresh leaves of *Liquidambar formosana* (1 kg) collected in November, were homogenized in 70% acetone, and filtered. After concentration, the resulting aqueous solution was extracted with Et₂O, ethyl acetate and *n*-butanol, successively, and each solvent was evaporated. A portion (6.58 g) of the *n*-butanol extract (27 g) was subjected to column chromatography over Sephadex LH-20 (2.2 $\times$ 68 cm) using 70% EtOH as the developer; 10-g fractions were collected. Combined fractions 59–73 (192 mg) were purified by column chromatography on Toyopearl HW-40 (fine grade) eluted with 70% EtOH, and further purified by column chromatography on Toyopearl HW-40 eluted with 50% EtOH, to afford **1** (14 mg).

Isolation of Isorugosin A (10) and Isorugosin D (11)—Fresh leaves of *L. formosana* (3.6 kg) collected in May, were treated in an analogous way, and gave 50 g of ethyl acetate extract. A portion (2.8 g) of the ethyl acetate extract was subjected to CPC (reversed-phase development), and was separated into four fractions. The second fraction (432 mg) was submitted to column chromatography on MCI-GEL CHP-20P (1.1 $\times$ 10 cm) eluted with H₂O, 20% MeOH, 40% MeOH and 60% MeOH, successively. The 40% MeOH eluate (203 mg) was further chromatographed over Toyopearl HW-40 (superfine grade) with 70% EtOH as the eluant, to give casuarictin²¹ and crude isorugosin A. Final purification was achieved by preparative HPLC [solvent system (R1)], to afford 2 mg of **10**. The 60% MeOH eluate (51 mg) from the column chromatography over MCI-GEL was submitted to column chromatography on Toyopearl HW-40 (superfine grade) eluted with 70% EtOH, 70% EtOH:70% acetone (9:1) and 70% EtOH:70% acetone (8:2), successively. The 70% EtOH:70% acetone (8:2) eluate afforded 25 mg of **11**.

Isorugosin B (1)—A light brown amorphous powder, $[\alpha]_D^{+28}$ ($c=1$, MeOH). *Anal.* Calcd for C₄₁H₃₀O₂₇·6H₂O: C, 46.34; H, 3.98. Found: C, 46.53; H, 3.83. FAB-MS: m/z 977 ([M+Na]⁺). UV λ_{max}^{MeOH} nm (log ϵ): 219 (4.93), 271 (4.56). IR ν_{max}^{KBr} cm⁻¹: 1740–1710 (ester carbonyl), 1620. CD (MeOH) $[\theta]$ (nm): +9.0 $\times 10^4$ (222), +3.4 $\times 10^4$ (238), -3.6 $\times 10^4$ (262), +3.8 $\times 10^4$ (288). ¹H-NMR: see text.

Methanolysis after Methylation of 1—A solution of **1** (5 mg) in ethanol (0.4 ml) was treated with ethereal diazomethane (0.4 ml) for 2 h at room temperature, and evaporated. The crude methyl ether was purified by preparative TLC using light petroleum-chloroform-acetone (4:6:3, *Rf* 0.30) as the developer, and then treated with 0.2% sodium methoxide in methanol (1 ml) overnight at room temperature. The mixture was acidified with acetic acid and then evaporated. The residue was subjected to preparative TLC with light petroleum-chloroform-acetone (6:3:1) as the developer, and gave methyl tri-*O*-methylgallate (**2**) (0.3 mg) [*Rf* 0.50. EI-MS: m/z 226 (M⁺)] and trimethyl octa-*O*-methylvaloneate (**3**) (0.4 mg) [*Rf* 0.24. EI-MS: m/z 660 (M⁺)].

Treatment of 1 with Hot Water—An aqueous solution (0.3 ml) of isorugosin B (1 mg) in a sealed tube was kept in a boiling water-bath for 18 h, and evaporated. 2,3-Di-*O*-galloyl-D-glucose (**4**) and valoneic acid dilactone (**5**) in the reaction mixture were identified by co-chromatography on HPLC [reversed-phase HPLC (R2) and normal-phase HPLC (N1)] with authentic samples. For the identification of **4**, reversed-phase HPLC using solvent system (R3) was also used.

Isorugosin A (10)—A light-brown amorphous powder. $[\alpha]_D^{+30}$ ($c=0.63$, acetone). *Anal.* Calcd for C₄₈H₃₄O₃₁·2H₂O: C, 50.45; H, 3.35. Found: C, 50.97; H, 4.16. UV λ_{max}^{MeOH} nm (log ϵ): 227 (4.94), 274 (4.59). IR ν_{max}^{KBr} cm⁻¹: 1730–1710 (ester carbonyl), 1620. ¹H-NMR: see text.

Partial Hydrolysis of 10 with Tannase—An aqueous solution of **10** (1 mg), containing one drop of tannase solution, was kept at 37 °C for 3 h. The mixture was acidified with 1% HCl to pH 2, and subjected to chromatography on a SEP-PAK C₁₈ cartridge (Waters Associates) eluted with water and then methanol. The methanol eluates afforded **1**, which was identified by ¹H-NMR, and co-chromatography on HPLC [reversed-phase HPLC (R1) and normal-phase HPLC (N1)] with an authentic sample.

Isorugosin D (11)—A light brown amorphous powder. $[\alpha]_D^{+75}$ ($c=0.5$, MeOH). *Anal.* Calcd for C₈₂H₅₈O₅₂·7H₂O: C, 49.20; H, 3.62. Found: C, 49.49; H, 3.77. UV λ_{max}^{MeOH} nm (log ϵ): 218 (5.33), 277 (4.86). IR ν_{max}^{KBr} cm⁻¹: 1730–1710 (ester carbonyl), 1620. CD (MeOH) $[\theta]$ (nm): +2.5 $\times 10^5$ (228), -6.0 $\times 10^4$ (255), +3.1 $\times 10^4$ (285). ¹H-NMR: see text.

Methylation of 11—An ethanol solution (0.5 ml) of **11** (5 mg) was treated with ethereal diazomethane (1 ml) and left to stand for 1 h. The solvent was evaporated off, and the residue was subjected to preparative TLC using

benzene-acetone (4:1, *R_f* 0.42), to give the nonacosamethylate (**12**) (1.5 mg), [α]_D + 3.5° (*c* = 0.23, acetone). ¹H-NMR (400 MHz, in acetone-*d*₆): δ 7.32, 7.29, 7.22, 7.21, 7.07 (2H each, s, galloyl × 5), 7.41, 6.97, 6.96, 6.78, 6.46 (1H each, s, HHDP and valoneoyl), 6.34 [1H, d, *J* = 8 Hz, glucose (glu) H-1], 6.28 (1H, d, *J* = 8.5 Hz, glu H-1), 5.92 (1H, t, *J* = 10 Hz, glu H-3), 5.73–5.68 (3H, glu H-2 × 2, glu H-3), 5.34 (1H, t, *J* = 10 Hz, glu H-4), 5.32 (1H, dd, *J* = 6.5, 13.5 Hz, glu H_a-6), 5.31 (1H, dd, *J* = 6.5, 13.5 Hz, glu H_a-6), 5.21 (1H, t, *J* = 10 Hz, glu H-4), 4.62 (1H, dd, *J* = 6.5, 10 Hz, glu H-5), 4.60 (1H, dd, *J* = 6.5, 10 Hz, glu H-5), 3.98–3.64 (CH₃O– × 29). The signals of two H_b-6 protons were overlapped by the methoxyl signals.

Methanolysis of Nonacosa-*O*-methylisorugosin D (12**)**—Compound **12** (0.5 mg) was treated with 0.5% sodium methoxide in methanol (0.1 ml) overnight at room temperature. After neutralization with acetic acid, the solvent was distilled off. HPLC analysis [normal-phase, solvent system (N2)] of the residue showed the presence of methyl tri-*O*-methylgallate (**2**), dimethyl hexamethoxybiphenylcarboxylate (**13**) and trimethyl octa-*O*-methylvaloneate (**3**) in a molar ratio of 1:1:5.

Partial Hydrolysis of **11**—Compound **11** (100 mg) was dissolved in 0.05 M acetate buffer (pH 6) and kept at 37 °C for 22 h. The reaction mixture was acidified with 10% HCl to pH 2, and passed through a SEP PAK C₁₈ cartridge with water and then methanol, as eluants. The methanol eluate was chromatographed over Toyopearl HW-40 (superfine grade) with 70% ethanol, and then with a mixture of 70% ethanol and 70% acetone (9:1), as eluants. The 70% ethanol eluate afforded 1,2,3-tri-*O*-galloyl-β-D-glucose (**15**) (5 mg) and tellimagrandin I (**14**) (23 mg). The 70% ethanol–70% acetone (9:1) eluate gave **10** (6 mg) and tellimagrandin II (**17**) (3 mg). An additional product (**16**) (3 mg) was also obtained from isorugosin D (120 mg), by preparative HPLC on a YMC A324 column [solvent system (R1)] after column chromatography of a mixture of hydrolyzates on Toyopearl HW-40. ¹H-NMR of **16** (400 MHz, in acetone-*d*₆): δ 7.62, 7.22, 7.15 (1H each, s, lactonized valoneoyl), 6.95, 6.93 (2H each, s, galloyl × 2), 6.66, 6.46 (1H each, s, HHDP), 6.11 (1H, d, *J* = 8 Hz, glu H-1), 5.75 (1H, t, *J* = 10 Hz, glu H-3), 5.54 (1H, dd, *J* = 8, 10 Hz, glu H-2), 5.26 (1H, dd, *J* = 6, 13 Hz, glu H_a-6), 5.17 (1H, dd, *J* = 10 Hz, glu H-4), 4.46 (1H, dd, *J* = 6, 10 Hz, glu H-5), 3.76 (1H, d, *J* = 13 Hz, glu H_b-6).

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