Tannins and Related Compounds. CV.¹⁾ Monomeric and Dimeric Hydrolyzable Tannins Having a Dehydrohexahydroxydiphenoyl Group, Supinanin, Euphorscopin, Euphorhelin and Jolkianin, from *Euphorbia* Species

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A chemical investigation of tannins in three *Euphorbia* species (*E. helioscopia*, *E. jolkini* and *E. supina*) has led to the isolation and characterization of four new hydrolyzable tannins, named supinanin (15), euphorscopin (16), euphorhelin (17) and jolkianin (18), together with fourteen known compounds (1–14). On the basis of chemical and spectroscopic evidence, the structures of supinanin and euphorscopin were established as 1,3,6-tri-*O*-galloyl-2,4-(*S*)-dehydrohexahydroxydiphenoyl- β -D-glucose (15) and 1,3-(*S*)-dehydrohexahydroxydiphenoyl-2-*O*-galloyl-4,6-(*S*)-hexahydroxydiphenoyl- β -D-glucose (16), respectively. Euphorhelin and jolkianin were characterized as dimeric hydrolyzable tannins (17 and 18, respectively), in which two glucopyranose units are linked *via* valoneoyl and dehydrodigalloyl groups, respectively, and each molecule possesses a dehydrohexahydroxydiphenoyl group.

Keywords *Euphorbia*; hydrolyzable tannin; supinanin; euphorhelin; euphorscopin; jolkianin; dehydrohexahydroxydiphenic acid; hexahydroxydiphenic acid; dehydrodigallic acid; tannin

In one²⁾ of the previous papers, we reported that *Euphorbia helioscopia* L., unlike other *Euphorbia* species so far examined, contains large amounts of novel ellagitannins, helioscopins A and B, which possess the 4,4',5,5',6,6'-hexahydroxydiphenoyl (HHDP) group at the 1,6-positions of the glucopyranose core. Further chemical study on tannins of this plant has led to the isolation of two minor hydrolyzable tannins named euphorscopin (16) and euphorhelin (17), together with eleven hydrolyzable tannins. Moreover, an extension of our examination to two other *Euphorbia* species, *E. supina* RAFIN and *E. jolkini* BOISS, has resulted in the isolation of ten and seven hydrolyzable tannins, respectively, among which two [supinanin (15) and jolkianin (18)] were found to be new. This paper deals with

the isolation and characterization of these compounds.

A combination of Sephadex LH-20, MCI-gel CHP 20P, Prep-pak 500/C₁₈, Fuji-gel ODS G3 and Bondapak C₁₈/Porasil B chromatographies of the aqueous acetone extract of the fresh whole plants of *E. helioscopia* afforded compounds 1, 2, 4–12, 16 and 17, while on similar treatment, the aqueous acetone extract of *E. jolkini* gave compounds 1, 2, 5–11 and 18. Furthermore, the extraction of *E. supina* yielded compounds 3, 8, 9 and 12–15. Compounds 1–14 were identified as 1-*O*- (1),³⁾ 1,6-di-*O*- (2),⁴⁾ 1,2,3-tri-*O*- (3),⁵⁾ 1,2,6-tri-*O*- (4),⁶⁾ 1,2,3,6-tetra-*O*- (5),⁷⁾ 1,3,4,6-tetra-*O*- (6)⁸⁾ and 1,2,3,4,6-penta-*O*-galloyl- β -D-glucoses (7),⁹⁾ corilagin (8),¹⁰⁾ geraniin (9),¹⁰⁾ helioscopin A (10),²⁾ carpinusin (11),²⁾ terchebin (12)¹¹⁾ and rugosins

Chart 1

D (**13**)¹² and E (**14**)¹² by comparisons of their physical and spectral data with those of authentic samples.

Supinanin (**15**) was obtained as a pale yellow crystalline powder (H₂O). In the proton nuclear magnetic resonance (¹H-NMR) spectrum, the observation of signals at δ 7.11, 7.15 and 7.26 (each 2H, s) indicated the presence of three galloyl ester groups in the molecule, and a pair of benzylmethine signals [δ 5.03 (d, $J=2$ Hz) and 5.29 (s), 1H in total] and olefinic proton signals [δ 6.33 (d, $J=2$ Hz) and 6.63 (s), 1H in total] were characteristic of a dehydrohexahydroxydiphenoyl (DHHDP) ester group existing as an equilibrium mixture of five- and six-membered hemiketal forms.¹⁰ The presence of the DHHDP ester group was also supported by carbon-13 nuclear magnetic resonance (¹³C-NMR) spectral analysis.²⁾

Upon treatment with *o*-phenylenediamine in an acidic solution, **15** yielded a phenazine derivative (**15a**). Subsequent methylation of **15a** with ethereal diazomethane, followed by alkaline hydrolysis and treatment with ethereal diazomethane, yielded methyl trimethoxybenzoate (**15b**) and a phenazine dimethyl ester (**15c**).²⁾ The negative sign of the optical rotation [-29.0° (CHCl₃)] of **15c** established the chirality of the DHHDP group to be in the *S*-series.²⁾

Partial hydrolysis of **15a** in hot water gave 1,3,6-tri-*O*-galloyl- β -D-glucose (**15d**), together with a phenazine bis-lactone (**15e**),²⁾ thus indicating that the DHHDP ester group is located at the glucose C-2 and C-4 hydroxyl groups. Furthermore, the orientation of the DHHDP ester group on the glucose moiety was determined chemically as follows. The treatment of **15** with triethylamine in acetonitrile¹³⁾ gave a product (**15f**), whose ¹H-NMR spectrum showed signals due to three galloyl groups [δ 7.04, 7.11,

7.15 (each 2H, s)] and a brevifolin carboxyl group¹⁴⁾ [δ 2.75 (1H, dd, $J=7, 19$ Hz), 4.50 (1H, br d, $J=7$ Hz), 7.17 (1H, s)]. The upfield shift of glucose H-4 [δ 4.05 (br d, $J=8$ Hz)], compared with that (δ 5.31) of the parent compound (**15**), indicated that the brevifolin carboxyl group is attached to the C-2 hydroxyl group of the glucose moiety, thus determining unequivocally the orientation of the DHHDP group.

On the basis of these findings, **15** was characterized as 1,3,6-tri-*O*-galloyl-2,4-(*S*)-DHHDP- β -D-glucose, in which the hydrated cyclohexenetetrone ring in the DHHDP group is located at the glucose C-2 position.

Euphorscopin (**16**) was obtained as a pale yellow amorphous powder. The ¹H-NMR spectrum of **16** showed the presence of a galloyl ester group [δ 7.23 (2H, s)], an HHDP ester group [δ 6.47 and 6.80 (each 1H, s)] and a glucose moiety. The observation of a characteristic benzylmethine singlet [δ 4.87 (1H)], an olefinic signal [δ 6.61 (1H, s)] and an aromatic one-proton singlet (δ 7.07) suggested the presence of a DHHDP ester group. Compound **16** gave a phenazine derivative (**16a**) on treatment with *o*-phenylenediamine in an acidic solution. Subsequent methylation of **16a** with ethereal diazomethane, followed by alkaline hydrolysis and ethereal diazomethane treatment, yielded methyl trimethyl gallate (**15b**), dimethyl hexamethoxydiphenate²⁾ (**16b**) and the phenazine methylate (**15c**). The negative sign of the optical rotations of **16b** and **15c** established the chirality of the HHDP and DHHDP ester groups to be both in the *S*-series. These findings indicated that compound **16** contains a galloyl, an (*S*)-HHDP and an (*S*)-DHHDP ester group on the glucose core, which was supported by the observation of the intense [M-H]⁻ ion

Chart 2

peak at m/z 951 in the negative fast atom bombardment mass spectrum (FAB-MS) of **16**.

The orientation and the location of each acyl group in the glucose moiety were determined as follows. The ^1H - ^{13}C long-range shift correlation (COSY) spectrum (Fig. 1) of

16 clearly showed the correlation between the DHHP aromatic one-proton singlet (δ 7.07) and a carboxyl carbon signal (δ 164.9) through a three-bond coupling, and this carboxyl carbon signal was also found to be correlated with the glucose C-1 proton signal (δ 6.54). Similarly, the glucose

Chart 3

Fig. 1. The ^1H - ^{13}C Long-Range COSY Spectrum of **16**

In acetone- d_6 + D_2O ($J_{\text{CH}} = 10$ Hz).

C-4 proton signal (δ 5.50) was shown to be correlated with the carboxyl carbon signal (δ 167.9), which also gave a cross peak with one (δ 6.47) of the HHDP proton signals. Furthermore, the glucose C-6 proton signal (δ 3.92) correlated with the carboxyl carbon signal (δ 169.0) also gave a cross peak with the HHDP proton signal (δ 6.83). These findings indicated that the HHDP ester group is located at the C-4 and C-6 positions of the glucose core, and the aromatic carboxyl of the DHHDP group is at the glucose C-1 position. Furthermore, treatment of **16** with tannase gave brevifagin II (**16c**)¹⁴ and gallic acid, thus confirming that the galloyl ester group is located at the glucose C-2 position and the DHHDP ester group at the glucose C-1 and C-3 positions.

Examination of the Dreiding model showed that bridging of the (*S*)-DHHDP group over the glucopyranose C-1 and C-3 positions is possible only in the case of the β -configuration at the anomeric center. Thus, euphorscopin was characterized as 1,3-(*S*)-DHHDP-2-*O*-galloyl-4,6-(*S*)-HHDP- β -D-glucose (**16**).

Euphorhelin (**17**) was obtained as a pale yellow amorphous powder. In the ¹H-NMR spectrum of **17**, the observation of a pair of benzylmethine proton signals [δ 4.93 (d, J =1.5 Hz) and 5.81 (s), 1H in total] and olefinic proton signals [δ 6.20 (d, J =1.5 Hz) and 6.52 (s), 1H in total] showed the presence of an equilibrated DHHDP ester group in the molecule. The ¹H-NMR spectrum of the phenazine derivative (**17a**), obtained by treatment of **17** with *o*-phenylenediamine, indicated the presence of three galloyl groups [(δ 6.97, 7.12 and 7.13 (each 2H, s)] one valoneoyl group [(δ 6.22, 7.03 and 7.18 (each 1H, s) and

one phenazine ester group [δ 7.50 (1H, s), 7.97–8.07, 8.27–8.35 (each 2H, m) and 8.33 (1H, s)]. In addition, two anomeric proton signals were observed at δ 5.83 (d, J =8 Hz) and 6.12 (d, J =6 Hz), indicating the presence of two sugar moieties in the molecule.

Methylation of **17a** with ethereal diazomethane, followed by alkaline hydrolysis and diazomethane treatment, yielded the products (**17b** and **17c**), together with **15b**. The positive signs of the optical rotations of **17b** and **17c** established the chirality of the DHHDP and valoneoyl ester groups to be all in the *R*-series. The ¹³C-NMR spectrum of **17a** showed twelve sugar carbon resonances, of which six (δ 63.9, 71.0, 73.8, 74.6, 75.4 and 93.7) were closely correlated with those found in 1,2,6-tri-*O*-galloyl- β -D-glucose (**4**), whereas the

17

Chart 4

Chart 5

TABLE I. $^1\text{H-NMR}$ Data for Sugar Moieties in Compounds 4, 9a, 17a, 19, 10a and 18a

	4 ^{a)}	9a ^{a)}	17a ^{b)}	19 ^{a)}	10a ^{a)}	18a ^{b)}
Glucose						
A-1	5.98 (d, $J=8$)		5.83 (d, $J=8$)		6.25 (brs)	6.23 (brs)
A-2	5.28 (t, $J=8$)		5.20 (t, $J=9$)		5.26 (brs)	5.49 (brs)
A-3	3.97 (t, $J=8$)		— ^{c)}		5.76 (brs)	5.71 (brs)
A-4	3.76 (t, $J=8$)		— ^{c)}		5.08 (brs)	4.97 (brs)
A-5	4.10 (m)		3.93 (m)		4.45 (m)	4.03 (dd, $J=5, 11$)
A-6	4.67 (br d, $J=12$)		4.75 (dd, $J=5, 12$)		5.15 (t, $J=11$)	5.33 (t, $J=11$)
	4.47 (dd, $J=4, 12$)		4.46 (dd, $J=4, 12$)		4.20 (dd, $J=5, 11$)	4.44 (dd, $J=5, 11$)
Glucose						
B-1		6.16 (d, $J=6$)	6.12 (d, $J=6$)	6.12 (d, $J=3$)		6.15 (d, $J=3$)
B-2		5.69 (d, $J=6$)	5.70 (d, $J=6$)	5.52 (dd, $J=3, 7$)		5.53 (dd, $J=3, 7$)
B-3		5.50 (m)	5.55 (d, $J=4$)	5.79 (t, $J=7$)		5.86 (t, $J=7$)
B-4		5.50 (m)	5.42 (d, $J=4$)	5.20 (dd, $J=2, 7$)		5.25 (dd, $J=3, 7$)
B-5		4.69—5.09 (m)	4.95 (dd, $J=4, 8$)	4.58 (m)		4.56 (m)
B-6		4.69—5.09 (m)	4.78 (dd, $J=8, 12$)	4.85 (t, $J=11$)		4.76 (t, $J=11$)
			4.56 (dd, $J=4, 12$)	4.43 (dd, $J=4, 11$)		4.54 (dd, $J=4, 11$)

In $\text{Me}_2\text{CO}-d_6 + \text{D}_2\text{O}$, values, J values in Hz. a) Measured at 100 MHz. b) Measured at 270 MHz. c) Overlapped with HOD signals.

Chart 6

chemical shifts of the remaining six signals [δ 65.8, 67.7, 68.6, 76.2 ($\times 2$) and 91.8] were almost identical with those of the phenazine derivative of geraniin (9a).⁴⁾ Similarly, the sugar signal pattern in the $^1\text{H-NMR}$ spectrum of 17a closely resembles those of 9a plus 4 (Table I).

From these findings, 17 was considered to be a dimeric ellagitannin composed of 1,2,6-tri-*O*-galloyl- β -D-glucose (4) and geraniin (9) units which are linked through the valoneoyl group. This was consistent with the negative FAB-MS data of 17. The orientation of the 3,6-positioned valoneoyl group in 17 was determined by generation of isomallotinic acid (17e),⁵⁾ together with 15e and 17f, on partial hydrolysis of 17a. The structure of 17f followed from the negative FAB-MS [m/z 1267 ($\text{M}-\text{H}$)⁻] and the observation of the significant high-field shift of the aromatic singlet (δ 6.22) due to the Hc proton⁵⁾ in the $^1\text{H-NMR}$ spectrum of 17f.

Based on the above chemical and spectroscopic evidence, the structure of euphorhelin was determined to be as represented by the formula 17. The $^1\text{H-NMR}$ spectrum of jolkianin (18) showed the presence of a DHHDG group [δ 4.93 (d, $J=2$ Hz) and 5.17 (s), 1H in total, δ 6.13 (d, $J=2$ Hz) 6.58 (s), 1H in total]. Treatment of 18 with *o*-phenylenediamine yielded the phenazine derivative (18a),

whose $^1\text{H-NMR}$ spectrum exhibited two one-proton signals at δ 6.15 (d, $J=3$ Hz) and 6.23 (brs) attributable to the anomeric protons, suggesting the presence of two sugar moieties in 18. The dimeric structure of 18 was also supported by the observation of twelve aliphatic resonances in the $^{13}\text{C-NMR}$ spectrum and of the prominent ($\text{M}-\text{H}$)⁻ ion peak at m/z 1941 in the FAB-MS of 18a. The $^1\text{H-NMR}$ spectrum of 18a showed, in the aromatic region, two galloyl singlets at δ 7.11 and 7.12, five one-proton singlets at δ 6.68, 6.83, 6.84, 7.04 and 7.17 and two *meta*-coupled doublets at δ 6.35 and 7.12 (each $J=2$ Hz), together with signals arising from the phenazine moiety.

Methylation of 18a with ethereal diazomethane, followed by alkaline hydrolysis and diazomethane treatment, yielded 15b, 16b, 15c and dimethyl penta-*O*-methyldehydrodigallate (18b)¹⁵⁾ in the molar ratio of 2:2:1:1. Comparison of the $^1\text{H-NMR}$ spectrum of 18a with those of 1,6-(*S*)-HHDP-2,3,4-tri-*O*-galloyl- β -D-glucose (19)⁴⁾ and the phenazine derivative of helioscopinin A (10a)²⁾ revealed a close structural relationship among these compounds. That is, in the $^1\text{H-NMR}$ spectrum of 18a, the chemical shifts and coupling patterns of signals arising from the two glucose moieties were closely correlated with those of 19 plus 10a (Table I).

These findings suggested that 18 is a dimeric ellagitannin consisting of moieties of 1,6-(*S*)-DHHDG-2,3,4-tri-*O*-galloyl- β -D-glucose (19)⁴⁾ and helioscopinin A (10), which are linked *via* the dehydrodigalloyl (DHDG) ester group.

To confirm the locations of each acyl group in the glucose moieties, partial hydrolysis of 18a was attempted. Brief treatment of 18a in hot water gave the hydrolysates (18c and 18d), together with 15e. Compound 18c was characterized as a product formed by hydrolysis of the phenazine ester on the ground that the $^1\text{H-NMR}$ spectra of 18a and 18c showed a close similarity in the aromatic and sugar regions, except for the lack of signals due to the phenazine moiety and the upfield shifts of the glucose C-2 and C-4 proton signals. The $^1\text{H-NMR}$ spectrum of 18d indicated the presence of two galloyl groups [δ 7.08 and 7.09 (each 2H, s)] and one DHHDG group [δ 6.75 and 7.19 (each 1H, d, $J=2$ Hz), 7.17 (1H, s)]. Although signals due

Chart 7

18a

- 1) methylation
- 2) hydrolysis
- 3) CH₂N₂/ether

Chart 8

Fig. 2. LSPD Experiments in **18c**

(a) Irradiation at δ 7.28 (H_b), (b) irradiation at δ 5.50 (glc. H-2'), (c) irradiation at δ 7.16 (H_a), (d) irradiation at δ 5.13 (glc. H-3), (e) non-decoupling.

C-2', C-3' and C-4' protons from ¹H-¹H COSY spectral analysis, indicating that these positions were acylated.

These findings indicated that the DHHD ester group is located at the C-2 and C-4 positions of the glucose A moiety and that the HHDP ester groups are at the C-1 and C-6 positions of the two glucose moieties. To confirm the location of the DHDG group, a long-range selective proton-decoupling (LSPD)¹⁵ experiment on **18c** was performed. The ¹³C-NMR spectrum of **18c** showed eight ester carbon signals. In the non-decoupling mode, the signal at δ 164.9 (C-7) was observed as a triplet, and this signal was changed into a doublet upon irradiation at δ 5.13 (glc. H-3) and δ 7.16 (DHDG-H_a). Accordingly, the C-7 ester group could be concluded to be located at the C-3 position of the glucose A moiety. On the other hand, the signal at δ 166.1 (C-7') was changed from a quartet into a sharp triplet on irradiation at δ 5.50 (glc. H-2') and δ 7.28 (DHDG-H_b). Accordingly, the location of the C-7' ester was shown to be at the C-2 position of the glucose B moiety.

Based on these findings, the structure of jolkianin was established to be as shown by the formula **18**.

Jolkianin (**18**) represents the first example of a dimeric hydrolyzable tannin possessing the HHDP group at the glucose 1,6-positions. The co-occurrence of hydrolyzable tannins having *R*- and *S*-DHHD groups in these *Euphorbia* species is of great interest from the viewpoint of plant physiology.

Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter. ¹H- and ¹³C-NMR spectra were recorded on JEOL FX-100 and JEOL GX-270 spectrometers, with

to the sugar moiety were found to be complicated owing to the anomerization at the C-1 position, the lowfield signals at δ 5.01 (dd, *J*=4, 10 Hz), 5.02 (t, *J*=10 Hz), 5.38 (t, *J*=10 Hz) and 6.00 (t, *J*=10 Hz) were assignable to the C-3,

tetramethylsilane as an internal standard, and chemical shifts are given in δ (ppm). FAB-MS were taken with a JEOL JMS DX-300 instrument. Column chromatography was carried out with Sephadex LH-20 (25–100 μ , Pharmacia Fine Chemical Industry Co., Ltd.), MCI-gel CHP 20P (75–150 μ , Mitsubishi Chemical Industry Co., Ltd.), Fuji-gel ODS G3 (43–65 μ , Fuji-gel Hanbai Co., Ltd.), Prep-pak 500/C₁₈ (37–75 μ , Waters Associates Inc.) and Bondapak C₁₈/Porasil B (37–75 μ , Waters Associates Inc.). Thin layer chromatography (TLC) was conducted on precoated Silica gel 60 F₂₅₄ plates (Merck) and precoated cellulose F₂₅₄ plates. Spots were visualized under UV illumination and by spraying 1% FeCl₃ (EtOH) and 5% sulfuric acid.

Isolation of Tannins a) From *Euphorbia helioscopia*: The fresh whole plants (48.5 kg) of *E. helioscopia*, collected in Fukuoka city in April 1988, were extracted with 80% aqueous acetone at room temperature. The acetone was removed and the insolubles were filtered off. The filtrate was concentrated and applied to a column of Sephadex LH-20. Elution with H₂O containing increasing proportions of MeOH afforded five fractions; I (80 g), II (335 g), III (65 g), IV (20 g) and V (23 g). Fraction I was rechromatographed over MCI-gel CHP 20P, Sephadex LH-20 and Fuji-gel ODS G3 (H₂O–MeOH) to give 1-*O*-galloyl- β -D-glucose (1) (22 g) and 1,6-di-*O*-galloyl- β -D-glucose (2) (380 mg). Fraction II was repeatedly chromatographed over MCI-gel CHP 20P, Fuji-gel ODS G3, Bondapak C₁₈/Porasil B (H₂O–MeOH) and Sephadex LH-20 (EtOH) to give helioscopinin A (10) (8.4 g), carpinusin (11) (18 g), corilagin (8) (660 mg), euphorscopin (16) (3.4 g) and geraniin (9) (69 g). On similar chromatographies, fraction III gave 1,2,6-tri-*O*-galloyl- β -D-glucose (4) (48 mg) and euphorhelin (17) (340 mg), while fraction IV yielded 1,2,3,6-tetra-*O*-galloyl- β -D-glucose (5) (38 mg) and 1,3,4,6-tetra-*O*-galloyl- β -D-glucose (6) (2 g). 1,2,3,4,6-Penta-*O*-galloyl- β -D-glucose (7) (51 mg) and terchebin (12) (3 g) were obtained from fraction V by similar chromatographic separation.

b) From *E. jolkini*: The fresh whole plants (50 kg) of *E. jolkini*, collected in Yobuko, Saga prefecture in April 1989, were extracted with 80% aqueous acetone and the extract was treated in a manner similar to that described for *E. helioscopia* to afford three fractions; I (30 g), II (200 g) and III (60 g). Fraction I was rechromatographed over MCI-gel CHP 20P, Fuji-gel ODS G3, Prep-pak 500/C₁₈ (H₂O–MeOH) and Sephadex LH-20 (EtOH) to give 1-*O*- (1) (410 mg) and 1,6-di-*O*-galloyl- β -D-glucoses (2) (55 mg). Fraction II was repeatedly chromatographed over MCI-gel CHP 20P, Bondapak C₁₈/Porasil B (H₂O–MeOH) and Sephadex LH-20 (60%, MeOH, EtOH) to give corilagin (8) (900 mg), geraniin (9) (9.5 g), helioscopinin A (10) (3.2 g), carpinusin (11) (1.3 g) and jolkianin (18) (340 mg). Similar chromatographies of fraction III gave 1,2,3,6-tetra-*O*- (5) (200 mg), 1,3,4,6-tetra-*O*- (6) (170 mg) and 1,2,3,4,6-penta-*O*-galloyl- β -D-glucoses (7) (94 mg).

c) From *E. supina*: The fresh whole plants (20 kg) of *E. supina*, collected in Fukuoka city in October 1989, were extracted with 80% aqueous acetone and the extract was treated in manner similar to that described for *E. helioscopia* to afford three fractions; I (120 g), II (14 g) and III (8 g). Fraction I was rechromatographed over MCI-gel CHP 20P, Fuji-gel ODS G3 (H₂O–MeOH) and Sephadex LH-20 (60% MeOH) to give corilagin (8) (18 g), supinanin (15) (400 mg) and geraniin (9) (20.4 g). On similar chromatographies, fraction II afforded 1,2,3-tri-*O*-galloyl- β -D-glucose (3) (293 mg). Terchebin (12) (120 mg) and rugosins D (13) (98 mg) and E (14) (340 mg) were obtained from fraction III by similar chromatographic separation.

Supinanin (15) A yellow crystalline powder (H₂O), mp 212–213°C, $[\alpha]_D^{22} + 38.2^\circ$ ($c=0.7$, acetone). Anal. Calcd for C₄₁H₃₀O₂₇·3/2H₂O: C, 50.26; H, 3.08. Found: C, 49.94; H, 3.56. Negative FAB-MS m/z : 953 [M–H][–]. ¹H-NMR (acetone-*d*₆+D₂O, 100 MHz) ppm: 5.03 (d, $J=2$ Hz, DHHDP-1), 5.29 (s, DHHDP-1), 6.33 (d, $J=2$ Hz, DHHDP-3), 6.53 (1H, brs, glc-1), 6.57 (s, DHHDP-3), 7.12, 7.15 (each 2H, s, galloyl-H), 7.28 (1H, s, DHHDP-3'). ¹³C-NMR (acetone-*d*₆+D₂O) ppm: 45.9, 51.7 (DHHDP-1), 62.3, 63.2, 65.1, 68.4, 69.3, 72.5, 73.1, 92.7 (glc-C), 92.1, 108.8 (DHHDP-6), 92.3, 96.2 (DHHDP-5), 110.0, 110.2 (galloyl-2, 6), 119.4, 119.5, 120.5 (galloyl-1), 125.8, 129.3 (DHHDP-3), 139.4, 140.1 (galloyl-4), 145.7, 145.9, 146.0 (galloyl-3,5), 148.6, 153.7 (DHHDP-2), 165.2, 165.5, 165.7, 167.3 (–COO–), 192.1, 194.9 (DHHDP-4).

Preparation of the Phenazine (15a) A mixture of 15 (100 mg), *o*-phenylenediamine (18 mg) and acetic acid (1.3 ml) in EtOH (5 ml) was left standing at room temperature for 15 h. The reaction mixture was diluted with water (2 ml), and evaporation of EtOH gave a yellow precipitate (15a) (64 mg). **15a**: A yellow powder (H₂O), mp > 300°C, $[\alpha]_D^{24} - 28.6^\circ$ ($c=0.7$, acetone). Anal. Calcd for C₄₇H₃₂N₂O₂₄·H₂O: C, 54.98; H, 3.14; N, 2.73. Found: C, 54.80; H, 3.42; N, 2.58. Positive FAB-MS m/z : 1009 [M+H]⁺. ¹H-NMR (acetone-*d*₆+D₂O, 100 MHz) ppm: 4.34 (3H in total, m, glc-5,

6), 5.35 (1H, brd, $J=4$ Hz, glc-2), 5.42 (1H, brd, $J=6$ Hz, glc-4), 5.80 (1H, d, $J=4$ Hz, glc-3), 6.65 (1H, brs, glc-1), 6.90, 7.03, 7.28 (each 2H, s, galloyl H), 7.45 [1H, s, phenazine (phe)-3'], 7.93–8.07, 8.22–8.33 (each 2H, m, phe-2', 3'', 4'', 5''), 8.33 (1H, s, phe-3). ¹³C-NMR (acetone-*d*₆+D₂O) ppm: 65.1, 66.3, 71.4, 71.7, 73.1, 94.8 (glc-C), 109.9, 110.5, 110.8 (galloyl-2, 6), 112.7 (phe-3'), 116.1, 117.1 (phe-1, 1'), 119.8, 120.0, 120.7, 121.0 (galloyl-1, phe-3), 130.1, 132.3 (phe-2', 3'), 136.0 (phe-2), 138.7, 138.9, 139.1, 139.6, 139.9 (galloyl-4, phe-5, 5'), 142.7, 142.9 (phe-1'', 6''), 145.9 (galloyl-3, 5), 152.2 (phe-6), 165.2, 165.6, 167.2, 168.1 (–COO–).

Methylation of 15a, Followed by Alkaline Hydrolysis A solution of 15a (50 mg) in MeOH (2 ml) was methylated with ethereal diazomethane for 20 h at 0°C. After removal of the solvent by evaporation, the residue was heated with 5% NaOH (2 ml) at 90°C for 30 min. The solution was acidified with 1N HCl and extracted with ether. The ether layer was washed with water, dried over Na₂SO₄ and concentrated to dryness. The residue was treated with ethereal diazomethane for 1 h. After evaporation of the solvent and the excess reagent, the residue was chromatographed over silica gel. Elution with benzene–acetone (25:1, v/v) yielded 15b (5 mg) as a white powder (MeOH), mp 81°C. Subsequent elution with benzene–acetone (25:2) afforded 15c as a yellow amorphous powder (11 mg), $[\alpha]_D^{23} - 29.0^\circ$ ($c=1.1$, CHCl₃).

Partial Hydrolysis of 15a A solution of 15a (50 mg) in H₂O–MeOH (1:1) (3 ml) was heated on a water bath for 3 h. The resulting red precipitate (15e) (7 mg) was collected by filtration. The filtrate was directly subjected to Sephadex LH-20 chromatography, and elution with 60% MeOH afforded 15d (23 mg).

Treatment of 15 with Triethylamine A solution of 15 (70 mg) in acetonitrile (2 ml) was heated with triethylamine (0.2 ml) under reflux for 10 min. The solution was acidified with 2N HCl. After concentration to ca. 2 ml, the solution was subjected to Sephadex LH-20 chromatography. Elution with 80% MeOH gave 15f (8 mg). **15f**: A pale yellow amorphous powder, $[\alpha]_D^{23} - 7.4^\circ$ ($c=0.8$, acetone). Anal. Calcd for C₄₀H₃₀O₂₅: C, 52.74; H, 3.30. Found: C, 52.72; H, 3.39. Negative FAB-MS m/z : 909 [M–H][–]. ¹H-NMR (acetone-*d*₆+D₂O) ppm: 2.75 [1H, dd, $J=7$, 19 Hz, brevifolin carboxyl (bre)-3)], 4.05 (1H, brd, $J=8$ Hz, glc-4), 4.50 (1H, brd, $J=7$ Hz, bre-2), 5.24 (1H, t, $J=8$ Hz, glc-2), 5.56 (1H, t, $J=8$ Hz, glc-3), 6.10 (1H, d, $J=8$ Hz, glc-1), 7.04, 7.11, 7.15 (each 2H, s, galloyl-H), 7.17 (1H, s, bre-3').

Euphorscopin (16) A pale yellow amorphous powder, $[\alpha]_D^{22} + 128.3^\circ$ ($c=0.5$, acetone). Anal. Calcd for C₄₁H₂₈O₂₇·5H₂O: C, 47.20; H, 3.64. Found: C, 47.34; H, 3.67. Negative FAB-MS m/z : 951 [M–H][–]. ¹H-NMR (acetone-*d*₆+D₂O, 270 MHz) ppm: 3.92 (1H, dd, $J=8$, 11 Hz, glc-6), 4.87 (1H, s, DHHDP-1), 4.90 (1H, t, $J=8$ Hz, glc-5), 5.06 (1H, dd, $J=8$, 11 Hz, glc-6), 5.30 (1H, dd, $J=1$, 4 Hz, glc-3), 5.50 (1H, d, $J=8$ Hz, glc-4), 5.84 (1H, dd, $J=1$, 4 Hz, glc-2), 6.54 (1H, d, $J=1$ Hz, glc-1), 6.47, 6.83 (each 1H, HHDP-H), 6.61 (1H, s, DHHDP-3), 7.07 (1H, s, DHHDP-3'), 7.23 (2H, s, galloyl-H). ¹³C-NMR (acetone-*d*₆+D₂O) ppm: 45.9, 51.8 (DHHDP-1), 64.6, 65.5, 69.1 ($\times 2$), 71.3 (glc 2–6), 92.4, 96.2, 109.9 (DHHDP-5, 6), 93.3 (glc-1), 108.4, 109.0 (DHHDP-3, 3'), 110.6 (galloyl-2, 6), 112.7 (DHHDP-3'), 115.2 (DHHDP-1'), 115.8 (HHDP-1), 116.7 (HHDP-1'), 119.8 (DHHDP-2), 120.1 (DHHDP-1), 124.4, 125.4 (HHDP-2, 2'), 125.6, 129.7 (DHHDP-3), 136.5, 138.8 (HHDP-5, DHHDP-5'), 140.2 (galloyl-3, 5), 143.2, 144.7 (DHHDP-6'), 144.4 (DHHDP-4'), 144.9 (HHDP-4'), 145.3, 145.7 (HHDP-4, 6, 6'), 146.0 (galloyl-4), 148.5, 153.6 (DHHDP-2), 164.0, 165.0, 165.3, 165.6, 166.4, 167.9, 169.0 (–COO–), 192.1, 195.0 (DHHDP-4).

Preparation of the Phenazine (16a) A mixture of 16 (30 mg), *o*-phenylenediamine (56 mg) and acetic acid (4 ml) in EtOH (16 ml) was left standing at room temperature for 25 min. The reaction mixture was diluted with water (6 ml) and evaporation of EtOH gave a precipitate (16a) (120 mg). **16a**: A yellow powder (H₂O), mp > 300°C, $[\alpha]_D^{23} + 91.8^\circ$ ($c=1.0$, acetone). Anal. Calcd for C₄₇H₃₀N₂O₂₄·5/2H₂O: C, 53.66; H, 3.33; N, 2.66. Found: C, 53.86; H, 3.23; N, 2.60. Positive FAB-MS m/z : 1007 [M+H]⁺. ¹H-NMR (acetone-*d*₆+D₂O, 270 MHz) ppm: 3.87 (1H, dd, $J=4$, 13 Hz, glc-6), 4.80 (1H, dd, $J=7$, 10 Hz, glc-5), 5.13 (1H, dd, $J=7$, 13 Hz, glc-6), 5.32 (1H, dd, $J=1$, 4 Hz, glc-3), 5.41 (1H, brs, glc-2), 5.68 (1H, dd, $J=4$, 10 Hz, glc-4), 6.33 (1H, brs, glc-1), 6.63, 6.67 (each s, 1H, HHDP-H), 7.10 (1H, s, phe-3'), 7.17 (2H, s, galloyl-H), 7.92 (1H, s, phe-3), 7.94–8.03, 8.17–8.39 (each 2H, m, phe-2', 3'', 4'', 5'').

Methylation of 16a, Followed by Alkaline Hydrolysis 16a (50 mg) was methylated with ethereal diazomethane at 0°C for 7 h. The tridecamethylate thus obtained was hydrolyzed with 5% NaOH (4 ml) at 90°C for 1 h. Work-up as above gave a mixture of hydrolysates, which was treated with ethereal diazomethane. The methylates were separated as before to give 15b (5 mg) and dimethyl-(*S*)-hexamethoxydiphenolate (16b) (11 mg) as a

yellow powder, $[\alpha]_D^{25} -27.6^\circ$ ($c=1.1$, CHCl_3) and **15c** (11 mg).

Enzymatic Hydrolysis of 16 A solution of **16** (60 mg) in H_2O (3 ml) was incubated with tannase at room temperature for 40 min. The reaction mixture was subjected to MCI-gel CHP 20P chromatography with an H_2O -MeOH system to yield gallic acid and a hydrolysate (**16c**) (28 mg), which was identified as brevifagin II by comparison of the ^1H - and ^{13}C -NMR spectral data with reported values. **16c**: A pale yellow amorphous powder, $[\alpha]_D^{25} +71.3^\circ$ ($c=1.0$, acetone). *Anal.* Calcd for $\text{C}_{34}\text{H}_{24}\text{O}_{23} \cdot 1/2\text{H}_2\text{O}$: C, 50.43; H, 3.09. Found: C, 50.40; H, 3.11. Negative FAB-MS m/z : 799 $[\text{M}-\text{H}]^-$. ^1H -NMR (acetone- d_6 + D_2O , 270 MHz) ppm: 4.55 (1H, dd, $J=1$, 3 Hz, glc-2), 4.90 (1H, s, DHHDP-1), 4.91 (1H, dd, $J=4$, 6 Hz, glc-5), 4.96 (1H, dd, $J=6$, 9 Hz, glc-6), 5.09 (1H, brd, $J=3$ Hz, glc-3), 5.38 (1H, brd, $J=4$ Hz, glc-4), 6.35 (1H, d, $J=1$ Hz, glc-1), 6.53, 6.54, 6.74, 6.75, 7.08 (4H in total, each s, HHDP and DHHDP-3, 3'). ^{13}C -NMR (acetone- d_6 + D_2O) ppm: 45.9, 51.7 (DHHDP-1), 63.8, 64.0, 64.4, 64.9, 68.1, 69.8, 74.2, 74.6 (glc 2-6), 95.3, 96.2 (glc-1), 92.5, 98.5, 108.9 (DHHDP-5, 6), 108.3, 109.7 (HHDP-3, 3'), 112.7 (DHHDP-3'), 115.0, 115.5 (HHDP-1, 1'), 115.7 (DHHDP-1'), 120.2 (DHHDP-2'), 125.3, 125.4 (HHDP-2, 2'), 126.1, 129.3 (DHHDP-3), 136.4, 136.9 (HHDP-5, 5'), 138.8 (DHHDP-5'), 143.3, 147.4 (DHHDP-6'), 145.0, 145.2 (HHDP-4, 4'), 145.8 (HHDP-6, 6'), 149.1, 154.2 (DHHDP-2), 164.5, 165.2, 166.6, 168.0, 168.1 (-COO-), 192.1, 194.9 (DHHDP-4).

Euphorhelin (17) A pale yellow amorphous powder, $[\alpha]_D^{20} -89.7^\circ$ ($c=1.0$, acetone). *Anal.* Calcd for $\text{C}_{68}\text{H}_{50}\text{O}_{45} \cdot 7\text{H}_2\text{O}$: C, 47.66; H, 3.73. Found: C, 47.59; H, 3.73. Negative FAB-MS m/z : 1585 $[\text{M}-\text{H}]^-$. ^1H -NMR (acetone- d_6 + D_2O , 270 MHz) ppm: 3.5-5.6 (12H in total, m, glc 2-6), 4.93 (d, $J=1.5$ Hz, DHHDP-1), 5.18 (s, DHHDP-1), 5.81 (1H, d, $J=8$ Hz, glc A-1), 6.20 (d, $J=1.5$ Hz, DHHDP-3), 6.52 (s, DHHDP-3), 6.56 (1H, d, $J=7$ Hz, glc B-1), 7.07, 7.11, 7.12, 7.13, 7.14, 7.16, 7.17, 7.22, 7.27 (11H in total, each s, aromatic H). ^{13}C -NMR (acetone- d_6 + D_2O) ppm: 45.9, 51.8 (DHHDP-1), 62.7, 63.9, 65.9, 66.8, 69.8, 70.2, 71.0, 72.4, 73.1, 73.7, 74.7, 75.3, 91.3, 93.6 (glc-A, B), 92.3, 96.1, 108.8 (DHHDP-5, 6), 104.6, 109.9, 110.2, 110.5, 113.6, 114.6, 115.7, 116.7, 116.8, 117.1, 118.8, 119.7, 121.0, 123.6, 124.8, 125.0, 128.7, 135.9, 136.6, 137.5, 137.8, 139.0, 139.8, 140.1, 140.4, 143.1, 143.4, 144.7, 144.9, 145.3, 145.9, 146.9, 147.5, 148.9, 154.1 (aromatic C), 164.9, 165.4, 165.6, 165.9, 166.6, 167.2, 168.8 (-COO-), 192.0, 194.8 (DHHDP-4).

Preparation of the Phenazine (17a) A mixture of **17** (200 mg) and *o*-phenylenediamine (18 mg) in acetic acid-EtOH (1:4, v/v) (15 ml) was treated at room temperature for 10 h. The solution was diluted with water (5 ml) and evaporation of EtOH gave a yellow precipitate (**17a**) (170 mg). **17a**: A yellow powder (H_2O), $[\alpha]_D^{25} -12.0^\circ$ ($c=0.2$, acetone). *Anal.* Calcd for $\text{C}_{74}\text{H}_{52}\text{N}_2\text{O}_{42} \cdot 2\text{H}_2\text{O}$: C, 52.90; H, 3.34; N, 1.67. Found: C, 53.13; H, 3.30; N, 1.69. ^1H -NMR (acetone- d_6 + D_2O , 270 MHz) ppm: 3.86 (1H, dd, $J=4$, 12 Hz, glc A-6), 3.93 (1H, m, glc A-5), 4.37 (1H, dd, $J=5$, 12 Hz, glc A-6), 4.56 (1H, brd, $J=12$ Hz, glc B-6), 4.78 (1H, dd, $J=8$, 12 Hz, glc B-6), 4.95 (1H, dd, $J=4$, 8 Hz, glc B-5), 5.20 (1H, t, $J=9$ Hz, glc A-2), 5.42 (1H, d, $J=3$ Hz, glc B-4), 5.55 (1H, d, $J=4$ Hz, glc B-3), 5.70 (1H, d, $J=6$ Hz, glc B-2), 5.83 (1H, d, $J=8$ Hz, glc A-1), 6.12 (1H, d, $J=6$ Hz, glc B-1), 6.22, 7.03, 7.18, 7.50, 8.31 [valoneoyl (val), phe-H], 6.97, 7.12, 7.13 (each 2H, s, galloyl-H). ^{13}C -NMR (acetone- d_6 + D_2O) ppm: 63.9 (glc A-6), 71.6 (glc A-4), 73.8 (glc A-2), 74.6 (glc A-3), 75.4 (glc A-5), 65.8, 67.7, 68.6, 76.6 ($\times 2$) (glc B 2-6), 91.8 (glc B-1), 93.7 (glc A-1), 105.3, 110.0, 110.3, 113.4, 114.7, 116.4, 116.5, 117.2, 119.4, 119.7, 120.1, 121.0, 123.7, 124.7, 129.8, 130.1, 132.7, 136.1, 136.7, 137.4, 139.0, 139.1, 139.6, 139.9, 140.2, 140.5, 142.9, 143.5, 144.7, 144.9, 145.9, 147.4, 152.2 (aromatic C), 165.2, 165.7, 166.1, 166.7 ($\times 2$), 167.4, 168.2, 169.1 (-COO-).

Methylation of 17a, Followed by Alkaline Hydrolysis A solution of **17a** (40 mg) in MeOH (3 ml) was methylated with ethereal diazomethane at 0°C for 15 h to give a methylate, which was treated with 5% NaOH (4 ml) at 90°C for 1 h. The hydrolysate mixture thus obtained was titrated with ethereal diazomethane and separated as described for **15a** to furnish **15b** (7 mg), the (*R*)-phenazine dimethyl ester (**17b**) (6 mg) $[\alpha]_D^{24} +35.4^\circ$ ($c=0.6$, CHCl_3), and trimethyl octa-*O*-methyl-(*R*)-valoneate (**17c**) (5 mg) $[\alpha]_D^{24} +14.7^\circ$ ($c=0.5$, CHCl_3).

Partial Hydrolysis of 17a A solution of **17a** (120 mg) in H_2O (6 ml) was heated on a water bath for 30 h. The resulting red precipitate (**15e**) (14 mg) was collected by filtration. The filtrate was directly subjected to MCI-gel CHP 20P chromatography and elution with H_2O -MeOH (1:0-0:1) gave 1,6-di-*O*-galloyl- β -D-glucose (**2**) (5 mg), isomallotinic acid (**17e**) (2 mg) and a hydrolysate (**17f**) (54 mg). **17f**: A pale brown amorphous powder, $[\alpha]_D^{23} -66.0^\circ$ ($c=0.6$, acetone). *Anal.* Calcd for $\text{C}_{54}\text{H}_{44}\text{O}_{36} \cdot 2\text{H}_2\text{O}$: C, 49.69; H, 3.68. Found: C, 49.54; H, 3.47. Negative FAB-MS m/z : 1267 $[\text{M}-\text{H}]^-$. ^1H -NMR (acetone- d_6 + D_2O , 270 MHz) ppm: 4.00-4.86 (11H in total, m, glc-H), 5.20 (1H, t, $J=9$ Hz, glc A-2), 5.82 (1H, d,

$J=9$ Hz, glc A-1), 6.35 (1H, d, $J=2$ Hz, glc B-1), 6.23 (1H, s, val-3'), 6.85 (1H, s, val-3), 7.12 (1H, s, val-3'), 7.10, 7.15 (6H in total, each s, galloyl-H).

Jolkianin (18) A pale brown amorphous powder, $[\alpha]_D^{24} -0.8^\circ$ ($c=0.8$, acetone). *Anal.* Calcd for $\text{C}_{82}\text{H}_{56}\text{O}_{53} \cdot 2\text{H}_2\text{O}$: C, 51.14; H, 3.11. Found: C, 50.89; H, 3.04. Negative FAB-MS m/z : 1887 $[\text{M}-\text{H}]^-$.

Preparation of the Phenazine (18a) A solution of **18** (100 mg) and *o*-phenylenediamine (9 mg) in 20% AcOH-EtOH (3 ml) was stirred at room temperature for 20 h. After removal of EtOH under reduced pressure, the aqueous solution was subjected to MCI-gel CHP 20P chromatography to give **18a** (67 mg). **18a**: A yellow powder (H_2O), mp $>300^\circ\text{C}$, $[\alpha]_D^{23} -68.3^\circ$ ($c=0.6$, acetone). *Anal.* Calcd for $\text{C}_{88}\text{H}_{58}\text{O}_{50}\text{N}_2$: C, 54.37; H, 2.98; N, 1.44. Found: C, 54.21; H, 2.79; N, 1.43. Negative FAB-MS m/z : 1941 $[\text{M}-\text{H}]^-$. ^1H -NMR (acetone- d_6 + D_2O , 270 MHz) ppm: 4.03 (1H, dd, $J=5$, 11 Hz, glc A-5), 4.44 (1H, dd, $J=5$, 11 Hz, glc A-6), 4.54 (1H, dd, $J=4$, 11 Hz, glc B-6), 4.56 (1H, m, glc B-5), 4.76 (1H, t, $J=11$ Hz, glc B-6), 4.97 (1H, brs, glc A-4), 5.49 (1H, brs, glc A-3), 5.25 (1H, dd, $J=3$, 7 Hz, glc B-4), 5.33 (1H, t, $J=11$ Hz, glc A-6), 5.53 (1H, dd, $J=3$, 7 Hz, glc B-2), 5.71 (1H, brs, glc A-3), 5.86 (1H, t, $J=7$ Hz, glc B-3), 6.15 (1H, d, $J=3$ Hz, glc B-1), 6.23 (1H, brs, glc A-1), 6.68, 6.74, 6.83, 6.84 (each 1H, s, HHDP-H), 6.85, 7.32 (each 1H, d, $J=2$ Hz, DHDG-H), 7.01 (1H, s, phe-3'), 7.11, 7.12 (each 2H, s, galloyl-H), 7.17 (1H, s, DHDG-H), 8.04 (1H, s, phe-3), 7.99-8.04, 8.28-8.33 (each 2H, m, phe-2', 3', 4', 5'). ^{13}C -NMR (acetone- d_6 + D_2O) ppm: 60.9, 64.0, 64.9, 67.7, 69.2, 70.7 ($\times 2$), 71.8, 72.7, 75.1, 90.1, 94.6 (glc A, B), 108.9, 109.4, 110.2, 111.3, 112.4, 114.8, 116.0, 116.2, 116.4, 116.6, 118.2, 118.6, 120.0, 120.1, 123.0, 124.7, 124.9, 125.3, 125.5, 130.1, 132.3, 135.7, 136.8, 137.0, 137.2, 137.9, 138.1, 138.5, 139.6, 140.5, 140.8, 142.9, 144.9, 145.0, 146.0, 146.3, 147.8, 152.6 (aromatic C), 162.0, 165.9, 166.2 ($\times 2$), 166.4 ($\times 2$), 166.8, 168.0, 168.5, 170.2 (-COO-).

Methylation of 18a, Followed by Alkaline Hydrolysis **18a** (70 mg) was treated with diazomethane in ether for 24 h at 0°C . After evaporation of the solvent, the residue was hydrolyzed with 5% NaOH (3 ml) at 90°C for 30 min. The reaction mixture was treated with ethereal diazomethane and separated as described before to give **15b** (13 mg), **16b** (16 mg), **15c** (11 mg) and dimethyl pentamethoxydehydrodigallate (**18b**) (13 mg). **18b**: An off-white amorphous powder. ^1H -NMR (CDCl_3) ppm: 3.74-4.05 (21H in total, each s, OCH_3), 6.80, 7.30 (each 1H, d, $J=2$ Hz), 7.27 (1H, s).

Partial Hydrolysis of 18a A solution of **18a** (100 mg) in H_2O -MeOH (4 ml) was heated at 90°C for 5 h. After cooling, the reaction mixture was concentrated, and chromatographed over Sephadex LH-20 and MCI-gel CHP 20P (H_2O -MeOH) to afford **18c** (50 mg), **18d** (5 mg) and **15e** (7 mg). **18c**: A pale brown amorphous powder, $[\alpha]_D^{25} -47.0^\circ$ ($c=0.9$, acetone). *Anal.* Calcd for $\text{C}_{68}\text{H}_{50}\text{O}_{44}$: C, 51.49; H, 3.37. Found: C, 51.89; H, 3.83. Negative FAB-MS m/z : 1569 $[\text{M}-\text{H}]^-$. ^1H -NMR (acetone- d_6 + D_2O , 400 MHz) ppm: 3.67 (1H, dd, $J=3$, 6 Hz, glc A-4), 4.03 (1H, dd, $J=6$, 12 Hz, glc A-6), 4.21 (1H, dd, $J=6$, 12 Hz, glc A-5), 4.42 (1H, dd, $J=5$, 12 Hz, glc B-6), 4.54 (1H, dd, $J=8$, 12 Hz, glc B-5), 4.66 (1H, t, $J=12$ Hz, glc B-6), 4.73 (1H, t, $J=12$ Hz, glc A-6), 5.13 (1H, t, $J=6$ Hz, glc A-3), 5.22 (1H, dd, $J=3$, 8 Hz, glc B-4), 5.50 (1H, dd, $J=3$, 8 Hz, glc B-2), 5.81 (1H, d, $J=3$ Hz, glc A-1), 5.82 (1H, t, $J=8$ Hz, glc B-3), 6.08 (1H, d, $J=3$ Hz, glc B-1), 6.74, 6.83 ($\times 2$), 6.85 (each 1H, s, HHDP-H), 6.88, 7.28 (each 1H, d, $J=2$ Hz, DHDG-H), 7.10, 7.11 (each 2H, s, galloyl-H), 7.16 (1H, s, DHDG-H). ^{13}C -NMR (acetone- d_6 + D_2O) ppm: 65.0, 68.1, 69.4, 70.7, 71.7, 73.1, 75.2, 76.2, 94.6, 96.1 (glc A, B), 108.3, 109.2, 109.5, 110.2, 110.3, 112.3, 114.3, 116.6, 119.8, 120.0, 124.7, 125.5, 125.9, 136.8, 137.0, 137.3, 139.6, 140.3, 140.6, 143.0, 144.7, 145.0, 146.0, 146.3, 148.1 (aromatic C), 164.9, 165.8, 166.1, 166.4, 167.1, 168.7, 169.4 (-COO-). **18d**: A pale brown amorphous powder, $[\alpha]_D^{25} 0^\circ$ ($c=0.5$, acetone). *Anal.* Calcd for $\text{C}_{40}\text{H}_{38}\text{O}_{28} \cdot \text{H}_2\text{O}$: C, 48.78; H, 4.06. Found: C, 48.96; H, 4.23. Negative FAB-MS m/z : 965 $[\text{M}-\text{H}]^-$. ^1H -NMR (acetone- d_6 + D_2O , 270 MHz) ppm: 3.14 (dd, $J=8$, 10 Hz, glc A- β -2), 4.60 (d, $J=8$ Hz, glc A- β -1), 5.01 (dd, $J=4$, 10 Hz, glc B- α -2), 5.02 (t, $J=10$ Hz, glc A- β -3), 5.12 (d, $J=4$ Hz, glc B- α -3), 6.75, 7.17 (each 1H, m, DHDG-H), 7.18, 7.19 (1H in total, each s, DHDG-H), 7.08, 7.09 (each 2H, s, galloyl-H).

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