Elaeagnatins A—G, *C*-Glucosidic Ellagitannins from *Elaeagnus umbellata*[1)]

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Seven new tannins, elaeagnatins A—G, have been isolated from the leaves of *Elaeagnus umbellata* (Elaeagnaceae) together with fifteen known tannins and related polyphenols, and their structures have been characterized as monomeric and dimeric *C*-glucosidic ellagitannins on the basis of spectral and chemical evidence. Elaeagnatins B, C and F are the first dimers composed of *C*-glucosidic monomer and ellagitannin monomer with a gluconic acid core.

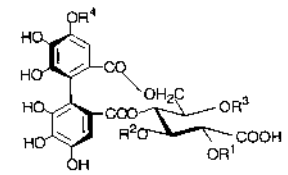
Key words *Elaeagnus umbellata*; Elaeagnaceae; *C*-glucosidic ellagitannin dimer; gluconic acid; lyxose; tannin

We previously reported the structures of hippophaenin A (**1**) and shephagenin A (**2**), a new class of ellagitannins based on a gluconic acid core, isolated from *Hippophae rhamnoides*[2)] and *Shepherdia argentea*[3)] (Elaeagnaceae), respectively. The inhibitory effect of these tannins on human immunodeficiency virus (HIV)-1 reverse transcriptase has also been reported.[3)] As part of our ongoing study to find further new tannins from the elaeagnaceous plants, we have now examined the polyphenols of *Elaeagnus umbellata* Thunb. whose leaves and fruits have been traditionally used as a tonic and an astringent to treat stomach and bowel disorders in Japan and China. Consequently, seven new tannins, named elaeagnatins A (**12**), B (**18**), C (**19**), D (**20**), E (**21**), F (**22**) and G (**23**), along with fifteen known tannins and related polyphenols were isolated from the leaf extract. We describe herein the structural elucidation of these new tannins.

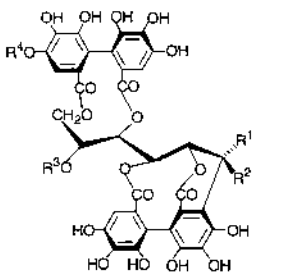
A concentrated solution of 70% aqueous acetone homogenate of the dried leaves of *E. umbellata* was partitioned with ether, ethyl acetate and 1-butanol, successively, to afford respective extracts and a water-soluble portion. The 1-butanol extract was subjected to a combination of column chromatography over Diaion HP-20, Toyopearl HW-40, MCI gel CHP-20P and Sephadex LH-20 to give 1,6-di-*O*-galloyl-β-D-glucose,[4)] pedunculagin,[5)] strictinin,[5)] punigluconin (**3**),[6)] lagerstannin C (**4**),[6)] and brevifolincarboxylic acid.[7)] Similar chromatographic separation of the water-soluble portion led to the isolation of elaeagnatins A—G and 12 known polyphenols. The known compounds were identified as 2,3-(*S*)-HHDP-D-glucose,[8)] valoneic acid dilactone, pedunculagin, strictinin, hippophaenin A (**1**),[2)] **3**, pterocarinin A (**6**),[9)] hippophaenin B (**7**),[2)] casuariin (**8**),[5)] desgalloylstachyurin (**9**),[10)] alienanin B (**16**)[11)] and casuglaunin A (**17**)[12)] by direct comparison with authentic specimens or by comparison of their physicochemical data with those reported in the literature.

Hippophaenin B (**7**) was first isolated together with **1** from *H. rhamnoides*. Evidence supporting the orientation of the valoneoyl group in **7**, which was proposed[2)] mainly based on the diagnostic chemical shifts[13)] of the valoneoyl proton signals in the ^{1}H-NMR spectrum, has now emerged from the ^{1}H–^{13}C long-range NMR shift correlation (COLOC) spectrum (Fig. 1). Namely, a signal at δ 6.20 which was assigned to the valoneoyl H_E by its correlation with ethereal carbon (δ 146.7) of the ring E was revealed to correlate with the glucose H-6 signal through a common ester carbonyl carbon (δ 169.0), confirming the binding mode of the valoneoyl group in **7**. The COLOC has established not only the connectivities of the other acyl protons with the glucose protons, as shown by arrows in Fig. 1, but also full assignments of the proton and carbon resonances of **7**, which had previously remained partly unsolved (see Experimental).

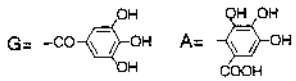
Elaeagnatin A (**12**) was isolated as a light-brown amorphous powder. The molecular formula was suggested to be $C_{53}H_{40}O_{35}$ based on a $(M+NH_4)^+$ ion peak at *m/z* 1254 in the electrospray ionization mass spectrum (ESI-MS) and the NMR spectral data described below. Although the ^{1}H-NMR and ^{13}C-NMR spectra of **12** were complicated, owing to multiple or broad signals arising from an equilibration at sugar moiety, the sugar proton and carbon signals were found to be almost superimposable on those of pterocarinin A (**6**) which possesses an equilibrated lyxose moiety at the C-1 β-position of an open-chain glucose residue. The difference in the ^{1}H-NMR spectra between **6** and **12** was indicated by the presence of an extra aromatic 1H-singlet in a major tautomer of the latter. Namely, **12** exhibited four 1H-singlets at δ 7.07, δ

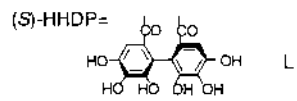


	R^1	R^2	R^3	R^4
1	(*S*)-HHDP		G	H
2	(*S*)-HHDP		G	A
2a	(*S*)-HHDP		H	A
3	G	H	G	H
4	H	H	G	H
5	(*S*)-HHDP		H	H



	R^1	R^2	R^3	R^4
6	H	L	G	H
7	OH	H	G	A
8	OH	H	H	H
9	H	OH	H	H
10	OH	H	G	H
11	H	OH	G	H
12	H	L	G	A





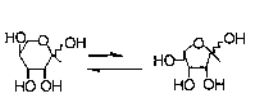


Chart 1

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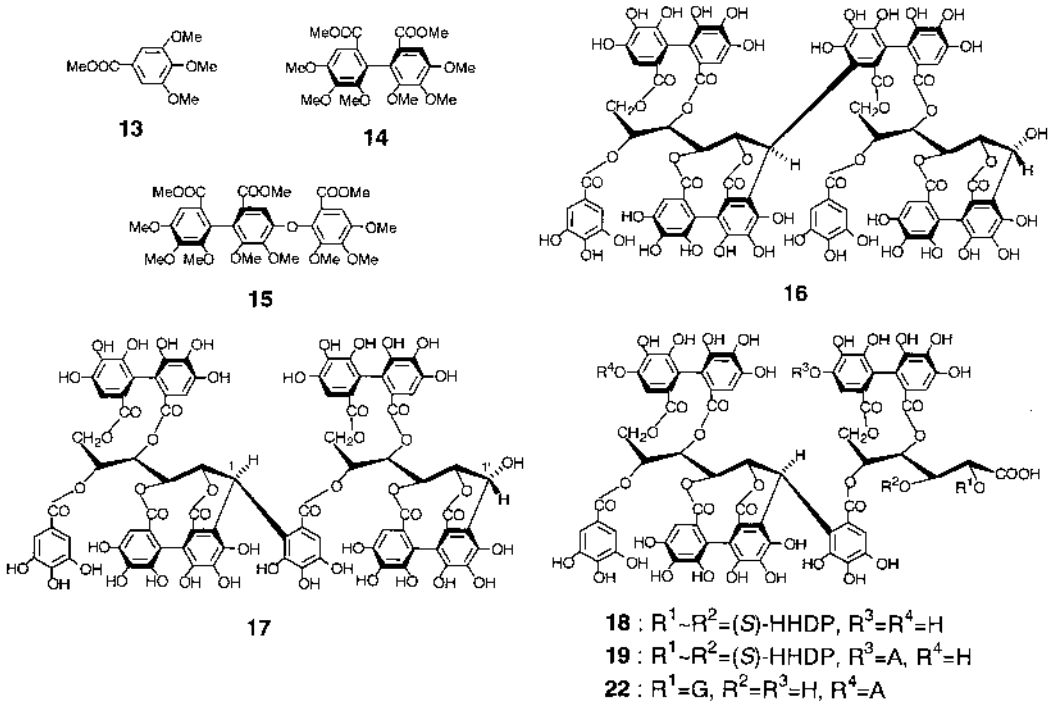


Chart 2

6.84, δ 6.45 and δ 6.20, as well as a 2H-singlet at δ 7.02 due to a galloyl group, suggesting that **12** has a valoneoyl group instead of one of two hexahydroxydiphenoyl (HHDP) groups in **6**. The presence of the valoneoyl group was verified by the methylation of **12**, followed by methanolysis yielding methyl tri-*O*-methylgallate (**13**) and trimethyl octa-*O*-methylvaloneate (**15**). This result also indicated that the valoneoyl group is at O-4/O-6 of the glucose core, but does not participate in *C*-glucosidic linkage. The position and orientation of the valoneoyl group were substantiated by long-range C–H correlations in the ^{1}H-detected heteronuclear multiple bond connectivity (HMBC) spectrum ($^{2,3}J_{C,H}$=6 Hz) of **12** as follows. The singlet signal (δ 6.20) at the highest field among the aromatic proton signals was assigned to H_E-3 of the valoneoyl group, based on the two-bond correlation with an ethereal phenyl carbon at δ 146.4.[14] The H_E-3 signal also showed a correlation with H-6 of the glucose through three bond couplings with a common ester carbonyl carbon at δ 168.6 (Fig. 2), thus providing definite evidence for binding sites of the valoneoyl group as shown in the formula. Atropisomerisms of the chiral HHDP and valoneoyl groups were both determined to be (*S*)-series by a large positive Cotton effect at 236 nm ([θ] $+1.5\times10^5$) in the circular dichroism (CD) spectrum.[15] Elaeagnatin A was thus assigned to the structure **12**.

Elaeagnatin B (**18**), a light-brown amorphous powder, showed a $(M+NH_4)^+$ ion peak at *m/z* 1888 and an $(M+H)^+$ ion peak at *m/z* 1871 in ESI- and FAB-MS, respectively. These data and elemental analysis of **18** were consistent with the molecular formula $C_{82}H_{54}O_{52}$. Based on the assignments of the ^{1}H-NMR signals by ^{1}H–^{1}H COSY (Table 1), this tannin was deduced to be a dimeric hydrolyzable tannin composed of two monomeric units having an open-chain glucose and a gluconic acid core. The chemical shifts and coupling patterns of the open-chain glucose core showed close similarity to those of stachyurin (**11**),[5] except for an upfield shift (δ 4.74) of the H-1 signal, as shown in Table 1. Similarly, the gluconic acid signals resembled those of hippophaenin A (**1**). These spectral features, along with aromatic proton signals [δ 7.13 (2H, s), δ 7.12, 6.92, 6.86, 6.68, 6.58, 6.57, 6.54, 6.53 (each 1H, s)], implied that the monomeric constituent units of **18** are **1** and **11**. This assignment was further substantiated by the close similarity of the sugar carbon resonances in the ^{13}C-NMR spectrum of **18** to those of **11** and **1**, except for a large upfield shift (*ca.* δ 25 ppm) of the C-1 resonance relative to that of the former. This upfield shift clearly indicates that dimerization between **1** and **11** occurred through C–C coupling at this position, removing a hydroxyl group. The configuration at C-1 in **18** was deduced based on a similarity of the coupling pattern of the H-1 to that of casuglaunin A (**17**). Methylation of **18** and subsequent methanolysis yielded **13** and dimethyl haxamethoxydiphenate (**14**). Treatment of **18** with tannase[16] gave a monomeric hydrolyzate in addition to gallic and ellagic acids. The partial hydrolyzate was identified with authentic lagerstannin A (**5**),[6] which was prepared from **1**. Based on these data, the structure of elaeagnatin B was assigned to **18**, which might be produced by intermolecular C–C coupling accompanied by dehydration between the glucose C-1 of **11** and the galloyl unit of **1**. The absolute configurations of the HHDP groups in **18** were determined to be all (*S*) by the strong positive Cotton effect at 235 nm in the CD spectrum.[15]

Elaeagnatin C (**19**) showed a pseudomolecular ion at *m/z* 2056 $(M+NH_4)^+$ in ESI-MS which is 168 mass units ($C_7H_4O_5$) larger than that of **18**. The molecular formula of **19** was thus assigned to $C_{89}H_{58}O_{57}$. The ^{1}H-^{1}H COSY spectrum of **19** revealed the presence of an open-chain glucose and a gluconic acid residue, as in **18**. Additionally, the sugar carbon resonances of **19** were almost superimposable on those of **18** (Table 2). On the other hand, the ^{1}H-NMR spectrum

Table 1. ^{1}H-NMR Spectral Data for the Sugar Moieties of Compounds **1**, **11** and **17**—**23**

Proton	**11**	**1**	**17**	**18**	**19**	**20**	**21**	**22**	**23**
H-1	4.93 d (2)		4.83 br s	4.74 br s	4.68 br s	4.75 br s	4.64 br s	4.92 br s	4.85 br s
H-2	4.86 t (2)		4.93 br s	4.93 br s	4.92 br s	4.92 br s	4.93 br s	4.92 br s	5.17 br s
H-3	4.98 t (2)		5.21 br s	5.20 br s	5.19 br s	5.26 br s	5.32 br s	5.28 br s	5.28 br s
H-4	5.62 dd (2, 9)		5.80 dd (2, 8)	5.78 br d (7.5)	5.74 br d (7)	5.74 br d (7.5)	5.73 dd (2, 7.5)	5.81 dd (2, 10.5)	5.76 br d (8.5)
H-5	5.36 dd (3, 9)		5.36 m (8.5)	5.33 br d (3.5, 7)	5.33 dd (7.5)	5.30 br d (7.5)	5.27 br d (8)	5.32 br d (3, 8.5)	5.35 dd
H-6	4.84 dd (3, 13)		4.94 dd (3.5, 13.5)	4.93 dd (3.5, 13.5)	4.89 dd (3.5, 12.5)	4.87 dd (3, 13)	4.84 dd (3, 13.5)	4.90 dd (3, 12)	4.89 dd (3, 13)
	4.02 d (13)		4.07 d (13.5)	4.03 d (13.5)	3.96 d (12.5)	3.99 d (13)	3.98 d (13.5)	3.99 d (12)	3.95 d (13)
H-1′			5.58 d (5)			5.61 d (5)	5.59 d (4.5)		6.05 d (8)
H-2′		5.36 d (10)	4.70 dd (2.5, 5)	5.38 d (9.5)	5.38 d (10)	4.72 dd (2, 5)	4.70 dd (2.5, 4.5)	5.43 d (4)	3.78 dd (8, 9.5)
H-3′		5.59 dd (1, 10)	5.46 t (5)	5.70 d (9.5)	5.72 br d (10)	5.44 m	5.46 m	4.57 dd (1.5, 4)	4.06 t (9.5)
H-4′		5.68 dd (1, 9)	5.44 dd (5, 11.5)	5.81 d (9)	5.76 br d (9)	5.44 m	5.41 dd (3.5, 9.5)	5.51 dd (1.5, 9)	4.90 t (9.5)
H-5′		5.60 dd (3.5, 9)	5.41 m	5.59 dd (3, 9)	5.55 dd (3, 9)	5.37 m	5.25 dd (3.5, 9.5)	5.84 dd (3, 9)	4.22 dd (5.5, 9.5)
H-6′		5.02 dd (3.5, 13.5)	4.99 dd (2.5, 13.5)	5.12 dd (3, 13.5)	5.13 dd (3, 13.5)	4.94 dd (3, 13)	4.96 dd (3.5, 13.5)	4.97 dd (3, 13)	5.20 dd (5.5, 13)
		4.06 d (13.5)	4.29 d (13.5)	4.36 d (13.5)	4.29 d (13.5)	4.25 d (13)	4.28 d (13.5)	4.14 d (13)	3.79 d (13)

500 MHz in acetone-d_6+D_2O, coupling constants (J in Hz) are given in parentheses.

Table 2. ^{13}C-NMR Spectral Data for the Sugar Moieties of Compounds **1**, **11**, **17**—**23** and Strictinin

Carbon	**11**	**1**	Strictinin	**17**	**18**	**19**	**20**	**21**	**22**	**23**
C-1	65.5			41.2	40.7	40.6	41.5	41.6	41.6	40.4
C-2	81.0			81.7	80.9	80.9	81.7	81.7	82.0	81.9
C-3	70.9			73.5	74.1	74.5	73.8	73.7	75.6	74.7
C-4	73.3			74.0	74.6	75.0	73.9	74.1	73.7	72.8
C-5	72.0			71.2	72.2	72.4	71.4	71.6	71.7	70.1
C-6	64.5			63.8	63.4	63.6	64.1	64.1	64.2	63.2
C-1′		168.6	95.5	67.0	168.7	169.4	67.2	67.4	171.1	94.7
C-2′		72.6	72.7	76.7	72.4	72.7	76.6	76.6	73.6	72.0
C-3′		73.6	75.5	70.9	73.0	73.4	70.9	71.1	74.3	74.3
C-4′		70.1	74.5	75.1	70.7	70.4	75.5	75.7	71.3	73.9
C-5′		70.1	73.0	73.0	69.3	69.4	72.9	72.8	69.8	72.5
C-6′		64.7	63.6	64.1	63.4	63.6	64.1	64.5	65.3	63.7

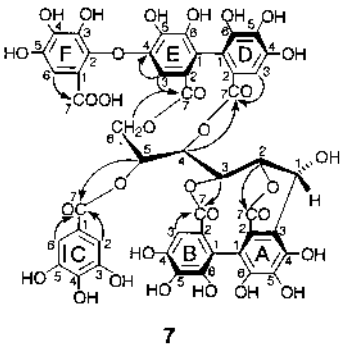
125.7 MHz in acetone-d_6+D_2O.

exhibited a galloyl signal (δ 7.11) and nine aromatic 1H singlets, δ 7.11, 7.04, 6.94, 6.89, 6.71, 6.59, 6.58, 6.53, 6.13. These spectral features clearly indicated that elaeagnatin C is a *C*-glucosidic ellagitannin dimer in which an HHDP group in **18** is replaced by a valoneoyl group. The presence of the valoneoyl group in elaeagnatin C was chemically confirmed by the methylation of **19** followed by methanolysis which yielded **15** in addition to **13** and **14**. Upon enzymatic hydrolysis with tannase, **19** yielded a monomeric hydrolyzate (**2a**) as judged by normal phase HPLC. The compound **2a** was identical with desgalloylshephagenin A (**2a**) obtained by similar treatment of **2**, indicating that the location of the valoneoyl group in **19** was at O-4/O-6 of the gluconic acid core. The (*S*)-configuration of both HHDP and valoneoyl groups in **19** were evidenced by a large positive Cotton effect ([θ] $+3.0\times10^5$) at 234 nm in the CD spectrum.[15] Consequently, the structure of elaeagnatin C was elucidated as **19**.

Elaeagnatin F (**22**) was obtained as a light-brown amorphous powder. The methylation of **22** followed by methanolysis yielded **13**, **14** and **15** common to those from **18** and **19**. The ^{1}H-NMR spectrum of **22** was closely similar to that of elaeagnatin C (**19**), except for the absence of an HHDP group and the existence of an extra galloyl group. Upon comparison of the sugar proton signals between **22** and **19** (Table 1), a remarkable upfield shift of the H-3′ signal ($\Delta\delta$ 1.15 ppm) in **22** was observed, indicating that the hydroxyl group at C-3′ of the gluconic acid core is not acylated. Actually, the gluconic acid signals were closely comparable to those of punigluconin (**3**). In addition, the ESI-MS of **22** showed a molecular ion species $(M+NH_4)^+$ at *m/z* 1906 ($C_{82}H_{56}O_{53}+NH_4$) corresponding to the loss of 150 mass units ($C_7H_2O_4$) from **19** (*m/z* 2056). Based on these data,

elaeagnatin F was presumed to be a *C*-glucosidic ellagitannin dimer in which an HHDP group at O-2′/O-3′ in **19** is replaced by a galloyl group at O-2′. The substitution mode of acyl groups in **22** was determined by the HMBC measurement ($^{2,3}J_{C,H}$=6 Hz) (Fig. 2). The aromatic proton signal at δ 6.18 was first assigned to H_E of the valoneoyl group based on its correlation through two-bond coupling with an ethereal carbon signal of C_E-4 (δ 146.8) of the valoneoyl E-ring,[14] and also through three-bond coupling with C_E-1 (δ 117.3). The H_E signal showed a correlation by three-bond coupling with the ester carbonyl carbon resonance at δ 168.6, which, in turn, correlated with the H-6 signal, δ 4.90, of the *C*-glucosidic unit. The location and orientation of the valoneoyl group in **22** was thus established, as shown in the formula. The HMBC spectrum displayed three-bond long-range couplings of the glucose H-1 with C-1 and C-3 of the H-ring, which was shown to be at O-5′ of the gluconic acid core based on long-range correlations of the aromatic proton, δ 7.22 (H_H-6), with the gluconic H-5′ through a common ester carbonyl carbon (δ 167.7). These data indicated an intermolecular linkage of monomers, as shown in the formula **22**. The locations of the other acyl groups on the sugars including those of the galloyl groups were also indicated by similar long-range correlations as shown by arrows in Fig. 2. The (*S*)-configuration of the valoneoyl group and HHDP groups in **22** was determined by CD spectral analogy to **18** and **19**.[15] Based on these data, the structure of elaeagnatin F was concluded to be represented by the formula **22**.

Elaeagnatin D (**20**), $[\alpha]_D$ +96.6° (MeOH) and elaeagnatin E (**21**), $[\alpha]_D$ +98.5° (MeOH), were obtained as light-brown amorphous powders, and were found to be ellagitannin dimers of the molecular formulae $C_{89}H_{58}O_{56}$ and $C_{96}H_{62}O_{61}$, respectively, as indicated by ESI-MS [*m/z* 2040 $(M+NH_4)^+$ for **20** and *m/z* 2208 $(M+NH_4)^+$ for **21**]. Their ^{1}H- and ^{13}C-NMR spectra in the aliphatic region are closely comparable to those of casuglaunin A (**17**), as shown in Tables 1 and 2, suggesting that these tannins are dimers composed of casuarinin (**10**) and stachyurin (**11**) units, in which both anomeric centers have the same configurations as those of **17**. The dis-



7

Fig. 1. Selected ^{1}H–^{13}C Long-range Correlations of **7**

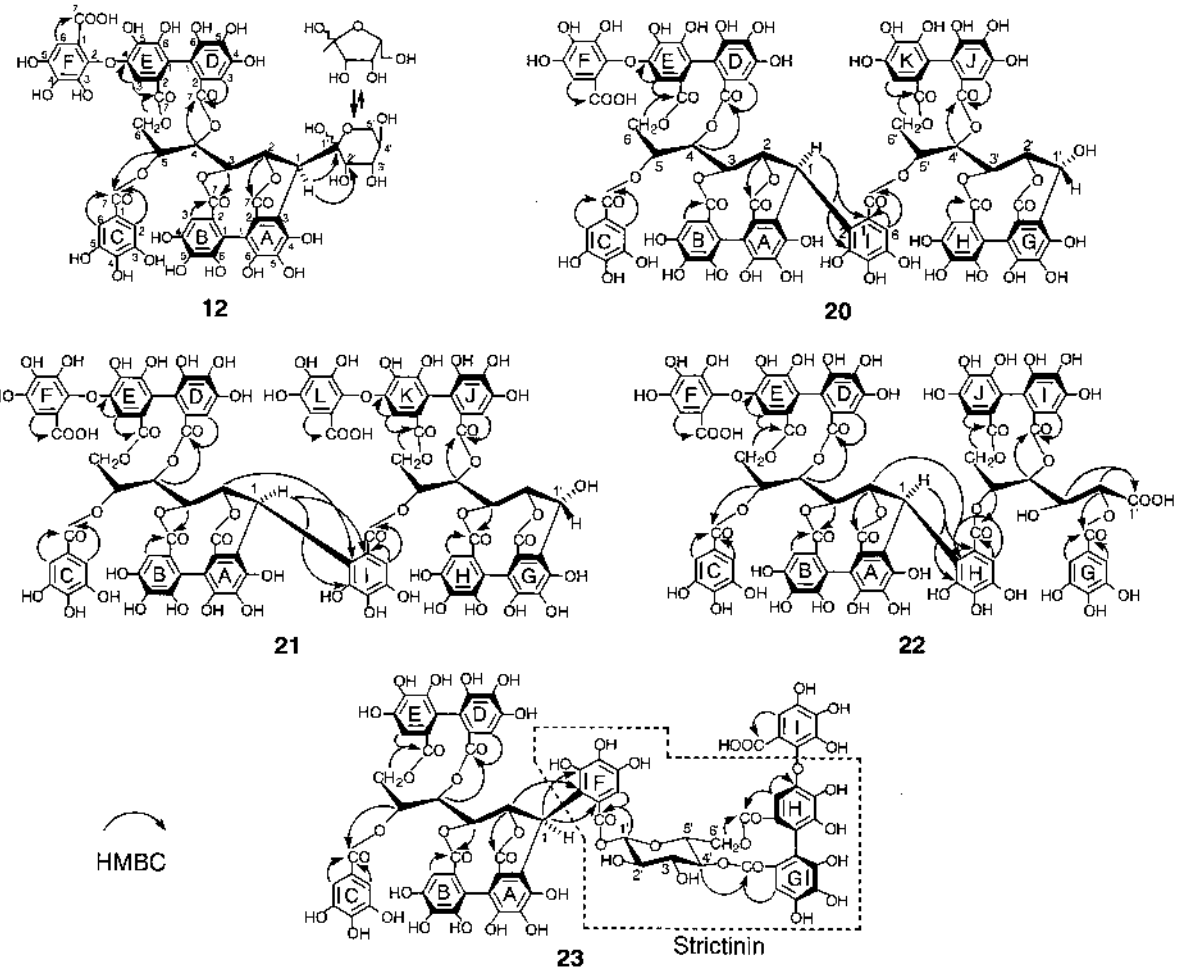


Fig. 2. Structures and Selected HMBC Correlations of **12** and **20**—**23**

tinguishing feature of the ^{1}H-NMR spectrum of these tannins from that of **17** was observed in the number of aromatic proton signals. Compound **20** showed eight 1H-singlets as well as a 2H-singlet, which include an extra 1H-singlet relative to **17**, while **21** exhibited nine 1H-singlets. Upon methylation and subsequent methanolysis, **20** afforded **13**, **14** and **15**, whereas **21** yielded **13** and **14** as major products. These findings indicate that these tannins are *C*-glucosidic ellagitannin dimers in which one HHDP group of **17** for **20** and two HHDP for **21** are replaced by the valoneoyl groups, respectively. This assumption is consistent with each increment of 190 mass units on going from **17** to **20** and **21** in the MS spectra. The binding modes of the valoneoyl groups of both **20** and **21** were clarified with the aid of HMBC spectra ($^{2,3}J_{C,H}$=6 Hz), as indicated by arrows in Fig. 2. The CD spectra of these tannins showed positive Cotton effects in the short-wavelength region ($[\theta]_{234}$ +3.4×10^5 and $[\theta]_{228}$ +2.8×10^5, respectively), confirming the (*S*)-configurations for all of the HHDP and valoneoyl groups in each compound.[15] On the basis of these data, the structures of elaeagnatins D and E were represented by **20** and **21**, respectively.

The structure **23** of elaeagnatin G was determined as follows. The molecular formula was determined to be $C_{75}H_{52}O_{48}$ based on ESI-MS [*m/z* 1738 $(M+NH_4)^+$], FAB-MS [*m/z* 1721 $(M+H)^+$] and elemental analysis. The ^{1}H-NMR spectrum (Table 1) exhibited sugar proton signals charasteristic of an open-chain glucose and a glucopyranose core with a $^4C_1$-conformation. The chemical shifts of the former were in agreement with the corresponding signals of **17**—**22**, indicating the presence of stachyurin unit with an intermolecular C–C linkage at the C-1 position. On the other hand, among the signals due to the $^4C_1$ glucopyranose residue, those at the upfield region [δ 3.78 (dd, *J*=8, 9.5 Hz) and δ 4.06 (t, *J*=9.5 Hz)] were assigned to H-2′ and H-3′ to indicate the presence of free hydroxyl groups at the concerned positions. The β-oriented acyl group at the anomeric center was evidenced by a large coupling constant (*J*=8 Hz) of the H-1′ signal at the downfield region (δ 6.05). Methylation of **23** followed by methanolysis yielded **13**, **14** and **15**. Taking into consideration the structural similarity to **17**—**22**, the aromatic proton signals (a 2H-singlet and seven 1H-singlets) in the ^{1}H-NMR spectrum of **23** were accounted for by the presence of a valoneoyl, two galloyl and two HHDP groups, among which each one of the galloyl and HHDP groups participate in the C–C linkage to the glucose. These assignments were confirmed by the ^{13}C-NMR spectrum of **23**, which exhibited sugar carbon resonances closely comparable to those of strictinin and the stachyurin moiety of **17**—**22** (Table 2) and nine ester carbonyl carbon resonances. The location and orientation of the valoneoyl group in **23** were unequivocally determined by HMBC spectrum (Fig. 2). The valoneoyl proton signal (H_G) at δ 6.79 was correlated with the H-4′ of a strictinin unit through three-bond coupling with the common ester carbonyl resonance at δ 167.7. Similarly, the valoneoyl H_H (δ 6.18) was correlated through a common ester carbon with the H-6′ signal of the strictinin unit. The absolute configurations at the biphenyl moieties in **23** were determined to be all (*S*), based on the CD spectrum of **23**, which showed a strong Cotton effect at 230 nm.[15] This evidence led us to establish the structure of elaeagnatin G as formula **23**.

Although ellagitannins linked to a lyxose moiety through a C–C bond have been isolated from Lythraceae, Myrtaceae, Juglandaceae, and Fagaceae, the isolation of **12** is the first example of an ellagitannin of this type in Elaeagnaceae. It is also noteworthy that **18**, **19** and **22** are the first examples of ellagitannin dimers composed of a *C*-glucosidic monomer and an ellagitannin monomer based on a gluconic acid core.

Experimental

Optical rotations were recorded on a JASCO DIP-1000 polarimeter. ^{1}H- and ^{13}C-NMR spectra were measured in acetone-d_6-D_2O and methanol-d_4 on Varian VXR-500 (500 MHz for ^{1}H-NMR and 125.7 MHz for ^{13}C-NMR) instruments. Chemical shifts are given in δ (ppm) values relative to that of the solvent [acetone-d_6 (δ_H 2.04; δ_C 29.8), methanol-d_4 (δ_H 3.35; δ_C 49.8)] on a tetramethylsilane scale. ESI-MS were carried out with a Micromass Auto Spec OA-Tof mass spectrometer (solvent: 50% MeOH+0.1% $AcONH_4$, flow rate: 20 μl/min). FAB-MS was taken on a VG 70-SE mass spectrometer using 3-nitrobenzyl alcohol as the matrix agent. CD spectra were measured on a JASCO J-720W spectrometer. Normal-phase HPLC was conducted on a YMC-Pack SIL A-003 (YMC Co., Ltd.) column (4.6 mm i.d.×250 mm) developed with *n*-hexane–MeOH–THF–formic acid (60 : 45 : 15 : 1) containing oxalic acid (500 mg/1.2 l) (solvent A) (flow rate, 1.5 ml/min; detection 280 nm), and *n*-hexane–EtOAc (2 : 1) (solvent B) at room temperature. Reversed-phase HPLC was performed on a YMC-Pack ODS-A A-302 (YMC Co., Ltd.) column (4.6×150 mm) developed with 10 mM H_3PO_4–10 mM KH_2PO_4–EtOH–EtOAc (45 : 45 : 8 : 2) (solvent C) (flow rate, 1 ml/min; detection 280 nm) at 40 °C. Detection was effected with a Simadzu SPD-6A spectrophotometric detector at 280 nm. A YMC-Pack A324 (YMC Co., Ltd.) (10×300 mm) column was used for preparative HPLC. Solvents were evaporated under reduced pressure below 40 °C.

Extraction and Isolation The dried leaves (1.7 kg) of *E. umbellata*, collected in July 1993, were homogenized in 70% acetone (10 l×3), and the concentrated solution (1.6 l) was extracted with ether (1 l×6), ethyl acetate (1.5 l×6) and 1-butanol saturated with water (1.2 l×6), successively. The H_2O extract (190 g) was chromatographed over Diaion HP-20 (6.7 cm i.d.×65 cm) with H_2O→aqueous MeOH (10%→20%→30%→40%→60% MeOH)→MeOH→70% acetone–H_2O. The eluate (8.4 g) from 10% MeOH was fractionated and purified by rechromatography over Toyopearl HW-40 (coarse grade, 2.2 cm i.d.×62 cm) and/or MCI-gel CHP-20P (75—150 μm, 1.1 cm i.d.×32 cm) with aqueous MeOH followed by preparative HPLC [YMC A-312 (10 mm i.d.×300 mm); solvent, 10 mM H_3PO_4–10 mM KH_2PO_4–EtOH–EtOAc (47.5 : 47.5 : 4 : 1)] to give valoneic acid dilactone (5 mg), hippophaenins A (**1**) (1.2 g), B (**7**) (1.6 g), punigluconin (**3**) (15 mg), casuariin (**8**) (6 mg), elaeagnatin A (**12**) (1.4 g), alienanin B (**16**) (53 mg), casuglaunin A (**17**) (61 mg), elaeagnatins D (**20**) (20 mg), E (**21**) (10 mg), F (**22**) (20 mg) and G (**23**) (33 mg). The 20% MeOH (7.7 g) and 30% MeOH (6.8 g) eluates were separately subjected to column chromatographies over Toyopearl HW-40 (coarse grade, 2.2 cm i.d.×70 cm) with aqueous MeOH, MCI-gel CHP-20P (75—150 μm, 1.1 cm i.d.×33 cm) with H_2O and aqueous MeOH, and/or Sephadex LH-20 (1.1 cm i.d.×30 cm) with EtOH and finally purified by preparative HPLC [YMC A-312 (10 mm i.d.×300 mm); solvent, 10 mM H_3PO_4–10 mM KH_2PO_4–EtOH–EtOAc (47.5 : 47.5 : 4 : 1)] to yield 2,3-(*S*)-HHDP-D-glucose (46 mg), pedunculagin (54 mg), strictinin (20 mg), **1** (806 mg), pterocarinin A (**6**) (1.1 g), **7** (50 mg), desgalloylstachyurin (**9**) (10 mg), **12** (39 mg), elaeagnatins B (**18**) (11 mg) and C (**19**) (11 mg). The 1-BuOH extract (65.8 g) was similarly fractionated and purified by a combination of column chromatographies over Diaion HP-20, Toyopearl HW-40 (coarse grade) and MCI-CHP-20P (75—150 μm) to give **1** (15 mg), lagerstannin C (**4**) (24 mg), brevifolincarboxylic acid (3 mg), 1,6-di-*O*-galloyl-β-D-glucose (14 mg), pedunculagin (69 mg) and strictinin (208 mg).

The known compounds were identified by comparison of their physical data with the reported values.

Hippophaenin B (7) ^{1}H-NMR (methanol-d_4) δ: 7.09 (2H, s, H_C-2, 6), 7.09 (1H, s, H_F-3), 6.85 (1H, s, H_D-3), 6.41 (1H, s, H_B-3), 6.20 (1H, s, H_E-3), 5.55 (1H, d, *J*=5 Hz, glucose (Glc) H-1), 5.45 (1H, dd, *J*=2, 9 Hz, Glc H-4), 5.42 (1H, dd, *J*=2, 2.5 Hz, Glc H-3), 5.29 (1H, dd, *J*=3, 9 Hz, Glc H-5), 4.89 (1H, dd, *J*=3, 13 Hz, Glc H-6), 4.73 (1H, dd, *J*=2.5, 5 Hz, Glc H-2), 4.04 (1H, d, *J*=13 Hz, Glc H-6). ^{13}C-NMR (methanol-d_4) δ: 64.3 (Glc C-6), 66.7 (Glc C-1), 69.5 (Glc C-3), 70.3 (Glc C-5), 73.7 (Glc C-4), 76.9 (Glc C-2), 104.3 (C_B-3), 104.5 (C_E-3), 108.0 (C_D-3), 109.3 (C_F-6), 109.5 (2C, C_C-2, 6), 114.6 (C_F-1), 115.4 (C_D-1), 115.6 (C_A-1), 115.9 (C_B-1), 117.1 (C_E-1), 119.1 (C_A-2), 119.8 (C_C-1), 116.7, 123.8, 125.8 (C_B, C_D, C_E-2), 126.5 (C_A-

3), 134.7 (C_B-5), 136.7 (C_E-5), 136.9 (C_D-5), 137.1 (C_F-2), 139.0 (C_A-5), 139.2 (C_F-3), 139.6 (C_C-4), 139.7 (C_F-4), 142.7 (C_F-5), 143.3, 143.4, 144.1, 144.4, 145.0, 145.6, 145.8 (C_A, C_B, C_D-4, 6, C_E-6), 145.3 (2C, C_C-3, 5), 146.7 (C_E-4), 165.9 (C_A-7), 166.2 (C_C-7), 167.9 (C_F-7), 168.5 (C_D-7), 169.0 (C_E-7), 169.8 (C_B-7).

Casuglaunin A (17) A light-brown amorphous powder, ESI-MS: *m/z* 1872 $(M+NH_4)^+$. ^{1}H-NMR (acetone-d_6+D_2O) δ: 7.13 (2H, s, galloyl), 7.06, 6.92, 6.73, 6.58, 6.57, 6.54, 6.38 (each 1H, s, galloyl and HHDP), sugar protons, see Table 1. ^{13}C-NMR (acetone-d_6+D_2O) δ: 105.4, 105.7, 107.5, 107.7, 108.6, 108.7, 115.2, 115.3 (HHDP C-3, 3′), 110.0 (2C), 110.9, 115.4 (galloyl C-2, 6), 115.4, 116.0, 116.1, 116.2, 116.5, 116.6, 117.5, 119.9 (HHDP C-1, 1′), 120.3, 120.8 (galloyl C-1) 122.4, 123.5, 124.9, 125.0, 126.3, 126.5, 127.3, 127.6 (HHDP C-2, 2′), 134.9, 135.0, 135.9, 136.1, 136.4, 136.8, 137.6, 137.8 (HHDP C-5, 5′), 138.9, 139.2 (galloyl C-4), 142.6, 142.8, 143.4, 143.6, 143.9, 144.1, 144.2, 144.2 (2C), 144.3, 145.0, 145.0, 145.1, 145.6, 145.7, 146.8 (HHDP C-4, 4′, 6, 6′), 145.9 (2C), 145.9 (2C), (galloyl C-3, 5), 165.3, 166.2, 168.0, 168.4 (2C), 168.4, 169.0, 169.1, 169.5, 170.3 (ester carbonyls), sugar carbons, see Table 2.

Elaeagnatin A (12) A light-brown amorphous powder, $[\alpha]_D$ +62.3° (*c*=0.5, MeOH). *Anal.* Calcd for $C_{53}H_{40}O_{35}\cdot 6H_2O$: C, 47.32; H, 3.9. Found: C, 47.21; H, 3.66. ESI-MS *m/z*: 1254 $(M+NH_4)^+$. FAB-MS *m/z*: 1237 $(M+H)^+$. UV λ_{max} (MeOH) nm (log ε): 220 (4.79), 265 (sh 4.44). CD (MeOH) [θ] (nm): $+1.5\times10^5$ (236), -2.5×10^4 (257), $+4.1\times10^4$ (283). ^{1}H-NMR (acetone-d_6+D_2O) δ: (major tautomer) 7.07 (1H, s, H_F-6), 7.02 (2H, s, H_C-2, 6), 6.84 (1H, s, H_D-3), 6.45 (1H, s, H_B-3), 6.20 (1H, s, H_E-3), 5.55 [1H, dd, *J*=2, 9 Hz, Glc H-4], 5.23 (1H, dd, *J*=3, 9 Hz, Glc H-5), 5.12 (1H, brs, Glc H-2), 4.90 (1H, d, *J*=2 Hz, Glc H-3), 4.81 (1H, dd, *J*=3, 13 Hz, Glc H-6), 3.96 (1H, d, *J*=13 Hz, Glc H-6), 3.94 [1H, d, *J*=3.5 Hz, lyxose (Lyx) H-2], 3.93 (1H, dd, *J*=6, 10 Hz, Lyx H-4), 3.85 (1H, dd, *J*=3, 10 Hz, Lyx H-3), 3.77 (1H, dd, *J*=6, 11 Hz, Lyx H-5), 3.65 (1H, d, *J*=11 Hz, Lyx H-5), 3.55 (1H, brs, Glc H-1). ^{13}C-NMR (MeOH-d_4) δ: (major tautomer) 45.9 (Glc C-1), 62.3 (Lyx C-5), 64.1 (Glc C-6), 66.0 (Lyx C-4), 69.8 (Glc C-5), 71.5 (2C) (Lyx C-2, 3), 72.8 (Glc C-4), 73.4 (Glc C-3), 74.6 (Glc C-2), 101.1 (Lyx C-1), 103.5 (C_B-3), 104.2 (C_E-3), 107.7 (C_D-3), 108.9 (C_F-6), 108.9 (2C) (C_C-2, 6), 113.9 (C_F-1), 114.4 (C_D-1), 115.1 (C_B-1), 115.4 (C_E-1), 116.0 (C_A-1), 119.4 (C_C-1), 123.3 (C_A-2), 116.3, 123.5 (C_B-2, C_D-2), 125.5 (C_E-2), 125.8 (C_A-3), 134.4 (C_B-5), 136.4 (C_E-5), 136.7 (C_D-5), 136.8 (C_F-2), 138.0 (C_A-5), 138.9 (C_F-3), 139.3 (C_C-4), 139.5 (C_F-4), 142.3 (C_F-5), 142.7 (C_A-4), 143.5 (C_B-6), 143.9 (C_A-6), 144.1 (C_E-6), 144.7 (C_D-6), 145.1(3C) (C_B-4, C_C-3, 5), 145.6 (C_D-4), 146.4 (C_E-4), 165.8 (C_C-7), 166.7 (C_A-7), 167.7 (C_F-7), 168.6 (C_E-7), 168.7 (C_D-7), 169.3 (C_B-7).

Methylation of 12 Followed by Methanolysis A mixture of **12** (1 mg), K_2CO_3 (10 mg) and $(CH_3)_2SO_4$ (0.01 ml) in acetone (1 ml) was stirred overnight at room temperature, then refluxed for 3 h. After removal of the inorganic material by centrifugation, the supernatant was evaporated to dryness. The residue was directly methanolyzed in 1% NaOMe in MeOH (1 ml) at room temperature for 6 h. After acidification with acetic acid and removal of the solvent, the residue was partitioned between EtOAc and H_2O. The EtOAc soluble portion was treated with CH_2N_2 (1 ml) for 1 h and the solvent was evaporated. Normal phase HPLC (solvent B) of the reaction mixture showed peaks identical with those of the authentic methyl tri-*O*-methyl gallate (**13**) and trimethyl octa-*O*-methylvaloneate (**15**).

Elaeagnatin B (18) A light-brown amorphous powder, $[\alpha]_D$ +74.8° (*c*=1.0, MeOH). UV λ_{max} (MeOH) nm (log ε): 222 (5.12), 261 (4.81). *Anal.* Calcd for $C_{82}H_{54}O_{52}\cdot 18H_2O$: C, 44.85; H, 4.13. Found: C, 44.83; H, 4.14. ESI-MS *m/z*: 1888 $(M+NH_4)^+$. FAB-MS *m/z*: 1871 $(M+H)^+$. CD (MeOH) [θ] (nm): $+3.3\times10^5$ (235), -7.9×10^4 (262), $+6.0\times10^4$ (284). ^{1}H-NMR (acetone-d_6+D_2O) δ: 7.13 (2H, s, galloyl), 7.12, 6.92, 6.86, 6.68, 6.58, 6.57, 6.54, 6.53 (each 1H, s, galloyl and HHDP), sugar protons, see Table 1. ^{13}C-NMR (acetone-d_6+D_2O) δ: 105.2, 106.7, 106.9, 107.3, 107.4, 107.5, 108.1, 109.9 (HHDP C-3, 3′, galloyl C-6′), 109.4 (2C) (galloyl C-2, 6), 113.1, 113.4, 114.4, 114.6, 114.8, 115.3, 115.4, 116.1 (HHDP C-1, 1′), 120.0, 120.1, 121.7, 121.8, 123.3, 124.5, 124.6, 125.3, 125.8, 125.9, 126.0, 127.3 (HHDP C-2, 2′, galloyl C-1, 1′, 2′), 134.3, 135.2, 135.4, 135.5 (2C), 135.7, 136.1, 136.9, 137.0, 138.4 (HHDP C-5, 5′, galloyl C-4, 4′), 142.0, 142.1, 143.3, 143.4, 143.48, 143.52, 143.54, 143.6, 143.8, 144.3 (5C), 144.4, 144.5, 144.8, 145.2 (2C), 146.0 (HHDP C-4, 6, 4′, 6′, galloyl C-3, 5, 3′, 5′), 164.7, 165.1, 167.0, 167.1, 167.6, 167.7, 168.0, 168.1, 168.1, 168.2 (ester carbonyls), sugar carbons, see Table 2.

Methylation of 18 Followed by Methanolysis To a solution of **18** (1 mg) in acetone (1 ml) were added $(CH_3)_2SO_4$ (0.01 ml) and K_2CO_3 (10 mg), and the mixture was stirred overnight at room temperature and refluxed for 3 h. After centrifugation, the supernatant was evaporated off and the reaction mixture was directly methanolyzed in 1% NaOMe in MeOH (1 ml) at room temperature for 6 h. After acidification with acetic acid and evaporation of the solvent, the residue was partitioned between EtOAc and H_2O. The EtOAc extract was further treated with CH_2N_2 (1 ml) for 1 h and the solvent was evaporated. The normal phase HPLC analysis (solvent B) of the residue revealed peaks identical with those of the authentic **13** and dimethyl hexamethoxydiphenate (**14**).

Partial Hydrolysis of 18 with Tannase A solution of **18** (0.2 mg) in H_2O (0.5 ml) was treated with tannase (3 drops) at 37 °C for 5 d. After the addition of EtOH, the reaction mixture was evaporated to dryness. The normal and reversed-phase HPLC (solvent A and B, respectively) showed, in addition to the peaks of gallic acid and ellagic acid, a peak due to a monomeric partial hydrolyzate which was identical with that of lagerstannin A (**5**) prepared from **1**.

Preparation of Lagerstannin A (5) from Hippophaenin A (1) An aqueous solution of **1** (10 mg/3 ml) was incubated with tannase (10 drops) at 37 °C for 72 h. The reaction mixture after concentration was chromatographed over Diaion HP-20 with H_2O and aq. MeOH. The H_2O eluate afforded lagerstannin A (**5**) (3.2 mg). **5**: A pale brown amorphous powder, $[\alpha]_D$ +107.2° (*c*=1.0, MeOH). FAB-MS *m/z*: 823 $(M+Na)^+$. ^{1}H-NMR (acetone-d_6+D_2O) δ: 6.64, 6.57, 6.52, 6.51 (each 1H, s, HHDP), 5.78 (1H, dd, *J*=2, 10 Hz, gluconic acid (GluA) H-3), 5.37 (1H, d, *J*=10 Hz, GluA H-2), 5.26 (1H, dd, *J*=2, 9 Hz, GluA H-4), 4.81 (1H, dd, *J*=4, 12.5 Hz, GluA H-6), 4.31 (1H, dd, *J*=4, 9 Hz, GluA H-5), 3.90 (1H, d, *J*=12.5 Hz, GluA H-6). These physical data were consistent with the reported data.[6)]

Elaeagnatin C (19) A light-brown amorphous powder, $[\alpha]_D$ +94.4° (*c*=1.0, MeOH). UV λ_{max} (MeOH) nm (log ε): 221 (5.13), 265 (4.79). *Anal.* Calcd for $C_{89}H_{58}O_{57}\cdot 22H_2O$: C, 43.88; H, 4.22. Found: C, 43.84; H, 4.03. ESI-MS *m/z*: 2056 $(M+NH_4)^+$. FAB-MS *m/z*: 2061 $(M+Na)^+$. CD (MeOH) [θ] (nm): $+3.0\times10^5$ (234), -7.7×10^4 (261), $+7.4\times10^4$ (284). ^{1}H-NMR (acetone-d_6+D_2O) δ: 7.11 (2H, s, galloyl), 7.11, 7.04, 6.94, 6.89, 6.71, 6.59, 6.58, 6.53, 6.13 (each 1H, s, galloyl and HHDP), sugar protons, see Table 1. ^{13}C-NMR (acetone-d_6+D_2O) δ: 103.6, 105.1, 106.9, 107.1, 107.7, 107.8, 108.0, 109.3, 109.9 (HHDP C-3, 3′, valoneoyl C-3, 3′, 6″, galloyl C-6′), 109.5 (2C) (galloyl C-2, 6), 113.1, 113.4, 114.2, 114.5, 114.6, 115.2, 115.4, 116.0, 116.2 (HHDP C-1, 1′, valoneoyl C-1, 1′, 1″), 119.6, 119.8, 121.7, 123.0, 123.8, 124.6, 124.7, 125.3, 125.4, 125.7, 126.9 (HHDP C-2, 2′, valoneoyl C-2, 2′, galloyl C-1), 134.5, 135.3, 135.4, 135.8, 135.9, 136.0, 136.1, 136.2, 137.1, 137.3, 138.7, 139.1, 139.2 (HHDP C-5, 5′, valoneoyl C-5, 5′, 2″, 30, 40, galloyl C-4, 3′, 4′), 142.0, 142.1, 142.3, 143.4, 143.6 (2C), 143.7, 143.8, 143.8, 143.9, 144.2, 144.3, 144.4, 144.5, 144.6, 144.7, 145.0, 145.2 (2C), 146.1, 146.4 (HHDP C-4, 4′, 6, 6′, valoneoyl C-4, 6, 5″, galloyl C-3, 5, 3′, 5′), 165.5, 166.8, 167.7, 167.8, 168.1 (2C), 168.2, 168.3, 168.8, 168.9 (2C) (ester carbonyls, valoneoyl C-7), sugar carbons, see Table 2.

Methylation of 19—23 Followed by Methanolysis Methylation of individual tannins (each 1 mg) was performed in a way similar to that for **12** and **18** described above. Each reaction mixture was directly methanolyzed in 1% NaOMe in MeOH (1 ml) at room temperature for 6 h. After a usual work-up, the reaction mixtures obtained from the individual tannins were analyzed by normal phase HPLC (solvent B) to commonly detect the peaks identical with those of the authentic **13**, **14** and **15**. In the case of **21**, **14** was detected as a minor product that was produced by ether cleavage of the valoneoyl group on methylation.

Partial Hydrolysis of 19 with Tannase A solution of **19** (0.2 mg) in H_2O (0.5 ml) was treated with tannase at 37 °C for 5 d. After the addition of EtOH, the reaction mixture was evaporated and analyzed by normal (solvent A) and reversed-phase HPLC (solvent C), which showed a peak due to a monomeric tannin identical with that of **2a** obtained from shephagenin A (**2**).

Degalloylation of Shephagenin A (2) with Tannase A solution of **2** (20 mg) in H_2O (20 ml) was incubated with tannase (4 ml) at 37 °C for 6 d. After concentration of the reaction mixture, the product was chromatographed over Diaion HP-20 with H_2O–MeOH. The 10% MeOH eluate gave desgalloylshephagenin A (**2a**) (2.5 mg). **2a**: A pale brown amorphous powder, FAB-MS *m/z*: 969 $(M+H)^+$. ^{1}H-NMR (acetone-d_6+D_2O) δ: 7.12, 6.63, 6.58, 6.53, 6.16 (each 1H, s, HHDP, valoneoyl), 5.75 (1H, dd, *J*=2, 10 Hz, GluA H-3), 5.36 (1H, d, *J*=10 Hz, GluA H-2), 5.30 (1H, dd, *J*=1.5, 10 Hz, GluA H-4), 4.72 (1H, dd, *J*=3.5, 12 Hz, GluA H-6), 4.27 (1H, dd, *J*=3.5, 8 Hz, GluA H-5), 3.82 (1H, d, *J*=12 Hz, GluA H-6).

Elaeagnatin D (20) A light-brown amorphous powder, $[\alpha]_D$ +96.6° (*c*=1.0, MeOH). UV λ_{max} (MeOH) nm (log ε): 222 (5.28), 268 (4.90). *Anal.* Calcd for $C_{89}H_{58}O_{56}\cdot 21H_2O$: C, 44.50; H, 4.19. Found: C, 44.24; H, 3.83. ESI-MS *m/z*: 2040 $(M+NH_4)^+$. FAB-MS *m/z*: 2023 $(M+H)^+$. CD (MeOH) [θ] (nm): $+3.4\times10^5$ (234), -8.6×10^4 (261), $+1.0\times10^5$ (284). ^{1}H-NMR (acetone-d_6+D_2O) δ: 7.10 (2H, s, H_C-2, 6), 7.09 (1H, s, H_F-6), 7.03 (1H, s,

H_I-6), 6.92 (1H, s, H_J-3), 6.74 (1H, s, H_D-3), 6.56 (1H, s, H_K-3), 6.52 (1H, s, H_B-3), 6.42 (1H, s, H_H-3), 6.19 (1H, s, H_E-3), sugar protons, see Table 1. ^{13}C-NMR (acetone-d_6+D_2O) δ: 104.8, 105.6, 105.8, 107.6, 108.6 (2C), 109.9, 110.6 ($C_{B,D,E,H,J,K}$-3, $C_{F,I}$-6), 110.2 (2C) (C_C-2, 6), 115.0 (C_D-1), 115.1 (C_K-1), 115.3 (C_J-1), 116.2 (C_F-1), 116.2, 116.3 ($C_{A,G}$-1), 116.7 (C_B-1), 116.7 (C_H-1), 117.2 (C_E-1), 117.6 (C_G-3), 120.2 (C_C-1), 120.5 (C_I-1), 120.7 (C_A-2), 122.5 (C_K-2), 122.5, 123.7, 124.7, 125.1, 126.3, 126.8, 127.3, 127.9 (C_A-3, $C_{B,D,E,G,H,I,J}$-2), 135.0 (C_B-5), 135.1 (C_H-5), 135.9 (C_K-5), 136.5 (C_J-5), 136.8 (C_E-5), 136.9 (C_F-2), 137.1 (C_D-5), 137.6, 137.8 ($C_{A,G}$-5), 139.0 (C_F-3), 139.2 (C_C-4), 139.7 (C_F-4), 142.9 (C_F-5), 140.0, 142.6, 142.7, 143.6, 143.7, 144.1, 144.2, 144.4, 144.5, 145.2, 145.3, 145.5 ($C_{A,B,G,J,I}$-4, $C_{A,B,D,E,G,H,J,K}$-6), 144.9 (C_K-4), 145.0 (C_D-4), 145.6 (C_I-5), 145.8 (2C) (C_C-3, 5), 146.0 (C_H-4), 146.9 (2C) (C_E-4, C_I-3), 165.0 (C_G-7), 166.1 (C_C-7), 167.2 (C_F-7), 168.1 (C_I-7), 168.2 (C_D-7), 168.4 (C_J-7), 168.4 (C_A-7) 168.7 (C_E-7), 169.2 (C_K-7), 169.5 (C_B-7), 170.4 (C_H-7), sugar carbons, see Table 2.

Elaeagnatin E (21) A light-brown amorphous powder, $[\alpha]_D$ +98.5° (c=1.0, MeOH). UV λ_{max} (MeOH) nm (log ε): 216 (5.27), 268 (4.94). *Anal.* Calcd for $C_{96}H_{62}O_{61}\cdot 14H_2O$: C, 47.18; H, 3.71. Found: C, 47.24; H, 3.82. ESI-MS *m/z*: 2208 $(M+NH_4)^+$. FAB-MS *m/z*: 2191 $(M+H)^+$. CD (MeOH) [θ] (nm): +2.8×10^5 (228), −7.3×10^4 (260), +1.0×10^5 (284). ^{1}H-NMR (acetone-d_6+D_2O) δ: 7.11 (1H, s, H_I-6), 7.09, 7.00 (each 1H, s, H_{EL}-6), 7.03 (2H, s, H_C-2, 6), 6.93 (1H, s, H_D-3), 6.72 (1H, s, H_J-3), 6.51, 6.44 (each 1H, s, $H_{B,H}$-3), 6.32 (1H, s, H_E-3), 6.22 (1H, s, H_K-3), sugar protons, see Table 1. ^{13}C-NMR (acetone-d_6+D_2O) δ: 105.0, 105.5, 105.8, 106.0, 108.3, 108.7, 109.8, 111.2 ($C_{B,D,E,H,J,K}$-3, C_{EL}-6), 109.9 (C_I-6), 110.2 (2C) (C_C-2, 6), 115.0 (C_D-1), 115.1, 115.6 ($C_{A,G}$-1), 116.0 (C_J-1), 116.3 (C_B-1), 116.4 (C_H-1), 116.8 (2C) ($C_{E,K}$-1), 117.3, 117.4 (C_{EL}-1), 120.3 (C_C-1), 120.8 (C_I-1), 122.5 (C_A-3), 122.7 (C_I-2), 123.9 (C_G-3), 117.6, 120.5, 124.6, 124.8, 126.4, 126.7, 127.4, 127.9 ($C_{A,B,D,E,G,H,J,K}$-2), 134.9 (C_B-5), 135.1 (C_H-5), 136.5 (C_D-5), 136.9, 137.9 ($C_{A,G}$-5), 136.9 (C_K-5), 137.0 (C_E-5), 137.3 (C_J-5), 137.7 (2C) (C_{EL}-2), 138.0, 138.9 (C_{EL}-3), 139.2, 139.8 ($C_{C,I}$-4), 140.0, 140.1 (C_{EL}-4), 142.3, 143.0 (C_{EL}-5), 142.8 (C_A-4), 143.0, 143.5, 143.8, 144.0, 144.2, 144.5, 145.3 ($C_{A,B,D,E,G,H,J,K}$-6), 144.8 (C_D-4), 144.9 (C_J-4), 145.5 (C_I-5), 145.6 (C_B-4), 145.7 (2C) (C_C-3, 5), 146.1 (C_H-4), 146.8 (C_E-4), 146.8 (C_K-4), 147.1 (C_I-3), 164.9, 166.1 ($C_{C,I}$-7), 167.2, 167.6 ($C_{A,G}$-7), 167.8, 168.2 (C_{EL}-7), 168.3 (C_D-7), 168.5 (C_J-7), 168.6 (C_K-7), 169.1 (C_E-7), 169.6 (C_B-7), 170.5 (C_H-7), sugar carbons, see Table 2.

Elaeagnatin F (22) A light-brown amorphous powder, $[\alpha]_D$ +50.8° (c=1.0, MeOH). UV λ_{max} (MeOH) nm (log ε): 220 (5.14), 264 (4.78). *Anal.* Calcd for $C_{82}H_{56}O_{53}\cdot 11H_2O$: C, 47.18; H, 3.77. Found: C, 47.42; H, 3.89. ESI-MS *m/z*: 1906 $(M+NH_4)^+$. FAB-MS *m/z*: 1889 $(M+H)^+$. CD (MeOH) [θ] (nm): +2.5×10^5 (232), −7.8×10^4 (262), +8.8×10^4 (284). ^{1}H-NMR (acetone-d_6+D_2O) δ: 7.27 (2H, s, H_G-2, 6), 7.22 (1H, s, H_H-6), 7.12 (2H, s, H_C-2, 6), 7.10 (1H, s, H_F-6), 7.02 (1H, s, H_I-3), 6.93 (1H, s, H_D-3), 6.54 (1H, s, H_B-3), 6.49 (1H, s, H_J-3), 6.18 (1H, s, H_E-3), sugar protons, see Table 1. ^{13}C-NMR (acetone-d_6+D_2O) δ: 104.9, 105.9, 107.1, 108.6, 110.0, 110.7 ($C_{B,D,E,I,J}$-3, C_F-6), 109.2 (C_H-6), 110.2 (2C) (C_C-2, 6), 110.6 (2C) (C_G-2, 6), 115.0 (C_F-1), 115.1 (C_J-1), 115.2 (C_D-1), 116.0 (C_I-1), 116.2 (C_A-1), 116.8 (C_B-1), 117.3 (C_E-1), 120.7 (C_G-1), 120.8 (C_C-1), 121.1 (C_H-2), 121.7 (C_H-1), 122.9 (C_A-3), 123.7, 124.9, 125.5, 126.5, 127.1, 128.2 ($C_{A,B,D,E,I,J}$-2), 135.0 (C_B-5), 135.7 (C_J-5), 136.6 (C_I-5), 136.6 (C_D-5), 136.9 (C_E-5), 137.4 (C_F-2), 137.7 (C_A-5), 137.9 (C_H-4), 139.2 (2C) ($C_{C,G}$-4), 139.7 (C_F-4), 140.2 (C_F-3), 142.7 (C_A-4), 143.0 (C_F-5), 144.1 (C_H-5) 142.8, 144.2, 144.3, 144.4, 144.6, 144.8 ($C_{A,B,D,E,I,J}$-6), 144.9 (C_I-4), 145.1 (C_J-4), 145.2 (C_D-4), 145.6 (C_B-4), 145.7 (2C) (C_G-3, 5), 145.9 (2C) (C_C-3, 5), 146.8 (C_E-4), 146.9 (C_H-3), 166.0 (C_C-7), 166.1 (C_G-7), 166.9 (C_F-7), 167.7 (C_H-7), 167.8 (C_A-7), 167.9 (C_I-7), 168.5 (C_D-7), 168.6 (C_E-7) 169.2 (C_J-7), 169.5 (C_B-7), sugar carbons, see Table 2.

Elaeagnatin G (23) A light-brown amorphous powder, $[\alpha]_D$ +89.5° (c=1.0, MeOH). UV λ_{max} (MeOH) nm (log ε): 217 (5.08), 264 (4.71). *Anal.* Calcd for $C_{75}H_{52}O_{48}\cdot 8H_2O$: C, 48.29; H, 3.67. Found: C, 48.53; H, 3.90. ESI-MS *m/z*: 1738 $(M+NH_4)^+$. FAB-MS *m/z*: 1721 $(M+H)^+$. CD (MeOH) [θ] (nm): +2.2×10^5 (230), −6.9×10^4 (261), +6.5×10^4 (284). ^{1}H-NMR (acetone-d_6+D_2O) δ: 7.41 (1H, s, H_F-6), 7.15 (2H, s, H_C-2, 6), 7.12 (1H, s, H_I-6), 6.90 (1H, s, H_E-3), 6.79 (1H, s, H_G-3), 6.60 (1H, s, H_D-3), 6.56 (1H, s, H_B-3), 6.18 (1H, s, H_H-3), sugar protons, see Table 1. ^{13}C-NMR (acetone-d_6+D_2O) δ: 104.1, 105.3, 106.9, 111.4 ($C_{B,F,G,H}$-3), 107.5 (C_D-3), 107.8 (C_E-3), 109.2 (C_I-6), 109.5 (2C) (C_C-2, 6), 114.3 (C_I-1), 114.6 (C_E-1), 115.0 (C_D-1), 115.5 (C_A-1), 115.5 (C_G-1), 116.1 (C_B-1), 116.7 (C_H-1), 118.4 (C_A-3), 120.1 (C_C-1), 122.2 (C_F-1), 122.5 (C_F-2), 122.6, 124.3, 125.6, 125.8, 126.0, 127.5 ($C_{A,B,D,E,G,H}$-2), 134.3 (C_B-5), 135.3 (C_D-5), 135.7 (C_G-5), 136.1 (C_E-5), 136.5 (C_H-5), 136.9 (C_I-2), 137.6 (C_F-4), 138.5 (C_A-5), 139.2 (C_C-4), 139.4 (2C) (C_I-3, 4), 142.0 (2C) (C_A-4, 6), 142.4 (C_I-5), 143.1 (C_F-5), 143.3, 143.6, 143.6, 143.8 ($C_{B,D,E,G,H}$-6), 144.1 (C_E-4), 144.3 (C_G-4), 144.5 (C_D-4) 144.8 (C_B-4), 145.2 (2C) (C_C-3, 5), 146.0 (C_F-3), 146.2 (C_H-4), 165.0 (C_C-7), 165.4 (C_F-7), 166.7 (C_I-7), 166.9 (C_A-7), 167.67 (C_G-7), 167.70 (C_E-7), 167.9 (C_D-7), 168.0 (C_H-7), 168.7 (C_B-7), sugar carbons, see Table 2.

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