

Tannins and Related Polyphenols of Euphorbiaceous Plants. XII.¹⁾ Euphorbins G and H, New Dimeric Hydrolyzable Tannins from *Euphorbia prostrata* and *Euphorbia makinoi*

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Two new ellagitannin dimers, euphorbins G (20) and H (21), together with 12 known polyphenols, were isolated from the leaves of *Euphorbia prostrata* (*E. chamaesyce*). Their structures, having ¹C₄ and ⁴C₁ glucopyranose cores in each molecule, were established by spectroscopic and chemical methods. These new dimers, and 13 known hydrolyzable tannins, among which six are the same as those from *E. prostrata*, were also isolated from *E. makinoi*.

Keywords *Euphorbia prostrata*; *Euphorbia makinoi*; Euphorbiaceae; tannin; euphorbin G; euphorbin H

In a previous study on the tannins of euphorbiaceous plants, we isolated and chemically characterized euphorbins A—F, dimeric hydrolyzable tannins of a new class having a geraniin moiety as a monomeric unit, from *Euphorbia hirta* L.²⁾ and *Euphorbia tirucalli* L.³⁾ We also isolated a new dimer, euprostin B, from *Euphorbia prostrata* AIT., collected in Fujian, China, together with rugosins D, E and G, which are oligomers of a type different from that of euphorbins.⁴⁾ During the survey of the tannins in the *Euphorbia* species, we found that *E. prostrata* (*E. chamaesyce* L.) collected in Okayama, Japan, shows different pattern in HPLC from that of the species collected in China. The present paper describes the isolation and structural elucidation of two additional members of euphorbin-type dimers, named euphorbins G and H, from *E. prostrata* collected in Okayama. These new dimers were also obtained from *E. makinoi* HAYATA, together with several known tannins which are the same as those from *E. prostrata*.

The aqueous acetone homogenate of the dried leaves of *E. prostrata* was extracted successively with ether, EtOAc and *n*-BuOH. The EtOAc extract was chromatographed over Toyopearl HW-40 and/or MCI-gel CHP 20P to yield the new tannin, euphorbin G (20), and nine known compounds. Among them, two were identified as quercitrin (1) and isoquercitrin (2), and the other seven were characterized as 2-*O*-galloyl-4,6-(*S*)-hexahydroxydiphenoyl- β -D-glucose (3),⁵⁾ strictinin (4),⁶⁾ tellimagrandin I (5),⁶⁾ casuarictin (6),⁶⁾ corilagin (8),⁷⁾ geraniin (9),⁷⁾ and rugosin F (11),⁸⁾ by comparison of their physical data with those of authentic samples. Similarly, the *n*-BuOH extract afforded euphorbins G (20) and H (21), 5, pedunculagin (7),⁶⁾ degalloylrugosin F (12)⁹⁾ and euphorhelin (13).¹⁰⁾

The *n*-BuOH-soluble portion of the aqueous acetone homogenate from the dried aerial parts of *E. makinoi* was also chromatographed in an analogous way to give euphorbins G (20) and H (21), along with 3, 5, 7, 8, 9, 12, praecoxin A (17),¹²⁾ furosins (18),¹⁴⁾ and mallotusinic acid (19).¹⁵⁾ 1,3,6-Tri-*O*-galloyl- β -D-glucose (14),¹¹⁾ 1,2,4,6-tetra-*O*-galloyl- β -D-glucose (15),¹¹⁾ 1,2,3,4,6-penta-*O*-galloyl- β -D-glucose (16),¹¹⁾ chebulagic acid (10)¹³⁾ and 9 were also obtained similarly from the EtOAc-soluble por-

tion.

Euphorbin G (20) and H (21) were suggested to be dimeric hydrolyzable tannins by positive color reactions with FeCl₃, and HOAc–NaNO₂ reagents¹⁶⁾ on a TLC plate, and by their large retention volume on normal-phase HPLC,¹⁷⁾ both of which are similar to those of 11 and 12. The dimeric nature of euphorbin G was also supported by the FAB-MS ion peak at *m/z* 1911 ascribable to (M + Na)⁺. Acid hydrolysis of 20 with hot 5% H₂SO₄ yielded glucose, as well as gallic acid, ellagic acid and valoneic acid dilactone, which were identified after methylation producing 27—29. The ¹H-NMR spectrum of 20 showed signals assignable to three galloyl groups and five pairs of one-proton singlets ascribable to a hexahydroxydiphenoyl (HHDP) group and a valoneoyl unit in the aromatic region. The pairs of methine proton signals [δ 5.12 (s) and 4.87 (d, *J* = 1.5 Hz), H-1''], vinyl proton signals [δ 6.48 (s) and 6.20 (d, *J* = 1.5 Hz), H-3''] and aromatic proton signals [δ 7.22 (s) and 7.12 (s), H-3'''], are characteristic of a dehydrohexahydroxydiphenoyl (DHHDP) group existing as an equilibrium mixture of six- and five-membered hemiacetal forms, as found in the geraniin (9) molecule.⁷⁾ Duplication of the signals were also observed for the sugar proton signals (Table I) and some other signals, and was thus attributed to the presence of a DHHDP group in 20. The paired signals due to the DHHDP group are also exhibited in the ¹³C-NMR spectrum of 20, by the signals of an α,β -unsaturated ketone system [δ 192.0, 195.0 (C-4''); 154.1, 149.3 (C-2''); 128.7 (C-3'')] and methine carbon signals [δ 46.0 and 52.0 (H-1'')].

Upon condensation with *o*-phenylenediamine in an acidic medium, 20 gave a phenazine derivative (22). Its ¹H-NMR spectrum, which is simplified by the absence of duplication of peaks, clearly indicated the presence of an HHDP and a valoneoyl group [δ 7.12, 6.97, 6.65, 6.64, 6.22 (each 1H, s)] in addition to a phenazine [δ 8.31, 7.49 (1H each, s) and 7.99 (2H, m), 8.32, 8.20 (1H each, br d, *J* = 9 Hz)] and three galloyl [δ 7.01 (2H, s), 6.95 (4H, s)] units. The sugar proton signals and the aromatic proton signals shown above are similar to those of the phenazine derivative (24)³⁾ from euphorbin F (23), except for the

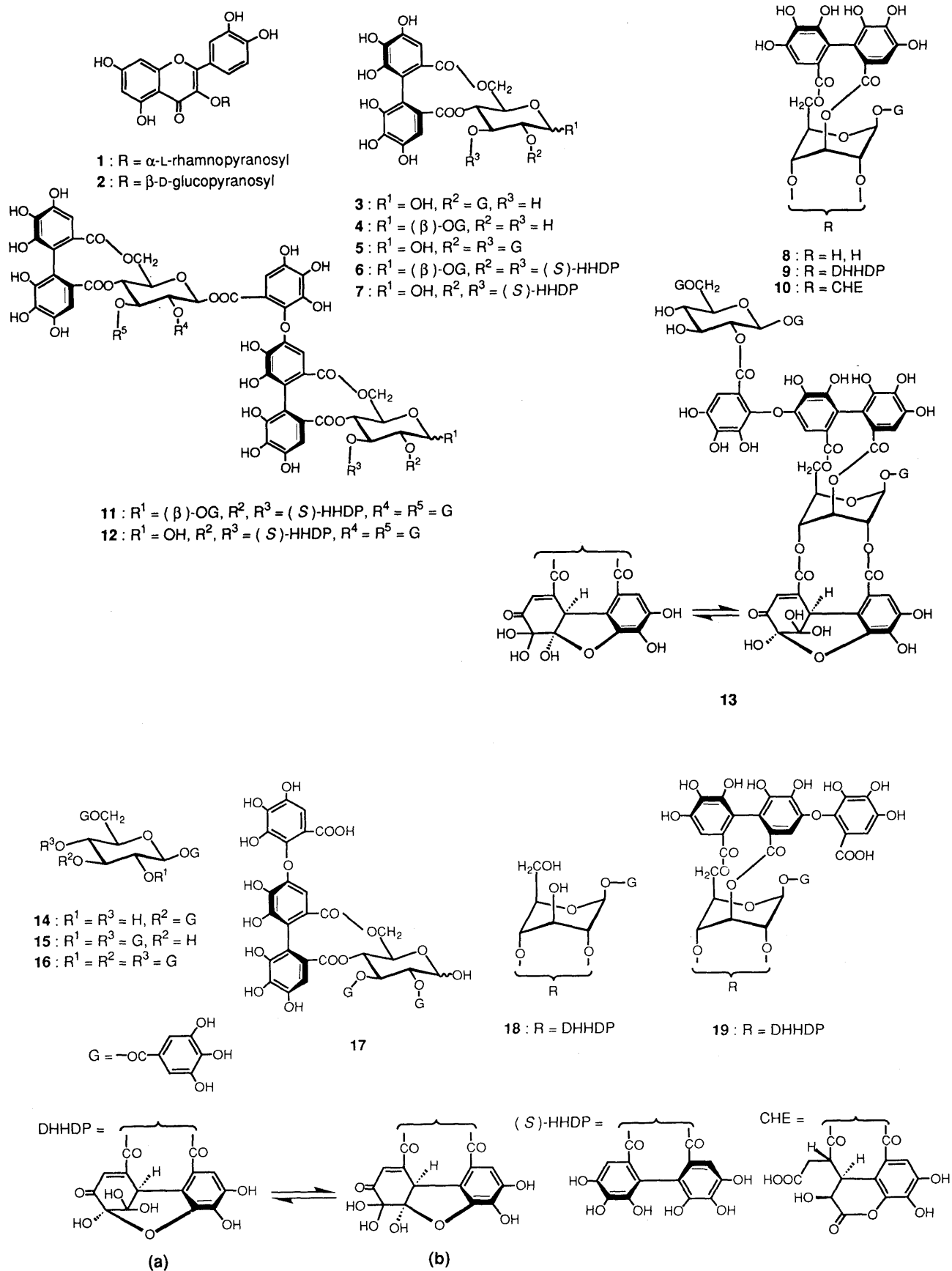


Chart 1

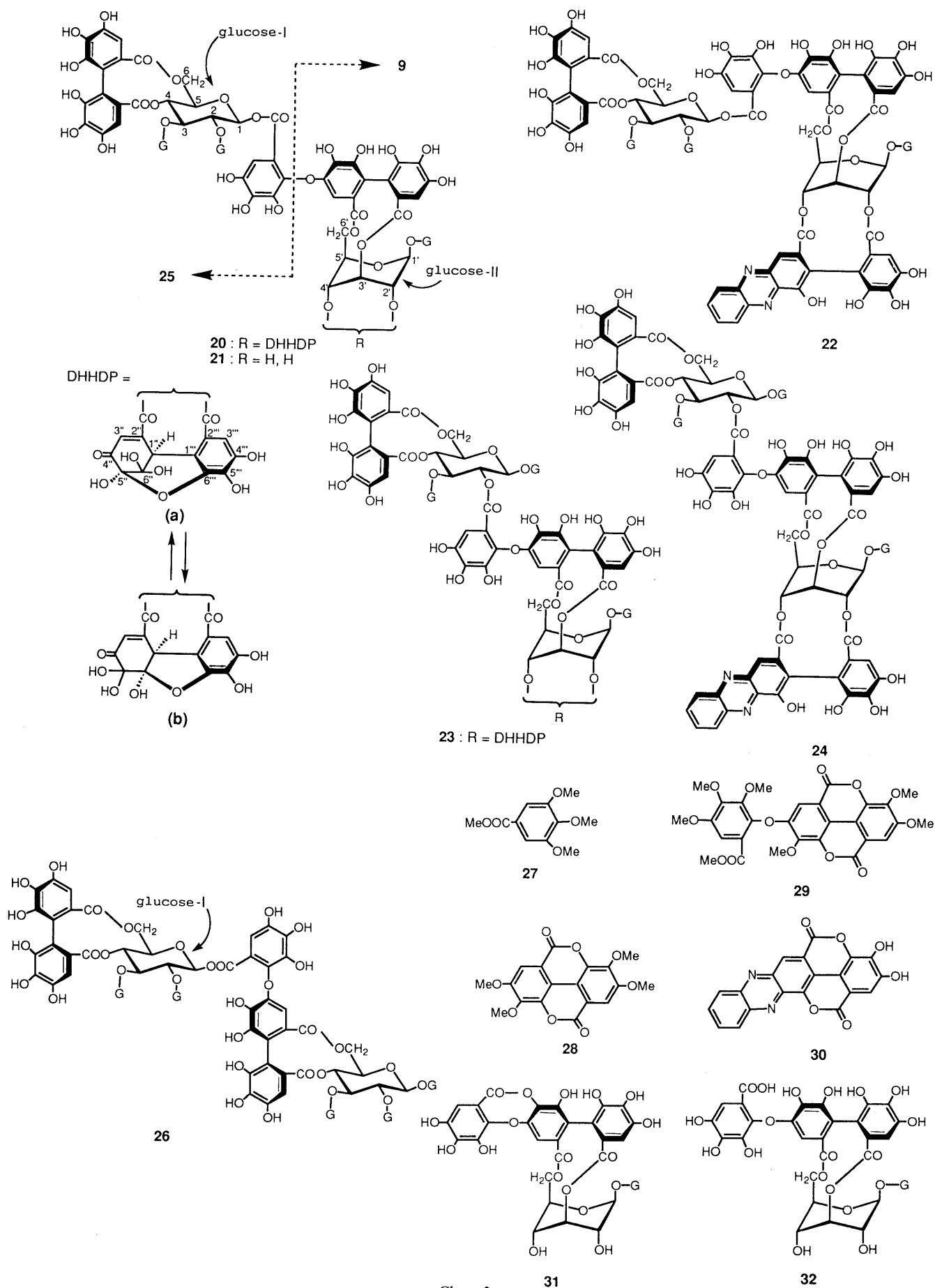


Chart 2

TABLE I. ^1H -NMR Spectral Data for the Glucose Moieties of **20**, **22** and **24** (500 MHz, Acetone- d_6 + D_2O , J in Hz)

Protons	20		22	24
	a-Form	b-Form		
Glucose-I				
H-1	6.01 (d, $J=8.5$)	6.01 (d, $J=8.5$)	6.05 (d, $J=8.5$)	5.95 (d, $J=9$)
H-2	5.56 (dd, $J=8.5, 10$)	5.56 (dd, $J=8.5, 10$)	5.57 (dd, $J=8.5, 10$)	5.60 (t, $J=9$)
H-3	5.77 (t, $J=10$)	5.77 (t, $J=10$)	5.78 (t, $J=10$)	5.31 (t, $J=9$)
H-4	5.17 (t, $J=10$)	5.17 (t, $J=10$)	5.17 (t, $J=10$)	5.09 (t, $J=10$)
H-5	4.48 (dd, $J=7, 10$)	4.48 (dd, $J=7, 10$)	4.49 (br dd, $J=6.5, 10$)	4.31 (dd, $J=6.5, 10$)
H-6	5.32 (dd, $J=7, 13$)	5.31 (dd, $J=7, 13$)	5.33 (dd, $J=6.5, 12$)	5.24 (dd, $J=6.5, 14$)
	3.88 (d, $J=13$)	3.87 (d, $J=13$)	3.87 (br d, $J=12$)	3.80 (d, $J=14$)
Glucose-II				
H-1'	6.52 (brs)	6.49 (brs)	6.10 (d, $J=6$)	6.11 (d, $J=6$)
H-2'	5.54 (brs)	5.53 (brs)	5.64 (d, $J=6$)	5.64 (d, $J=6$)
H-3'	5.40 (brs)	5.51 (brs)	5.78 (d, $J=4$)	5.51 (d, $J=4$)
H-4'	5.42 (brs)	5.32 (brs)	5.50 (d, $J=4$)	5.47 (d, $J=4$)
H-5'	} 4.71	4.86 (br t, $J=8$)	4.90 (dd, $J=4, 8.5$)	4.92 (dd, $J=4, 8$)
H-6'		4.56 (dd, $J=8, 11$)	4.59 (dd, $J=8.5, 12$)	4.73 (dd, $J=8, 12$)
		4.34 (dd, $J=8, 11$)	3.97 (dd, $J=4, 12$)	4.02 (dd, $J=4, 12$)
	4.22 (br t)			

chemical shift of H-3 ($\Delta\delta 0.47$ ppm) (Table I). In the ^{13}C -NMR spectrum of **22**, 12 sugar carbon signals are also closely similar to those of **24**, indicating that euphorbin G is an analog of **23** composed of geraniin (**9**) and tellimagrandin II (**25**) units, which are connected with each other, accompanied by the formation of a valoneoyl group. The molecular formula of **20** is thus $\text{C}_{82}\text{H}_{56}\text{O}_{53}$, which is consistent with the FAB-MS data. One of the main features distinguishing **20** from **23** in the ^{13}C -NMR spectra was the chemical shift of the C-1 signal ($\Delta\delta 0.4$ ppm) and C-3 signal ($\Delta\delta 0.8$ ppm) as shown in Table II. The ^{13}C resonances of the glucose-I signals were notably similar to those of rugosin D (**26**),⁸ suggesting that euphorbin G (**20**) is an isomer of **23** concerning the location of the galloyl part of the valoneoyl group on the glucose-I. The position of the acyl group on the glucose-I was determined by the production of tellimagrandin I (**5**), phenazine C (**30**),⁷ and the hydrolyzate 1 (**21**), upon mild partial hydrolysis of **22** in hot water (30 min). The ^1H -NMR spectrum of the hydrolyzate 1 showed the presence of three galloyl groups and an HHDP and a valoneoyl group, and two glucopyranose residues. It also showed that the H-2 and H-4 signals of the $^1\text{C}_4$ glucose core are shifted upfield ($\delta 4.05$ and 4.37) compared with those of **22**. These data, together with the FAB-MS data [m/z 1593 ($\text{M}+\text{Na})^+$], indicated structure **21** for this hydrolyzate. The production of **5** in this hydrolysis confirmed the position of the galloyl part of the valoneoyl group at O-1 on the glucose-I. Upon treatment with a weak alkali, **22** afforded, besides **5** and **30**, the hydrolyzate 2 (**31**). The ^1H -NMR spectrum of **31** showed signals due to a galloyl and a valoneoyl group, and glucose proton signals similar to those of **8**. The chemical shifts of the valoneoyl protons ($\delta 7.14$, 6.95 and 6.86), which are analogous to those of euprostin C,⁴ along with the FAB-MS data, indicated that this product has a depsidone structure (**31**) which is also consistent with the ^{13}C -NMR spectrum.⁴ Following treatment with hot water, **31** yielded isomallotinic acid (**32**),¹⁸ thus providing evidence

TABLE II. ^{13}C -NMR Data for the Glucose Moieties of **20**, **23** and **26** (127 MHz, Acetone- d_6 + D_2O)

Carbons	20		23		26
	a-Form	b-Form	a-Form	b-Form	
Glucose-I					
C-1	93.2		93.6		93.1
C-2	71.6		71.6, 71.5		71.7
C-3	73.2		74.0		73.2 ^a
C-4	70.5		70.4		70.5 ^b
C-5	72.8, 72.9		72.7		72.8 ^c
C-6	63.0		62.9		63.0 ^d
Glucose-II					
C-1'	91.0	91.9	91.0	92.0	93.5
C-2'	70.0	70.8	70.0	70.8	71.7
C-3'	63.3	62.5	63.3	62.5	73.1 ^a
C-4'	65.8	66.9	65.9	66.9	70.6 ^b
C-5'	72.4	73.2	72.5	73.4	72.9 ^c
C-6'	63.6	63.9	63.8	64.1	62.9 ^d

a–d) Values with the same superscript are interchangeable.

for the orientation and absolute configuration of the valoneoyl group at O-3/O-6 of glucose-II.

Euphorbin H was obtained as an off-white amorphous powder. Its ^1H -NMR spectrum indicated the presence of three galloyl groups, an HHDP and a valoneoyl group in the aromatic field. Two sets of sugar proton signals were in agreement with the sum of **25** and **8**. These spectral characteristics were the same as those of the hydrolyzate 1 (**21**) derived from **22** as mentioned above. The identity of euphorbin H as **21** was confirmed by the direct comparison of their physical data.

The similarity in ellagitannin composition found by the present study shows the chemotaxonomic resemblance between *E. prostrata* and *E. makinoi*, since five monomeric ellagitannins (**3**, **5**, **7–9**) and three dimers (**12**, **20**, **21**) among eleven (from *E. makinoi*)-thirteen (from *E. prostrata*) ellagitannins, are commonly present in both species of the plants. The present study has also revealed that the tannins produced by *E. prostrata*

collected in Okayama (Japan) are different from those⁴⁾ produced by the plant collected as "*E. prostrata*" in Fujian (China).¹⁹⁾ Because of prolific naturalization of the *Euphorbia* species in east Asia, further establishment of chemotaxonomy with components of various types, based on firm morphological evidence, should be required.

Experimental

¹H- and ¹³C-NMR spectra were measured in acetone-*d*₆ + D₂O unless otherwise stated, on a Varian VXR-500 instrument (500 MHz for ¹H-NMR and 127 MHz for ¹³C-NMR). Chemical shifts are given in δ values (ppm) relative to that of the solvent [acetone-*d*₆ (δ_H 2.04; δ_C 29.8)] on a tetramethylsilane scale. Details of the other instruments and chromatographic conditions used throughout this work are the same as described in the previous paper.¹⁾

Isolation of Tannins from *E. prostrata* *E. prostrata* was collected in Okayama City, Japan, in October 1989. The identity of plant material was confirmed by direct comparison with the voucher specimen (ED-M8-1990)²⁰⁾ deposited at the Department of Botany, Faculty of Science, Kyoto University. The dried leaves (1 kg) were homogenized in 70% aqueous acetone (10 l $\times$ 3) and filtered. The concentrated solution (ca. 2 l) was extracted with Et₂O (0.6 l $\times$ 3), EtOAc (0.6 l $\times$ 10) and *n*-BuOH saturated with H₂O (0.6 l $\times$ 10), successively, to give the Et₂O extract (4.1 g), EtOAc extract (28 g) and *n*-BuOH extract (31 g). A part (5 g) of the EtOAc extract was chromatographed over Toyopearl HW-40 (coarse) (2.2 cm i.d. $\times$ 60 cm) with EtOH-H₂O (6:4 $\rightarrow$ 7:3 $\rightarrow$ 8:2) $\rightarrow$ EtOH-acetone-H₂O (7:1:2 $\rightarrow$ 6:2:2 $\rightarrow$ 5:3:2) $\rightarrow$ acetone-H₂O (7:3) in a stepwise gradient mode. The eluate with EtOH-H₂O (6:4) gave quercitrin (**1**) (50.2 mg) and isoquercitrin (**2**) (11 mg). The eluate with EtOH-H₂O (7:3) afforded corilagin (**8**) (62 mg), tellimagrandin I (**5**) (183 mg), geraniin (**9**) (62 mg), 2-*O*-galloyl-4,6-(*S*)-hexahydroxydiphenoyl-D-glucose (**3**) (19 mg) and strictinin (**4**) (36 mg). Euphorbin G (**20**) (318 mg) and rugosin F (**11**) (46 mg) were obtained from the eluate with EtOH-acetone-H₂O (6:2:2), and (5:3:2), respectively.

The *n*-BuOH extract (10 g) was subjected to column chromatography over Dia-ion HP-20 (2.8 i.d. $\times$ 28 cm) and developed with MeOH-H₂O (5:95 $\rightarrow$ 1:9 $\rightarrow$ 2:8 $\rightarrow$ 3:7 $\rightarrow$ 4:6 $\rightarrow$ 5:5 $\rightarrow$ 7:3) in a stepwise gradient mode. The eluate with MeOH-H₂O (2:8) gave pedunculagin (**7**) (822 mg). The eluate with MeOH-H₂O (4:6) (1.6 g) was further chromatographed over MCI-gel CHP-20P with aqueous MeOH to give tellimagrandin I (**5**) (41 mg), euphorhelin (**13**) (41 mg), euphorbin G (**20**) (96 mg) and degalloylrugosin F (**12**) (41 mg). The eluate with MeOH-H₂O (7:3) was similarly purified by column chromatography on MCI-gel CHP-20P to afford euphorbin H (**21**) (39 mg).

Isolation of Tannins from *E. makinoi* The dried aerial parts (260 g) of *E. makinoi*,²¹⁾ collected in Zhengzhou, China, were extracted in a similar way to *E. prostrata* to give Et₂O extract (3.8 g), EtOAc extract (7.6 g) and *n*-BuOH extract (11.0 g). A part (3 g) of the EtOAc extract was chromatographed over Toyopearl HW-40 (coarse) (2.2 i.d. $\times$ 30 cm) with MeOH-H₂O (5:5 $\rightarrow$ 6:4 $\rightarrow$ 7:3) to give chebulagic acid (**10**) (5 mg), geraniin (**9**) (165 mg), 1,3,6-tri-*O*-galloyl- β -D-glucose (**14**) (5 mg), 1,2,4,6-tetra-*O*-galloyl- β -D-glucose (**15**) (7 mg) and 1,2,3,4,6-tetra-*O*-galloyl- β -D-glucose (**16**) (5 mg).

The combination of column chromatographies of the *n*-BuOH extract over Dia-ion HP-20 and MCI-gel CHP-20P, as described for the *n*-BuOH extract of *E. prostrata*, afforded **3**, **5**, **7**, **8**, **9**, **12**, praecoxin A (**17**), furosin (**18**), mallotusinic acid (**19**), and euphorbins G (**20**) and H (**21**). Yields of the tannins from the *n*-BuOH extract (% in *n*-BuOH extract) were as follows: **3** 0.28%, **5** 0.09%, **7** 0.16%, **8** 0.18%, **9** 14.5%, **12** 1.73%, **17** 0.06%, **18** 0.06%, **19** 0.4%, **20** 0.19%, **21** 0.08%.

Euphorbin G (20**)** A light-brown amorphous powder, $[\alpha]_D -43^\circ$ ($c=1.0$, MeOH). Anal. Calcd for C₈₂H₅₆O₅₃·7H₂O: C, 48.87; H, 3.50. Found: C, 48.97; H, 3.62. UV λ_{max}^{MeOH} nm (log ϵ): 220 (5.14), 276 (4.79). FAB-MS m/z : 1911 (M+Na)⁺. CD (MeOH) $[\theta]$ (nm): +12 $\times 10^4$ (236); -2.6 $\times 10^4$ (286). ¹H-NMR δ : 7.13, 6.99, 6.94 (each 2H, s, galloyl), 7.22, 7.17 (each s, 1H in total), 7.09, 7.04 (each s, 1H in total), 7.08 (1H, s), 6.67, 6.66 (each s, 1H in total), 6.48, 6.46 (each s, 1H in total), 6.20, 6.18 (each s, 1H in total, HHDP and valoneoyl), glucose protons, see Table I. ¹³C-NMR δ : 162.3, 166.1, 166.3, 166.5, 167.7, 168.2 (ester carbonyl), glucose carbons, see Table II.

Acid Hydrolysis of Euphorbin G (20**)** A solution of **20** (5 mg) in 5% H₂SO₄ (2 ml) was heated in a boiling-water bath for 5 h. After cooling,

the reaction mixture was extracted with EtOAc. The aqueous layer was neutralized with ion-exchange resin [Amberlite IRA-410 (OH form)] and evaporated to dryness. The syrupy residue was analyzed after trimethylsilylation by GLC [capillary column, G-250 (1.2 mm i.d. $\times$ 40 m); column temperature, 170 $^\circ$; detection, hydrogen flame ionization detector (FID)] to show the liberation of glucose. The residue obtained from the EtOAc extract was methylated with CH₂N₂-Et₂O overnight at room temperature. After removal of the solvent, the methylated products were purified by preparative TLC [benzene-acetone (15:1)] to give methyl tri-*O*-methylgallate (**27**) (1.0 mg), tetra-*O*-methylellagic acid (**28**) (0.6 mg) and methyl hexa-*O*-methylvalonate dilactone (**29**) (0.9 mg).

Formation of Phenazine Derivative (22**) from **20**** A mixture of **20** (10 mg) and *o*-phenylenediamine (1.9 mg) in MeOH (4 ml) and 15% AcOH (12 ml) was left standing overnight at room temperature. After removal of the solvent, the residue was suspended in water. The yellowish insoluble materials were washed with H₂O, and then dissolved in a small amount of acetone. Reprecipitation by adding a large amount of CHCl₃ gave the phenazine derivative (**22**) (6 mg). $[\alpha]_D +31^\circ$ ($c=0.3$, MeOH). UV λ_{max}^{MeOH} nm (log ϵ): 218 (5.22), 279 (5.02). CD (MeOH) $[\theta]$ (nm): -5.4 $\times 10^4$ (214); +16 $\times 10^4$ (238); -8.3 $\times 10^4$ (283). ¹H-NMR, see text and Table I. ¹³C-NMR δ : 93.2 [glucose (Glc) C-1], 71.6 (Glc C-2), 73.2 (Glc C-3), 70.5 (Glc C-4), 72.8 (Glc C-5), 63.0 (Glc C-6), 91.5 (Glc C-1'), 76.4 (Glc C-2'), 68.5 (Glc C-3'), 67.6 (Glc C-4'), 76.6 (Glc C-5'), 65.2 (Glc C-6'), 105.3, 107.7, 108.1, 109.4, 109.7, 109.9 (2C), 110.0 (4C), 112.7, 113.1, 115.6, 115.8, 116.3, 116.5, 117.0 (2C), 119.4, 119.5, 119.7, 119.9 (2C), 123.7, 124.6, 125.4, 125.9, 130.0 (2C), 132.2, 132.4, 135.9, 136.3, 136.5, 136.8, 137.3, 138.9, 139.2, 139.4, 139.6, 139.7, 140.3, 141.3, 142.6, 142.7, 143.3, 144.2 (2C), 144.9 (2C), 145.0, 145.1 (2C), 145.2, 145.3, 145.7 (2C), 145.9 (4C), 146.7, 152.1 (aromatic), 162.4, 164.9, 166.3, 166.4, 166.5, 166.6, 167.7, 167.9, 168.1, 168.3 (ester carbonyl).

Partial Hydrolysis of **22** a) A suspension of **22** (63 mg) in H₂O (30 ml) was heated on a water-bath at 80 $^\circ$ C for 30 min. The brownish precipitate was collected by suction, then crystallized from tetrahydrofuran to afford phenazine C (**30**) (6.2 mg). The filtrate of the precipitate was evaporated and subjected to column chromatography over Toyopearl HW-40 (fine) with EtOH-H₂O (5:5 $\rightarrow$ 6:4 $\rightarrow$ 7:3). The eluates with EtOH-H₂O (6:4) and EtOH-H₂O (7:3) gave tellimagrandin I (**5**) (13.5 mg) and the hydrolyzate 1 (**21**) (11.6 mg), respectively. The latter was identified with euphorbin H by comparison of the physical data.

Hydrolyzate 1 (= Euphorbin H, **21**): A pale yellowish amorphous powder, $[\alpha]_D -12^\circ$ ($c=1.0$, MeOH). Anal. Calcd for C₆₈H₅₀O₄₄·16H₂O: C, 43.93; H, 4.45. Found: C, 43.63; H, 4.15. UV λ_{max}^{MeOH} nm (log ϵ): 218 (5.06), 275 (4.73). FAB-MS m/z : 1593 (M+Na)⁺. ¹H-NMR δ : 6.95, 7.00 (each 2H, s, galloyl), 6.24, 6.46, 6.68, 6.82, 7.13 (each 1H, s, HHDP and valoneoyl), glucose protons, see Table I.

b) A solution of **22** (140 mg) in 0.1 M NaOAc (35 ml) was heated at 60 $^\circ$ C for 30 min. After acidification with dil.-HCl followed by removal of the insoluble material [phenazine C (**30**)], the reaction mixture was chromatographed over MCI-gel CHP-20P with MeOH-H₂O (25:75 $\rightarrow$ 30:70 $\rightarrow$ 35:65 $\rightarrow$ 40:60) to give tellimagrandin I (**5**) (30 mg) (from the eluate with MeOH-H₂O (30:70) and the hydrolyzate 2 (**31**) (16.4 mg) (from the eluate with MeOH-H₂O 40:60).

Hydrolyzate 2 (**31**): An off-white amorphous powder, $[\alpha]_D -129^\circ$ ($c=1.0$, MeOH). UV λ_{max}^{MeOH} nm (log ϵ): 218 (4.75), 278 (4.36). FAB-MS m/z : 807 (M+Na)⁺. ¹H-NMR δ : 7.07 (2H, s, galloyl), 7.14, 6.95, 6.86 (each 1H, s, depsidonic valoneoyl), 6.34 (1H, d, $J=2.5$ Hz, H-1), 4.06 (1H, brs, H-2), 4.75 (1H, brs, H-3), 4.48, 4.49 (2H, overlapped signal, H-4, H-5), 4.71 (1H, t, $J=11$ Hz, H-6), 4.21 (1H, dd, $J=8, 11$ Hz, H-6). ¹³C-NMR δ : 94.4 (Glc C-1), 69.2 (Glc C-2), 71.3 (Glc C-3), 61.8 (Glc C-4), 75.3 (Glc C-5), 64.9 (Glc C-6), 109.7, 110.0, 110.3, 110.4 (2C), 110.9, 115.4, 120.6, 122.4, 132.3, 135.3, 137.2, 137.3, 139.4, 141.8, 143.5, 143.8, 145.2, 145.4, 145.8 (2C), 149.0, 151.7 (aromatic), 164.2, 165.6, 167.0, 167.4 (ester carbonyl).

Formation of Isomallotinic Acid (32**) from **31**** An aqueous solution of **31** (6 mg) was heated on a water-bath at 80 $^\circ$ C for 1 h, and the concentrated solution was subjected to column chromatography over MCI-gel CHP-20P with aqueous MeOH to give isomallotinic acid (**32**) (3.7 mg), $[\alpha]_D -93^\circ$ ($c=1.0$, MeOH). UV λ_{max}^{MeOH} nm (log ϵ): 217 (4.76), 265 (4.41). FAB-MS m/z : 825 (M+Na)⁺. ¹H-NMR δ : 7.07 (2H, s, galloyl), 7.04, 6.80, 6.45 (each 1H, s, valoneoyl), 6.32 (1H, d, $J=2$ Hz, H-1), 4.04 (1H, brs, H-2), 4.80 (1H, brs, H-3), 4.38 (1H, brs, H-4), 4.45 (1H, brdd, $J=8, 11$ Hz, H-5), 4.77 (1H, t, $J=11$ Hz, H-6), 4.05 (1H, dd, $J=8, 11$ Hz, H-6).

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