Galloyl and Hexahydroxydiphenoyl Esters of Phenylpropanoid Glucosides, Phenylpropanoids and Phenylpropanoid Glucosides from Rhizome of *Balanophora fungosa*

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Five new galloyl and (*S*)-hexahydroxydiphenyl (HHDP) esters of phenylpropanoid glucosides; 1-*O*-(*E*)-coumaroyl-3-galloyl-4,6-(*S*)-HHDP-β-D-glucopyranose (21), 1-*O*-(*E*)-coumaroyl-3,4,6-trigalloyl-β-D-glucopyranose (22), 1-*O*-(*E*)-caffeoyl-3,4,6-trigalloyl-β-D-glucopyranose (23), 1-*O*-(*E*)-cinnamoyl-3-galloyl-4,6-(*S*)-HHDP-β-D-glucopyranose (24), and 1-*O*-(*E*)-cinnamoyl-4-galloyl-β-D-glucopyranose (25), together with twenty known compounds which were identified as four triterpenes (1, 2, 3, 5), one steroid (4), one lignan (6), three phenylpropanoids (7, 8, 14), five phenylpropanoid glucosides (10, 12, 13, 15, 16), five galloyl and HHDP esters of phenylpropanoid glucosides (11, 17—20), and one bischroman (9). Their structures were determined on the basis of 1D and 2D spectroscopic data.

Key words *Balanophora fungosa*; Balanophoraceae; phenylpropanoid; phenylpropanoid glucoside; hexahydroxydiphenoyl ester; galloyl ester

Balanophora fungosa is a parasitic plant growing on the root of various plants and belongs to the family Balanophoraceae. It is known as "Ka-noon-din", "Kok-mag-pasi", "Head-hin", "Wan-dok-din" and "Bua-pud" in Thai. It is monoecious or rarely dioecious, with yellowish brown rhizome and 10—15 cm in height.[1] In Thai traditional medicine, *B. fungosa* is used for ear discharge and as an antiseptic.[2] Previous phytochemical investigation of *Balanophora* species have resulted in the isolation of various types of compounds such as lignans,[3] phenylpropanoids,[3] steroids,[4] triterpene,[5] fatty acid,[5] phenylpropanoide glucosides, galloyl and hexahydroxydiphenoyl esters of phenylpropanoid glucosides,[6] and ellagitannins.[7] The present study deals with the isolation and characterization of five new compounds (**21**—**25**), together with twenty known compounds (**1**—**20**) from *B. fungosa* which grew on the root of *Diospyros mollis*. It should be noted that compounds **9**, **11** and **14** are the first isolation from Balanophoraceae.

Results and Discussion

The hexane, EtOAc and MeOH extracts of rhizomes of *B. fungosa* were fractionated by column chromatography on silica gel PF60, cosmosil ($75C_{18}$-OPN), lichroprep RP-18 and sephadex LH-20. Chromatotron and preparative thin layer chromatography (TLC) gave twenty known compounds; β-amyrin palmitate (**1**),[5] lupeol acetate (**2**),[3] lupeol (**3**),[8] β-

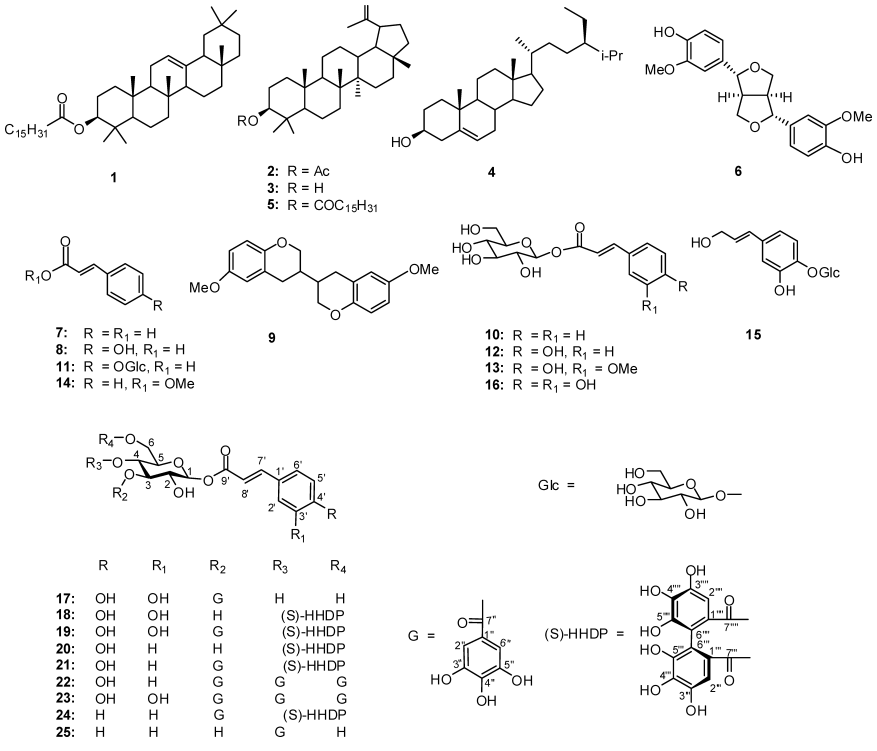

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Table 1. ^{1}H-NMR Spectral Data (δ, ppm) in CD_3OD for Compounds **21**—**25** (400 MHz)[a)]

Position	21	22	23	24	25
1-Glucose	5.75 d (8.2)	5.83 d (8.2)	5.83 d (8.2)	5.78 d (8.1)	5.69 d (8.2)
2	3.83 br t (8.2)	3.88 br t (8.2)	3.89 t (8.2)	3.88 t (8.1)	3.57 t (8.2)
3	5.43 t (9.4)	5.56 t (9.4)	5.53 t (9.4)	5.44 t (9.5)	3.79 t (9.4)
4	5.08 t (10.0)	5.44 t (9.4)	5.44 t (9.4)	5.08 t (10.0)	5.02 t (9.4)
5	4.24 br dd (6.2, 10.0)	4.42 br d (9.4)	4.12 m	4.26 br dd (6.2, 10.0)	3.72 ddd (2.0, 5.4, 8.2)
6a	5.30 dd (6.2, 13.2)	4.46 br d (12.3)	4.49 br d (12.2)	5.32 dd (6.2, 13.2)	3.65 br dd (2.0, 12.1)
6b	3.85 d (13.2)	4.30 dd (4.9, 12.3)	4.23 dd (4.8, 12.2)	3.88 br d (13.2)	3.54 dd (4.7, 12.0)
	1′-Coumaroyl	1′-Coumaroyl	1′-Caffeoyl	1′-Cinnamoyl	1′-Cinnamoyl
2′	7.49 d (8.4)	7.40 d (8.2)	7.04 d (1.7)	7.62 m	7.64 m
3′	6. 82 d (8.4)	6.80 d (8.2)		7.42 m	7.42 m
4′				7.42 m	7.42 m
5′	6. 82 d (8.4)	6.80 d (8.2)	6.77 d (8.2)	7.42 m	7.42 m
6′	7.49 d (8.4)	7.40 d (8.2)	6.83 dd (1.7, 8.2)	7.62 m	7.64 m
7′	7.75 d (15.9)	7.72 d (16.0)	7.66 d (15.9)	7.83 d 16.0	7.82 d (16.0)
8′	6.38 d (15.9)	6.30 d (16.0)	6.27 d (15.9)	6.58 d (16.0)	6.59 d (16.0)
1″-Galloyl		1″-Galloyl	1″-Galloyl	1″-Galloyl	1″-Galloyl
2″, 6″	7.02 s	6.99 s	7.01 s	7.05 s	7.10 s
1-HHDP		1-Galloyl	1-Galloyl	1-HHDP	
2‴	6.45 s	6.94 s	6.95 s	6.48 s	
6‴		6.94 s	6.95 s		
1⁗-HHDP		1⁗-Galloyl	1⁗-Galloyl	1-HHDP	
2‴	6.60 s	7.07 s	7.07 s	6.59 s	
6⁗		7.07 s	7.07 s		

a) Figure in parentheses are multiplicities and coupling constants in Hz.

sitosterol (**4**),[9)] lupeol palmitate (**5**),[10)] pinoresinol (**6**),[3)] cinnamic acid (**7**),[3)] *p*-hydroxycinnamic acid (**8**),[3)] 3,3′-bis(3,4-dihydro-6-methoxy-2*H*-1-benzopyran) (**9**),[11)] cinnamoyl-β-D-glucopyranose (**10**),[12)] *p*-glucosylcinnamic acid (**11**),[13)] *p*-hydroxycinnamoyl-β-D-glucopyranose (**12**),[6)] 4′-hydroxy-3′-methoxycinnamoyl-β-D-glucopyranose (**13**),[12)] methyl cinnamate (**14**),[12)] coniferin (**15**),[3)] caffeoyl-β-D-glucopyranose (**16**),[4)] 1-*O*-(*E*)-caffeoyl-3-galloyl-β-D-glucopyranose,[4)] 1-*O*-(*E*)-caffeoyl-4,6-(*S*)-hexahydroxydiphenyl (HHDP)-β-D-glucopyranose (**18**),[6)] 1-*O*-(*E*)-caffeoyl-3-galloyl-4,6-(*S*)-HHDP-β-D-glucopyranose (**19**),[6)] 1-*O*-(*E*)-coumaroyl-4,6-(*S*)-HHDP-β-D-glucopyranose (**20**)[6)] and five new compounds (**21**—**25**).

Compound **21** was obtained as a yellow powder and it was assigned the molecular formula $C_{36}H_{28}O_{20}$ from the high resolution electrospray ionization time-of-flight mass spectrometry (HR-ESI-TOF-MS) (observed *m*/*z* 781.1252 $[M+H]^+$). The IR spectrum showed absorption bands of hydroxyl (3427 cm^{-1}) and ester carbonyl (1722 cm^{-1}) groups. The ^{1}H- and ^{13}C-NMR spectra of **21** were similar to those of **19**,[6)] except for the absence of the caffeoyl group which was replaced by a coumaroyl unit. The ^{1}H-NMR spectrum (Table 1) showed four sets of signals arising from the coumaroyl group at δ 7.49 (2H, d, *J*=8.4 Hz, H-2′, 6′), 6.82 (2H, d, *J*=8.4 Hz, H-3′, 5′), 7.75 (1H, d, *J*=15.9 Hz, H-7′) and 6.38 (1H, d, *J*=15.9 Hz, H-8′); the galloyl unit at δ 7.02 (2H, s, H-2″, 6″); the HHDP moiety at δ 6.45 (1H, s, H-2‴), and 6.60 (1H, s, H-2⁗); and the glucose moiety at δ 5.75 (1H, d, *J*=8.2 Hz, H-1), 5.43 (1H, t, *J*=9.4 Hz, H-3), 5.30 (1H, dd, *J*=6.2, 13.2 Hz, H-6a), 5.08 (1H, t, *J*=10.0 Hz, H-4), 4.24 (1H, br dd, *J*=6.2, 10.0 Hz, H-5), 3.83 (1H, br t, *J*=8.2 Hz, H-2), and 3.85 (1H, d, *J*=13.2 Hz, H-6b). The ^{13}C-NMR spectrum (Table 2) of **21** showed four ester carbonyl carbons which were assigned to the coumaroyl, galloyl, and HHDP groups. The location of each acyl group on the glucose core was determined by heteronuclear multiple bond correlation

Table 2. ^{13}C-NMR Spectral Data (δ, ppm) in CD_3OD for Compounds **21**—**25** (100 MHz)

Position	21	22	23	24	25
1	94.6	94.2	94.2	94.7	94.3
2	71.3	71.1	71.1	71.3	72.8
3	74.7	74.9	74.9	74.7	74.5
4	70.0	68.6	68.6	69.9	70.6
5	72.0	72.8	72.8	72.0	75.6
6	62.5	61.9	61.9	69.5	60.5
1′	125.5	125.6	126.1	134.1	134.2
2′	130.1	130.1	114.0	128.0	128.0
3′	115.5	115.5	145.4	128.7	128.7
4′	160.2	160.2	148.6	130.6	130.4
5′	115.5	115.5	115.1	128.7	128.7
6′	130.1	130.1	122.0	128.0	128.0
7′	147.0	147.0	147.4	146.8	146.4
8′	112.6	112.6	112.6	116.4	116.7
9′	166.0	166.0	166.0	165.4	165.6
1″	119.6	119.6	119.6	119.6	119.7
2″	109.2	109.1	109.1	109.2	108.9
3″	144.9	145.0	145.0	144.9	145.3
4″	138.5	138.5	138.5	138.5	138.4
5″	144.9	145.0	145.0	144.9	145.3
6″	109.2	109.1	109.1	109.2	108.9
7″	166.6	166.3	166.3	166.6	166.3
1‴	115.3	119.7	119.7	115.0	
2‴	124.9	109.1	109.1	124.5	
3‴	106.9	145.0	145.0	106.5	
4‴	144.4	138.7	138.7	144.5	
5‴	136.2	145.0	145.0	136.2	
6‴	143.0	109.2	109.2	143.4	
7‴	167.9	165.7	165.7	167.9	
1⁗	115.3	119.7	119.7	115.3	
2⁗	124.9	109.1	109.1	124.9	
3⁗	107.2	145.0	145.0	107.1	
4⁗	144.5	138.6	138.6	144.9	
5⁗	136.2	145.0	145.0	136.2	
6⁗	143.4	109.1	109.1	143.4	
7⁗	168.2	166.6	166.6	168.2	

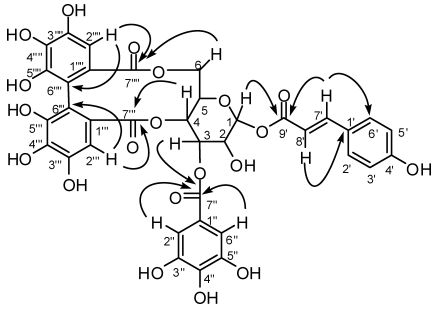

Fig. 1. Selected HMBC Correlations of **21**

(HMBC) correlation (Fig. 1) of H-1 to coumaroyl (166.0, C-9′), H-3 to galloyl (166.6, C-7″), and H-4 and H-6a,b to HHDP carbonyl carbons (167.9, C-7‴ and 168.2, C-7⁗, respectively).

The atropisomerism of the HHDP biphenyl bond at C-4 and C-6 of glucose was assigned to be an *S* configuration from analysis of the circular dichroism (CD) spectrum which showed a negative Cotton effect at 273 nm ($\Delta\varepsilon$ −19.7) and a positive one at 240 nm ($\Delta\varepsilon$ 43.1), and the specific rotation value (−32.7), as well as the deshielded resonance signals of methine proton, H-4 (δ 5.08) and methylene protons, H-6 (δ 5.30, 3.85). These data were comparable to the related compound, 1-*O*-*p*-(*E*)-coumaroyl-4,6-(*S*)-HHDP-β-D-glucopyranose.[6] The absolute configuration on the glucose unit was assigned on the basis of their coupling constants. The *J* values of 8.2—10.0 Hz for the coupling of H-1 through H-5 revealed that those protons were in axial positions. On the basis of the above data, the structure of **21** was assigned as 1-*O*-(*E*)-coumaroyl-3-galloyl-4,6-(*S*)-HHDP-β-D-glucopyranose.

The molecular formula of compound **22** was determined as $C_{36}H_{30}O_{20}$ by HR-ESI-TOF-MS (observed *m*/*z* 783.1409 $[M+H]^+$). The ^{1}H- and ^{13}C-NMR spectra of **22** were similar to those of **21**, except for the absence of the HHDP group which was displaced by two sets of galloyl units at δ_H 6.94 (2H, s, H-2‴, 6‴) and 7.07 (2H, s, H-2⁗, 6⁗). The HMBC correlation of **22** also confirmed the connection of coumaroyl and tri-galloyl units to the glucose unit at C-1, C-3, C-4 and C-6, respectively, *via* the correlation of H-1 to C-9′ (δ_C 166.0), H-3 to C-7″ (δ_C 166.3), H-4 to C-7‴ (δ_C 165.7) and H-6 to C-7⁗ (δ_C 166.6). The complete assignment of protons and carbons in **22** (Tables 1, 2) were established by analyses of correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), and HMBC spectra. On the basis of the above data the structure of **22** was deduced as 1-*O*-(*E*)-coumaroyl-3,4,6-trigalloyl-β-D-glucopyranose.

Compound **23** was shown to be caffeoyl-trigalloyl-glucose by comparisons of the ^{1}H- and ^{13}C-NMR spectra with those of **22** and the observation of a $[M+H]^+$ peak at *m*/*z* 799.1358 in the HR-ESI-TOF-MS ($C_{36}H_{30}O_{21}$) which has one more oxygen in the structure. The ^{1}H- and ^{13}C-NMR spectra of **23** were similar to those of **22**, except for the absence of the coumaroyl group which was displaced by a caffeoyl group at δ_H 7.04 (1H, d, *J*=1.7 Hz, H-2′), 6.83 (1H, dd, *J*=1.7, 8.2 Hz, H-6′), and 6.77 (1H, d, *J*=8.2 Hz, H-5′). The HMBC spectrum revealed the correlation of H-1 to caffeoyl (δ_C 166.0, C-9′), H-3 to galloyl (δ_C 166.3, C-7″), H-4 to galloyl (δ_C 165.7, C-7‴) and H-6 to galloyl (δ_C 166.6, C-7⁗) carbonyl carbons. The complete assignment of protons and carbons in **23** (Tables 1, 2) were established by analyses of COSY, HSQC, and HMBC spectra. Consequently, the structure of compound **23** was assigned as 1-*O*-(*E*)-caffeoyl-3,4,6-trigalloyl-β-D-glucopyranose.

The ^{1}H- and ^{13}C-NMR spectral data of **24** (Tables 1, 2) were similar to those of **21**, except for the presence of a cinnamoyl unit at δ_H 7.83 (1H, d, *J*=16.0 Hz, H-7′), 6.58 (1H, d, *J*=16.0 Hz, H-8′); 7.62 (2H, m, H-2′ and H-6′); and 7.42 (3H, m, H-3′, H-4′ and H-5′). The resonances of galloyl, HHDP and glucose units also showed splitting patterns similar to those of **21**. The CD spectrum of **24** showed a negative Cotton effect at 297 nm ($\Delta\varepsilon$ −6.7) and a positive one at 240 nm ($\Delta\varepsilon$ 33.6)[6] which showed similar pattern to compound **21**. Analyses of the HSQC, HMBC and COSY spectra led to the complete assignment of protons and carbons (Tables 1, 2). The HMBC correlation of **24** confirmed the connection of cinnamoyl, galloyl and HHDP groups to the glucose unit at C-1, C-3, C-4 and C-6, respectively *via* the correlations of H-1 to C-9′, H-3 to C-7″, H-4 to C-7‴, and H-6 to C-7⁗. The structure of **24** was finally established as 1-*O*-(*E*)-cinnamoyl-3-galloyl-4,6-(*S*)-HHDP-β-D-glucopyranose.

Compound **25** was obtained as a yellow amorphous solid and it was assigned the molecular formula $C_{22}H_{22}O_{11}$ from the HR-ESI-TOF-MS (observed *m*/*z* 463.1186 $[M+H]^+$). The ^{1}H- and ^{13}C-NMR spectra of **25** (Tables 1, 2) were similar to those of **24** except for the absence of the HHDP group at C-4 and C-6 of the glucose unit. The HMBC correlation of **25** confirmed the connection of cinnamoyl and galloyl units to the glucose unit at C-1, and C-4, respectively *via* the correlations of H-1 to C-9′ and H-4 to C-7″. Thus, the structure of **25** was assigned as 1-*O*-(*E*)-cinnamoyl-4-galloyl-β-D-glucopyranose.

Experimental

General Procedures Optical rotations were obtained using a JASCO DIP-1000 digital polarimeter, where CD spectra were obtained using a JASCO J-810 apparatus. UV spectra were measured on an Agilent 8453 UV–visible spectrophotometer. IR spectra were recorded as KBr disks, using Perkin Elmer Spectrum One FTIR spectrophotometer. The ^{1}H- and ^{13}C-NMR spectra were obtained from Varian Mercury Plus 400 spectrometer. Chemical shifts were reported on δ (ppm) scale using $CDCl_3$, CD_3OD and DMSO-d_6 with the solvents and tetramethylsilane (TMS) as the internal standards HR-ESI-MS were recorded on a Micromass LCT mass spectrometer. Column chromatography was carried out on MERCK silica gel 60 (less than 0.063 mm and 0.063—0.200 mm), cosmosil (75C_{18}-OPN), lichroprep RP-18 (particle size 40—63 μm) and sephadex LH-20 (Amersham Pharmacia Biotech AB, Sweden). Chromatotron plates were coated with MERCK silica gel 60 PF_{254} containing gypsum. TLC were performed with precoated MERCK silica gel 60 PF_{254} aluminum sheets, the spots were visualized under UV light (254 nm and 366 nm) and further by spraying with anisaldehyde and cesium sulphate reagents and then heating until charred.

Plant Materials The rhizomes of *B. fungosa* were collected from roots of *Diospyros mollis* at Loei province, Thailand in January 2003. The plant material was identified by Prof. Dr. Pranom Chantaranothai, Department of Biology, Khon Kaen University, where a voucher specimen (S. Kanokmedhakul, 8) was deposited.

Extraction and Isolation Air-dried rhizomes of *B. fungosa* (370 g) were ground into powder and then extracted successively with hexane (3×0.8 l), EtOAc (3×0.8 l) and MeOH (3×0.8 l), to yield crude hexane (31.6 g), EtOAc (14.6 g) and MeOH (141.5 g) extracts, respectively. The hexane extract (31.6 g) was separated on silica gel flash column chromatography (FCC), gradient eluting with hexane–CH_2Cl_2 and EtOAc–MeOH to give 6 fractions designated as F_1—F_6. Fraction F_2 yielded **1** (2.690 g). Fraction F_5 was purified over silica gel column chromatography (CC), eluted with a gradient system of hexane–EtOAc to yield **2** (1.08 g). Fraction F_6 was applied to silica gel CC, eluted with a gradient system of hexane–CH_2Cl_2 to

yield **3** (61.1 mg) and **4** (53.2 mg). The EtOAc extract (14.6 g) was dissolved with hexane (3×100 ml) and then MeOH (3×100 ml). The solvents were evaporated to dryness to give hexane–S (3.38 g) and MeOH–S (10.69 g). The hexane–S extract was separated on silica gel CC, eluted with a gradient system of hexane–CH_2Cl_2, CH_2Cl_2–EtOAc followed by MeOH to give an additional amount of **1** (817.8 mg), **2** (240.0 mg) and **5** (72.3 mg). The MeOH–S extract was applied on silica gel CC, eluted with a gradient system of CH_2Cl_2–MeOH to afford 9 fractions, F''_1—F''_9. Fraction F''_1 was purified on siligca gel CC, eluted with a gradient system of hexane–EtOAc to give 4 subfractions designated as $F''_{1.1}$—$F''_{1.4}$. Subfraction $F''_{1.4}$ was purified by preparative TLC by using 50% hexane–CH_2Cl_2 as eluent (developed×4) to give **6** (11.0 mg). Fraction F''_3 was subjected to silica gel CC, eluted with a gradient system of hexane–CH_2Cl_2 to give 5 subfractions, $F''_{3.1}$—$F''_{3.5}$. Subfraction $F''_{3.1}$ was dissolved with hexane to give a white solid which further recrystallized from CH_2Cl_2–hexane to yield a white solid of **7** (8.9 mg). Fraction F''_4 was purified on silica gel CC, eluted with a gradient system of hexane–CH_2Cl_2 to afford 6 fractions designated as $F''_{4.1}$—$F''_{4.6}$. Subfraction $F''_{4.1}$ was dissolved with CH_2Cl_2 to yield compound **8** (9.5 mg) and the filtrate was purified by preparative TLC by using CH_2Cl_2 as eluent to yield pale-yellow needles of **9** (2.9 mg). Fraction F''_7 was subjected to sephadex LH-20 CC, eluted with MeOH to afford 6 fractions, $F''_{7.1}$—$F''_{7.6}$. Fraction $F''_{7.1}$ was separated on a silica gel CC, eluted with an isocratic system of 2% MeOH–EtOAc to yield **10** (32.8 mg). Fraction $F''_{7.4}$ was purified over preparative TLC by using CH_2Cl_2–MeOH–H_2O (20 : 3 : 1×1, 15 : 3 : 1×1, 10 : 3 : 1×1) to give **12** (5.3 mg) and **13** (12.8 mg). Fraction F''_8 was isolated on silica gel CC, eluted with a gradient system of CH_2Cl_2–MeOH–H_2O (30 : 3 : 1—5 : 3 : 1) to give **7** fractions ($F''_{8.1}$—$F''_{8.7}$). Fraction $F''_{8.3}$ was purified over silica gel CC, gradient elution to afford 5 fractions designated as $F''_{8.3.1}$—$F''_{8.3.5}$. Fraction $F''_{8.3.2}$ was washed with MeOH to yield **11** (6.0 mg). The MeOH extract (141.5 g) was dissolved in MeOH to give an insoluble solid (1.86 g). The filtrate was then partitioned successively between hexane–H_2O, EtOAc–H_2O and *n*-BuOH–H_2O to yield hexane–P (0.36 g), EtOAc–P (112.3 g) and *n*-BuOH–P (4.9 g) extracts, respectively. The EtOAc–P extract (34.0 g) was applied over silica gel CC, eluted with a gradient system of CH_2Cl_2–MeOH–H_2O (30 : 3 : 1—6 : 4 : 1) to obtain 12 fractions, F'''_1—F'''_{12}. Fractions F'''_1 was purified by preparative TLC using CH_2Cl_2 as eluent to yield **14** (40.0 mg). Fraction F'''_8 was applied to silica gel CC, eluted with a gradient system of CH_2Cl_2–MeOH to afford 5 fractions, $F'''_{8.1}$—$F'''_{8.5}$. Fraction $F'''_{8.4}$ was dissolved with 10% MeOH–CH_2Cl_2 to give an additional amount of **10** (67.7 mg). Fraction F'''_9 was purified by chromatotron to yield an additional amount **10** (62.9 mg) and **13** (32.8 mg). Fraction F'''_{10} was further separated by chromatotron, eluted with an isocratic system of 1% MeOH–EtOAc to afford **15** (21.0 mg). Fraction F'''_{11} was separated on chromatotron to obtained an additional amount of **12** (221.0 mg) and **13** (2.5 mg). Fraction F'''_{12} (0.89 g) was purified by chromatotron, eluted with an isocratic system of 2% MeOH–EtOAc to yield compound **16** (24.0 mg). Fraction F'''_{12} (3 g) was purified on cosmosil (75-C_{18}-OPN) CC, eluted with a gradient system of MeOH–H_2O to furnish 10 fractions, $F'''_{12a.1}$—$F'''_{12a.10}$. Fraction $F'''_{12a.4}$ was applied on lichroprep RP-18 CC, eluted with a gradient system of MeOH–H_2O to afford **17** (9.0 mg), **18** (10.0 mg) and **19** (51.0 mg). Fraction $F'''_{12a.6}$ was subjected to lichroprep RP-18 CC, eluted with a gradient system of MeOH–H_2O to give **20** (14.0 mg) and **21** (86.6 mg). Fraction $F'''_{12a.7}$ was purified by lichroprep RP-18 CC, eluted with a gradient system of MeOH–H_2O to yield **22** (14.0 mg), **23** (9.7 mg), **24** (27.0 mg) and **25** (7.0 mg).

1-*O*-(*E*)-Coumaroyl-3-galloyl-4,6-(*S*)-HHDP-*β*-D-glucopyranose (**21**): A yellow powder, $[\alpha]_D^{21}$ −32.7 (c=0.3, MeOH). UV λ_{max} (EtOH) mn (log ε): 219 (4.57), 299 (4.30). CD (2.6×10^{-5} M, EtOH) $\Delta\varepsilon_{273}$ −19.7, $\Delta\varepsilon_{240}$ 43.1. IR (KBr) cm^{-1}: 3427, 1722, 1603, 1448, 1350, 1236, 1032. ^{1}H- and ^{13}C-NMR see Tables 1 and 2. HR-ESI-TOF-MS m/z: 781.1252 $[M+H]^+$ (Calcd for $C_{36}H_{28}O_{20}$+H: 781.1174).

1-*O*-(*E*)-Coumaroyl-3,4,6-galloyl-*β*-D-glucopyranose (**22**): A yellow powder, $[\alpha]_D^{24}$ −9.2 (c=0.3, MeOH). UV λ_{max} (EtOH) mn (log ε): 218 (4.15), 285 (3.80). IR (KBr) cm^{-1}: 3384, 1710,1608, 1448, 1340, 1224, 1036. ^{1}H- and ^{13}C-NMR see Tables 1 and 2. HR-ESI-TOF-MS m/z: 783.1409 $[M+H]^+$ (Calcd for $C_{36}H_{30}O_{20}$+H: 783.1330).

1-*O*-(*E*)-Caffeoyl-3,4,6-galloyl-*β*-D-glucopyranose (**23**): A yellow powder, $[\alpha]_D^{24}$ −23.2 (c=0.3, MeOH). UV λ_{max} (EtOH) mn (log ε): 219 (6.01), 293 (5.67), 330 (5.43). IR (KBr) cm^{-1}: 3384, 1707, 1606, 1447, 1342, 1230, 1064. ^{1}H- and ^{13}C-NMR see Tables 1 and 2. HR-ESI-TOF-MS m/z: 799.1358 $[M+H]^+$ (Calcd for $C_{36}H_{30}O_{21}$+H: 799.1280).

1-*O*-(*E*)-Cinnamoyl-3-galloyl-4,6-(*S*)-HHDP-*β*-D-glucopyranose (**24**): A pale yellow powder, $[\alpha]_D^{21}$ −16.1 (c=0.3, MeOH). UV λ_{max} (EtOH) mn (log ε): 218 (4.91), 377 (4.78). CD (1.4×10^{-6} M, EtOH) $\Delta\varepsilon_{297}$ −6.7, $\Delta\varepsilon_{240}$ 33.6. IR (KBr) cm^{-1}: 3420, 1723, 1626, 1449, 1350, 1236, 1032.^{1}H- and ^{13}C-NMR see Tables 1 and 2. HR-ESI-TOF-MS m/z: 765.1303 $[M+H]^+$ (Calcd for $C_{36}H_{28}O_{19}$+H: 765.1225).

1-*O*-(*E*)-Cinnamoyl-4-galloyl-*β*-D-glucopyranose (**25**): A yellow powder, $[\alpha]_D^{24}$ −30 (c=0.3, MeOH). UV λ_{max} (EtOH) mn (log ε): 204 (4.43), 218 (4.41), 279 (4.13). IR (KBr) cm^{-1}: 3401, 1711, 1627, 1447, 1331, 1231, 1073. ^{1}H- and ^{13}C-NMR see Tables 1 and 2. HR-ESI-TOF-MS m/z: 463.1186 $[M+H]^+$ (Calcd for $C_{22}H_{22}O_{11}$+H: 463.1162).

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