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# Tannins and Related Compounds. XCIV.[1] Isolation and Characterization of Seven New Hydrolyzable Tannins from the Leaves of *Macaranga tanarius* (L.) MUELL. *et* ARG.

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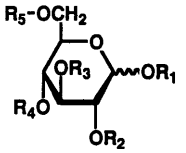
**A chemical examination of the tannins in the leaves of *Macaranga tanarius* (L.) MUELL. *et* ARG. (Euphorbiaceae) has led to the isolation of seven new hydrolyzable tannins (22—28), together with twenty-one known tannins (1—21). On the basis of chemical and spectroscopic evidence, the structures of compounds 22—28 were established as 1,4-di-*O*-galloyl-α-D-glucopyranose (22), 3,4-di-*O*-galloyl-D-glucopyranose (23), galloylpunicafolin (24), galloylgeraniin (25), 1-*O*-galloyl-3-*O*-brevifolincarboxyl-β-D-glucopyranose (26), 1,2,4-tri-*O*-galloyl-3,6-(*S*)-hexahydroxydiphenoyl-β-D-glucopyranose (macaranganin) (27) and 1,2,4-tri-*O*-galloyl-3,6-(*R*)-dehydrohexahydroxydiphenoyl-β-D-glucopyranose (tanarinin) (28).**

**Keywords** *Macaranga tanarius*; Euphorbiaceae; hydrolyzable tannin; *S*-hexahydroxydiphenic acid; *R*-dehydrohexahydroxydiphenic acid; brevifolincarboxylic acid; macaranganin; tanarinin; atropisomerism

*Macaranga tanarius* (L.) MUELL. *et* ARG. is a common tropical tree distributed from southern Asia to northern Australia.[2] The bark and leaves are known to be rich in tannins and have been used as a folk medicine for diarrhea and wounds, and also as an antiseptic.[3] As part of our studies on tannins of Euphorbiaceous plants, we have examined the leaves of *M. tanarius*, and isolated seven new hydrolyzable tannins (**22**—**28**), along with twenty-one known compound (**1**—**21**). This paper deals with the isolation and structure elucidation of these tannins.

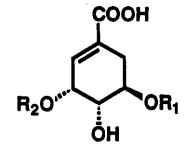
The aqueous acetone extract of the leaves, collected in Taiwan, was subjected to a combination of column chromatographies over Sephadex LH-20, MCI-gel CHP 20P, Fuji-gel ODS G-3, Bondapak $C_{18}$/Porasil B and Avicel cellulose, to afford compounds **1**—**28**. Compounds **1**—**21** were identified as known galloylglucoses [1(β)-*O*- (**1**),[4] 4-*O*- (**2**),[5] 6-*O*- (**3**),[6] 2,3-di-*O*- (**4**),[7] 1(β),2,6-tri-*O*- (**5**),[8] 2,4,6-tri-*O*- (**6**),[9] 1(β),2,3,4,6-tetra-*O*- (**7**),[10] 1(β),2,4,6-tetra-*O*- (**8**)[11] and 1(β),2,3,4,6-penta-*O*- (**9**)[12] galloylglucoses], galloyl-(−)-shikimic acids [3-*O*- (**10**)[13] and 5-*O*- (**11**)[14] galloylshikimic acids], galloylquinic acids [4-*O*- (**12**)[15] and 3,4-di-*O*- (**13**)[15] galloylquinic acids], 3,6-(*S*)-hexahydroxydiphenoyl (HHDP)-D-glucopyranose (**14**),[16] corilagin (**15**),[17] punicafolin (**16**),[18] furosin (**17**),[19] terchebin (**18**),[20] geraniin (**19**),[21] mallotusinic acid (**20**)[19] and repandusinic acid A (**21**),[22] by comparisons of their spectroscopic and physical data with those of authentic samples.

Compounds **22** and **23** showed a dark blue coloration with the ferric chloride reagent and exhibited the same $[M-H]^-$ ion peak at *m/z* 483 in the negative ion fast atom bombardment mass spectra (FAB-MS).[23] Acid hydrolysis of these compounds yielded gallic acid and glucose. In the proton nuclear magnetic resonance ($^1$H-NMR) spectra, the appearance of singlet signals at δ 7.25 and 7.19 (each 2H) in

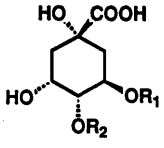


| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ |
|---|---|---|---|---|---|
| 1 | (β)G | H | H | H | H |
| 2 | H | H | H | G | H |
| 3 | H | H | H | H | G |
| 4 | H | G | G | H | H |
| 5 | (β)G | G | H | H | G |
| 6 | H | G | H | G | G |
| 7 | (β)G | G | G | H | G |
| 8 | (β)G | G | H | G | G |
| 9 | (β)G | G | G | G | G |

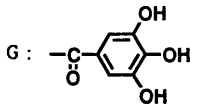
| | $R_1$ | $R_2$ | $R_4$ | $R_3$ | $R_5$ |
|---|---|---|---|---|---|
| 14 | H | H | H | (*S*)HHDP | |
| 15 | (β)G | H | H | (*R*)HHDP | |
| 16 | (β)G | G | G | (*R*)HHDP | |
| 17 | (β)G | DHHDP | H | H | |
| 18 | (β)G | DHHDP | G | G | |
| 19 | (β)G | DHHDP | (*R*)HHDP | | |
| 20 | (β)G | DHHDP | VAL | | |
| 21 | (β)G | H DCHE | (*R*)HHDP | | |

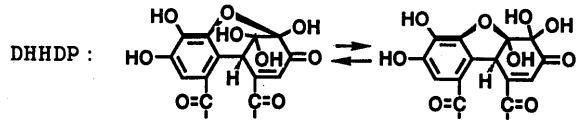


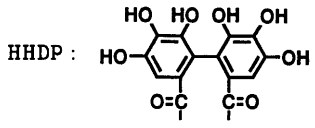
| | $R_1$ | $R_2$ |
|---|---|---|
| 10 | G | H |
| 11 | H | G |

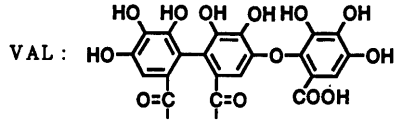


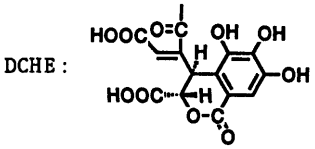
| | $R_1$ | $R_2$ |
|---|---|---|
| 12 | H | G |
| 13 | G | G |











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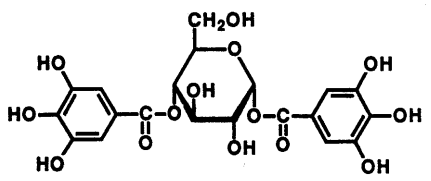
**22** and $\delta$ 7.03, 7.04 and 7.10 (4H in total) in **23** indicated the presence of two galloyl ester groups in each molecule. The result of $^1H$–$^1H$ shift correlation spectroscopy (COSY) of **22** clearly showed that the two lowfield methine signals at $\delta$ 6.36 (1H, d, $J$=4 Hz) and 5.13 (1H, t, $J$=10 Hz) were attributable to the glucose anomeric and $C_4$ protons, respectively, thus confirming the location of the two galloyl groups at these positions. The small coupling constant ($J$= 4 Hz) of the anomeric proton signal showed the configuration of the anomeric center to be $\alpha$. Accordingly, compound **22** was characterized as 1,4-di-*O*-galloyl-α-D-glucopyranose (**22**).

On the other hand, in the $^1H$-NMR spectrum of **23**, complex signal patterns arising from the glucose moiety, as well as the appearance of the anomeric signals at $\delta$ 5.32 (d, $J$=4 Hz, α-form) and $\delta$ 4.82 (d, $J$=8 Hz, β-form) in the ratio of 2:1, indicated that **23** is an anomer mixture. Furthermore, the observation of two pairs of triplet signals in the lowfield region [$\delta$ 5.69 and 5.20 (each 2/3, t, $J$=10 Hz, α-form), $\delta$ 5.47 and 5.17 (each 1/3H, t, $J$=10 Hz, β-form)] suggested the location of the galloyl groups to be at the $C_3$ and $C_4$ positions of the glucose core. Further support for this was obtained by methylation of **23**, which yielded the α- and β- anomers (**23a** and **23b**). The $^1H$-NMR spectrum of the α-anomer (**23a**) clearly indicated that the two lowfield triplets ($\delta$ 5.33 and 5.73 (each 1H, $J$=10 Hz)] are not coupled with the anomeric signal [$\delta$ 4.96 (d, $J$=4 Hz)]. Based on these findings, the structure of **23** was established to be 3,4-di-*O*-galloyl-D-glucopyranose (**23**).

Compounds **24** and **25** gave $^1H$-NMR spectra closely related to those of punicafolin (**16**) and geraniin (**19**), respectively, except for the complexity of the aromatic signals. In the negative FAB-MS, **24** and **25** exhibited $[M-H]^-$ ion peaks at $m/z$ 1089 and 1103, which were 152 mass units (corresponding to one galloyl group) more than those of **16** ($m/z$ 937) and **19** ($m/z$ 951), respectively.

Mild methanolysis with methanolic acetate buffer (pH 5.4)[12] yielded punicafolin (**16**) and geraniin (**19**), along with methyl gallate. This result indicated that the additional galloyl group is attached depsidically to the phenolic hydroxyl group in each molecule. As for the location of the depside galloyl group in **24**, it is evident from the appearance of the $^1H$-NMR galloyl signals as doublets [$\delta$ 7.42, 7.46, 7.52, 7.54 (each d, $J$=2 Hz)][24] that the depside galloyl



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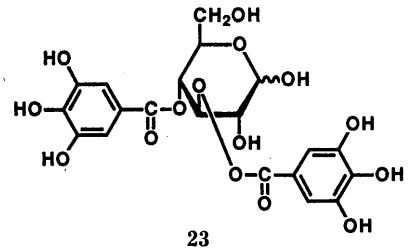

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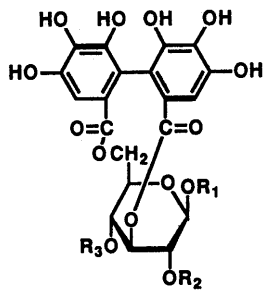

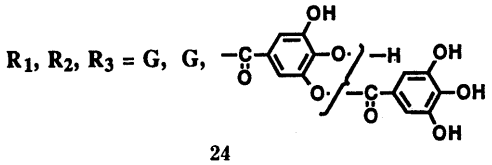


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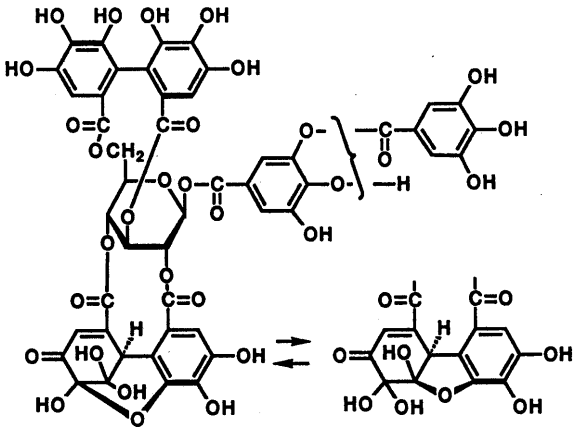

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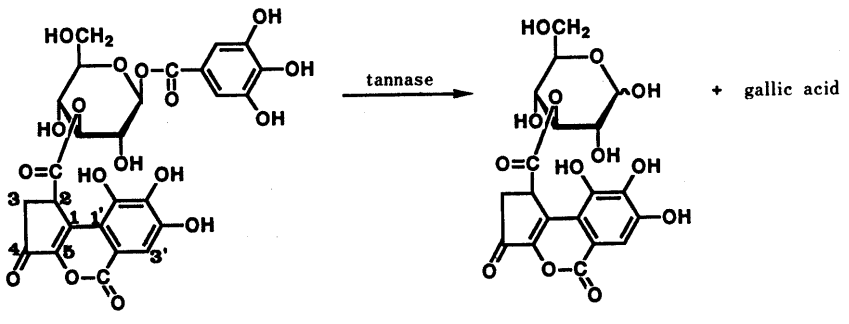


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26a

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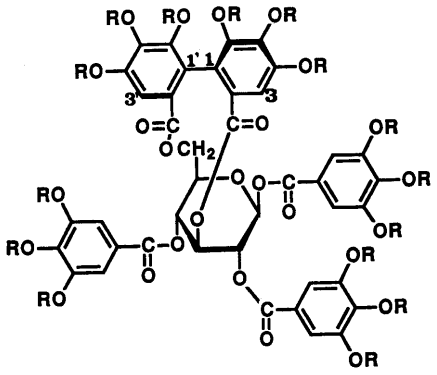
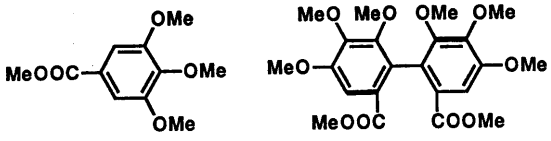
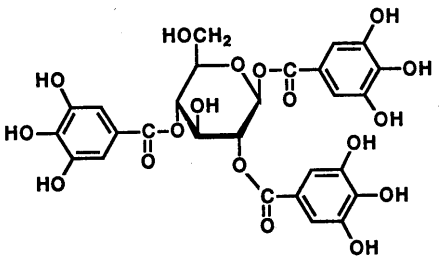


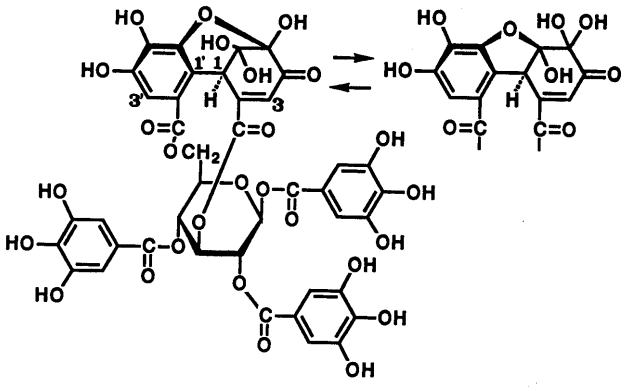
27 : R=H
27a : R=Me



27b 27c



27d



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group is attached to the proximal galloyl group, but its location could not be definitively determined owing to the lack of sufficient sample. In the case of **25**, the $^1$H-NMR spectrum of the phenazine derivative (**25a**) clearly showed the splitting of the galloyl signals into doublets [$\delta$ 7.25, 7.31 (each d, $J$=2 Hz)], thus indicating that the depsidically linked galloyl group is located at the anomeric galloyl hydroxyls. In addition, taking into account the observation of small galloyl singlet peaks ($\delta$ 7.16 in **24**, $\delta$ 7.06 in **25a**), a *p*-depside galloyl derivative was considered to exist as a minor component in each case. On the basis of these observations, compounds **24** and **25** were concluded to be galloylpunicafolin and 1-*O*-di-galloyl-2,4-(*R*)-dehydrohexahydroxydiphenoyl (DHHDP)-3,6-(*R*)-HHDP-$\beta$-D-glucopyranose.

Compound **26** showed a prominent $[M-H]^-$ ion peak at *m/z* 605 in the negative FAB-MS, and exhibited the presence of one galloyl group [$\delta$ 7.19 (2H, s)] and a sugar moiety [$\delta$ 5.78 (1H, d, $J$=8 Hz, anomeric H)] in the $^1$H-NMR spectrum. The observation of an aromatic singlet at $\delta$ 7.45 and aliphatic ABX-type signals at $\delta$ 2.73 (1H, dd, $J$= 2 and 19 Hz), 3.13 (1H, dd, $J$=8 and 19 Hz) and 4.72 (1H, dd, $J$=2 and 8 Hz) suggested the occurrence of a brevifolincarboxylic acid moiety,[25] which was alo consistent with the $^{13}$C nuclear magnetic resonance ($^{13}$C-NMR) spectrum [$\delta$ 196.0 (carbonyl), 42.3, 38.2 (>CH–$CH_2$–), 140.6, 150.4 (>C=C–O–)]. The component acids and sugar were confirmed unequivocally by acid hydrolysis yielding gallic acid, brevifolincarboxylic acid and glucose.

The location of each acyl group was determined as follows. In the $^1$H–$^1$H COSY spectrum, the lowfield shifts of the anomeric [$\delta$ 5.78 (d, $J$=8 Hz)] and $C_3$ [$\delta$ 5.15 (t, $J$= 9 Hz)] proton signals apparently indicated these positions to be acylated. Partial hydrolysis with tannase afforded gallic acid and a hydrolysate (**26a**). In the $^1$H-NMR spectrum of **26a**, the signal arising from the galloyl group disappeared and the anomeric proton signal was found to be shifted to upper field [$\delta$ 4.64 (d, $J$=8 Hz, $\beta$-form) and 5.20 (d, $J$=4 Hz, $\alpha$-form)]. This fact indicated the galloyl group to be located at the anomeric position. Furthermore, in the $^1$H-NMR spectrum of **26**, a large coupling constant ($J$=8 Hz) of the anomeric signal indicated the $\beta$-configuration. Thus, **26** was represented as 1-*O*-galloyl-3-*O*-brevifolincarboxyl-$\beta$-D-glucopyranose (**26**).

Compound **27** (name macaranganin) showed, in the negative FAB-MS, an $[M-H]^-$ ion peak at *m/z* 937 identical to that of punicafolin (**16**). The $^1$H-NMR spectrum of **27** suggested the presence of three galloyl groups ($\delta$ 7.00, 7.14 and 7.26 (each 2H, s)], one HHDP group [$\delta$ 7.18 and 7.20 (each 1H, s)] and a $\beta$-glucopyranose moiety [$\delta$ 6.48 (1H, d, $J$=9 Hz, H-1), 5.68—5.46 (2H, m, H-2, 3), 5.19 (1H, d, $J$=12 Hz, H-6), 5.07 (1H, brs, H-4), 4.48 (1H, brs, $J_{1/2w}$=4 Hz, H-5) and 4.13 (1H, dd, $J$=4 and 12 Hz, H-6)].

Methylation of **27** with dimethyl sulfate and anhydrous potassium carbonate in dry acetone gave the pentadecamethyl ether (**27a**), [$M^+$ *m/z*: 1148, field desorption mass spectrum (FD-MS)]. Alkaline hydrolysis of **27a**, followed by methylation with diazomethane, afforded methyl 3,4,5-trimethoxybenzoate (**27b**) and dimethyl 4,4′,5,5′,6,6′-hexamethoxydiphenoate (**27c**). The negative value [−32.9° (acetone)] of the specific optical rotation of **27c** confirmed the chirality of the biphenyl bond to be in the *S*-series.[26]

To determine the location of each acyl group in the glucose moiety, **27** was subjected to partial hydrolysis in boiling water, which yielded ellagic acid and 1,2,4-tri-*O*-galloyl-$\beta$-D-glucopyranose (**27d**).[27] This result indicated the location of the HHDP group to be at the 3,6-positions. Thus, macaranganin was characterized as 1,2,4-tri-*O*-galloyl-3,6-(*S*)-HHDP-$\beta$-D-glucopyranose (**27**).

Compound **28** (tanarinin) was obtained as a yellow amorphous powder. The $^1$H-NMR spectrum of **28**, although duplicated, exhibited signals corresponding to three galloyl groups [$\delta$ 7.16, 7.20 and 7.32 (each 3/2H, s), 7.31,

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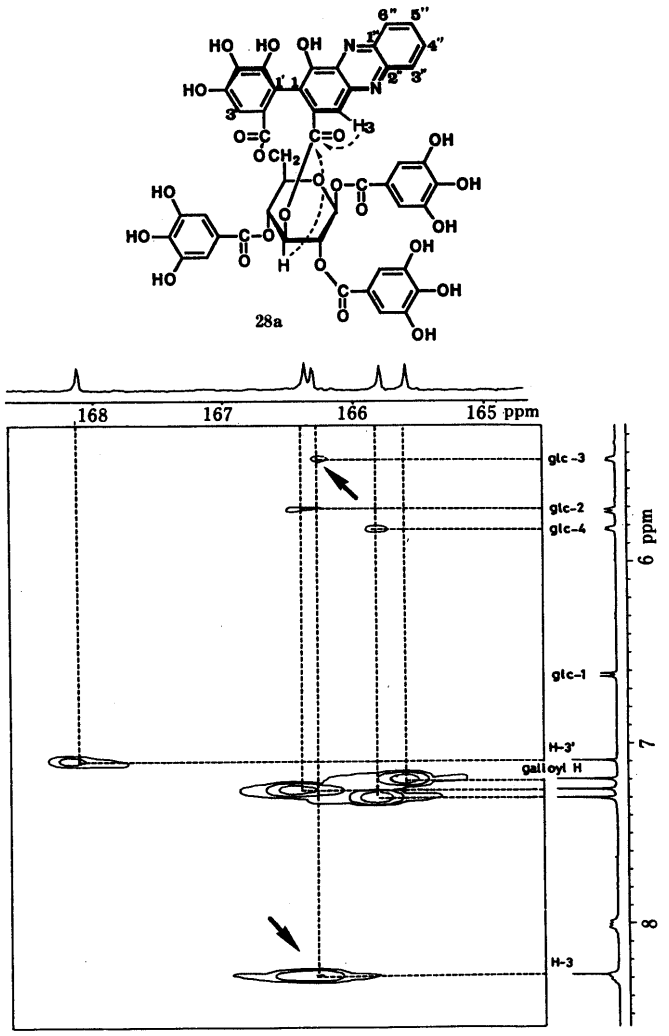


Fig. 1. $^{1}H$–$^{13}C$ Long-Range Shift Correlation Spectrum of **28a** in Acetone-$d_6$ ($J_{CH}$ = 10 Hz)

7.18 and 7.13 (each 1/2H, s)], and one DHHDP group [$\delta$ 7.28 (1H, s), 6.71 (3/4H, s), 6.33 (1/4H, d, $J$ = 2 Hz), 5.33 (3/4H, s) and 4.92 (1/4H, d, $J$ = 2 Hz)]. When reduced with sodium hydrosulfite,[28] **28** afforded punicafolin (**16**), thus confirming not only the location of each acyl group but also the *R*-configuration of the DHHDP group.

The orientation of the DHHDP group was determined by $^{1}H$–$^{13}C$ long-range COSY of the phenazine derivative (**28a**). In the spectrum, the glucose $C_3$-signal at $\delta$ 5.39 was found to be correlated with the ester carbon resonance at $\delta$ 166.3 through a three-bond coupling, and this ester carbon signal was also correlated with the aromatic proton signal at $\delta$ 8.25 which was assignable to H-3 of the phenazine moiety. Accordingly, the hydrated cyclohexenetrione moiety was determined to be attached to the glucose $C_3$ position, and the structure of tanarinin was concluded to be as represented by the formula **28**.

The accumulation of geraniin (**19**) in this plant was similar to those of other Euphorbiaceous plants, but the presence of unusual 3,6-(*S*)-HHDP-glucopyranoses (**14** and **27**) was rather characteristic, since the HHDP group attached to the 3,6-positions of the glucopyranose moiety usually possesses *R*-configuration.

## 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. $^{1}H$- and $^{13}C$-NMR spectra were taken with a JEOL FX-100 spectrometer, with tetramethylsilane as an internal standard; chemical shifts are given on a $\delta$ (ppm) scale. FAB- and FD-MS were recorded on JEOL JMS DX-300 and D-300 spectrometers. Column chromatography was carried out with Sephadex LH-20 (25—100 $\mu$, Pharmacia Fine Chemical Co., Ltd.), MCI-gel CHP 20P (75—150 $\mu$, Mitsubishi Chemical Industries, Ltd.), Fuji-gel ODS G-3 (43—65 $\mu$, Fuji Gel Hanbai Co., Ltd.), Bondapak $C_{18}$/Porasil B (37—75 mesh, Waters Associates, Inc.) and silica gel 60 (70—230 mesh, Merck), Avicel cellulose (Funakoshi). Thin-layer chromatography (TLC) was performed on precoated Silica gel 60 $F_{254}$ plates (0.2 mm thick, Merck) with benzene–ethyl formate–formic acid (1 : 7 : 1, 1 : 7 : 1.5 or 1 : 5 : 1.5) and precoated Cellulose $F_{254}$ plates (0.1 mm thick, Merck) with 2% acetic acid, and spots were detected by the use of ultraviolet (UV) light or by spraying 1% ferric chloride, 10% sulfuric acid or aniline–hydrogen–phthalate reagents.

**Isolation** The dried leaves (6.0 kg) of *M. tanarius*, collected in February 1987, in Taipei, Republic of China, were extracted three times with 70% aqueous acetone at room temperature. The extract was concentrated under reduced pressure, and the resulting precipitates, consisting mainly of chlorophylls and waxes, were removed by filtration. The filtrate was applied to a column of Sephadex LH-20. Elution with $H_2O$ containing increasing amounts of MeOH, and finally with 50% aqueous acetone afforded fractions I (138 g), II (135 g), III (410 g) and IV (75 g).

Repeated chromatography of fr. I on Sephadex LH-20 ($H_2O$–MeOH, EtOH), MCI-gel CHP 20P ($H_2O$–MeOH) and Fuji-gel ODS G-3 ($H_2O$–MeOH) yielded 1-*O*-galloyl-$\beta$-D-glucose (**1**) (210 mg), 4-*O*-galloyl-D-glucose (**2**) (60 mg), 6-*O*-galloyl-D-glucose (**3**) (520 mg), 5-*O*-galloyl-(−)-shikimic acid (**11**) (240 mg), 4-*O*-galloylquinic acid (**12**) (390 mg), 3,6-(*S*)-HHDP-D-glucose (**14**) (160 mg), and repandusinic acid A (**21**) (210 mg). Fraction II was repeatedly chromatographed over Sephadex LH-20 (EtOH–$H_2O$–$Me_2CO$, EtOH, 80% MeOH) and MCI-gel CHP 20P ($H_2O$–MeOH) to give 2,3-di-*O*-galloyl-D-glucose (**4**) (40 mg), 2-*O*-galloyl-(−)-shikimic acid (**10**) (90 mg), 3,4-di-*O*-galloylquinic acid (**13**) (60 mg), corilagin (**15**) (1.28 g) and compounds **22** (320 mg), **23** (140 mg) and **26** (90 mg). Fraction III yielded 1,2,6-tri-*O*-galloyl-$\beta$-D-glucose (**5**) (80 mg), 2,4,6-tri-*O*-galloyl-D-glucose (**6**) (230 mg), furosin (**17**) (490 mg), terchebin (**18**) (90 mg) and mallotusinic acid (**20**) (240 mg) on repeated chromatography over MCI-gel CHP 20P ($H_2O$–MeOH), Sephadex LH-20 (EtOH–$H_2O$–$Me_2CO$, EtOH, 80% MeOH), Fuji-gel ODS G-3 ($H_2O$–MeOH), Bondapak $C_{18}$/Porasil B ($H_2O$–MeOH) and Avicel cellulose (2% AcOH). Similar repeated chromatography of fr. IV yielded 1,2,3,6-tetra-*O*-galloyl-$\beta$-D-glucose (**7**) (100 mg), 1,2,4,6-tetra-*O*-galloyl-$\beta$-D-glucose (**8**) (130 mg), 1,2,3,4,6-penta-*O*-galloyl-$\beta$-D-glucose (**9**) (200 mg), punicafolin (**16**) (690 mg), geraniin (**19**) (36.45 g), and compounds **24** (280 mg), **25** (220 mg), **27** (140 mg) and **28** (340 mg).

**Compound 22** A white powder ($H_2O$), mp 195—197 °C, $[\alpha]_D^{21}$ +37.3° ($c$ = 0.6, MeOH). Negative FAB-MS $m/z$: 483 $[M-H]^-$. *Anal.* Calcd for $C_{20}H_{20}O_{14}\cdot 3H_2O$: C, 44.61; H, 4.87. Found: C, 44.73; H, 4.75. $^{1}H$-NMR (acetone-$d_6$ + $D_2O$) $\delta$: 3.58—3.62 (2H, m, H-6), 3.89 (1H, dd, $J$ = 4, 10 Hz, H-2), 4.08 (1H, d, $J$ = 10 Hz, H-5), 4.27 (1H, t, $J$ = 10 Hz, H-3), 5.13 (1H, t, $J$ = 10 Hz, H-4), 6.36 (1H, d, $J$ = 4 Hz, H-1), 7.19, 7.25 (each 2H, s, galloyl H). $^{13}C$-NMR (acetone-$d_6$ + $D_2O$) $\delta$: 61.6 (glc C-6), 70.0 (2C), 72.4, 73.7 (glc C-2, 3, 4, 5), 93.0 (glc C-1), 110.2 (4C, galloyl C-2,6), 120.7, 120.9 (galloyl C-1), 139.2, 139.5 (galloyl C-4), 145.9 (4C, galloyl C-3,5), 166.1 167.0 (–COO–).

**Acid Hydrolysis of 22** A solution of **22** (2 mg) in 1 N $H_2SO_4$ (1 ml) was heated at 90 °C for 2 h. After cooling, the reaction mixture was extracted with ethyl acetate. TLC examination of the ethyl acetate layer showed the presence of gallic acid [silica gel/benzene–ethyl formate–formic acid (2 : 7 : 1), *Rf*: 0.69]. The aqueous layer was neutralized with Amberlite MB-3 ion exchange resins, and analyzed by cellulose TLC [solvent, *n*-BuOH–pyridine–$H_2O$ (6 : 4 : 3), detection, aniline–hydrogen–phthalate reagent]. A spot (*Rf*: 0.39) corresponding to glucose was detected.

**Compound 23** An off-white amorphous powder, $[\alpha]_D^{21}$ −46.2° ($c$ = 0.7, MeOH). Negative FAB-MS $m/z$: 483 $[M-H]^-$. $^{1}H$-NMR (270 MHz, acetone-$d_6$ + $D_2O$) $\delta$: 4.00—4.10 [1/3H, m, ($\beta$)H-5], 4.18—4.24 (2/3H, m, ($\alpha$)H-5], 4.82 [1/3H, d, $J$ = 8 Hz, ($\beta$)H-1], 5.17 [1/3 H, d, $J$ = 10 Hz, ($\beta$)H-4], 5.20 [2/3 H, t, $J$ = 10 Hz, ($\alpha$) H-4), 5.32 [2/3 H, d, $J$ = 4 Hz, ($\alpha$) H-1], 5.47 [1/3H, t, $J$ = 10 Hz, ($\beta$)H-3], 5.69 [2/3 H, t, $J$ = 10 Hz, ($\alpha$)H-3], 7.03, 7.04, 7.10 [4H in total, each s, galloyl H].

**Acid Hydrolysis of 23** **23** (5 mg) was treated with 1 N $H_2SO_4$ (1 ml) as described for **22**, and the spots of gallic acid and glucose were detected by TLC.

**Methylation of 23** A mixture of **23** (58 mg), dimethyl sulfate (0.3 ml)

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and anhydrous potassium carbonate (600 mg) in dry acetone (6 ml) was heated under reflux for 2 h. After removal of the inorganic precipitate by filtration, the filtrate was concentrated to dryness under reduced pressure. The residue was separated by preparative TLC [solvent: $CHCl_3$–MeOH (19:1 v/v)] to afford **23a** (5 mg) and **23b** (2 mg). **23a**: an off-white amorphous powder, FD-MS *m/z*: 582 ($M^+$). $^1$H-NMR (270 MHz, $CDCl_3$) $\delta$: 3.55 (3H, s, $OCH_3$), 3.85, 3.87 (each 9H, s, $OCH_3 \times 6$), 4.96 (1H, d, $J$=4 Hz, H-1), 5.33 (1H, t, $J$=10 Hz, H-4), 5.73 (1H, t, $J$=10 Hz, H-3), 7.19, 7.20 (each 2H, s, galloyl H). **23b**: an off-white amorphous powder, FD-MS *m/z*: 582 ($M^+$). $^1$H-NMR (270 MHz, $CDCl_3$) $\delta$: 3.64 (3H, s, $OCH_3$), 3.86 (9H, s, $3 \times OCH_3$), 3.87 (3H, s, $OCH_3$), 3.88 (6H, s, $2 \times OCH_3$), 4.48 (1H, d, $J$=8 Hz, H-1), 5.39 (1H, t, $J$=10 Hz, H-4), 5.60 (1H, t, $J$=10 Hz, H-3), 7.19, 7.21 (each 2H, s, galloyl H).

**Compound 24** A tan amorphous powder, $[\alpha]_D^{21}$ −14.5° ($c$=0.8, MeOH). Negative FAB-MS *m/z*: 1089 $[M-H]^-$, 937 $[M-\text{galloyl}]^-$. *Anal.* Calcd for $C_{48}H_{34}O_{30} \cdot 4H_2O$: C, 49.57; H, 3.61. Found: C, 49.41; H, 3.71. $^1$H-NMR (acetone-$d_6$ + $D_2O$) $\delta$: 4.40—5.00 (3H, m, H-5,6), 5.20 (1H, d, $J$=3 Hz, H-3), 5.54 (1H, d, $J$=5 Hz, H-2), 5.89 (1H, d, $J$=3 Hz, H-4), 6.59 (1H, d, $J$=5 Hz, H-1), 6.77, 6.78, 6.80, 7.05, 7.09 (2H in total, HHDP-H), 7.16 (1/2H, s, *p*-depside galloyl H), 7.18, 7.19, 7.22, 7.25, 7.27, 7.28, 7.30 (6H in total, galloyl H), 7.42, 7.46, 7.52, 7.54 (3/2H in total, each d, $J$=2 Hz, *m*-depside galloyl H). $^{13}$C-NMR (acetone-$d_6$) $\delta$: 64.5 (2C) (glc C-4,6), 70.8, 72.4, 75.6 (glc C-2,3,5). 91.8 (glc C-1), 107.9, 110.0 (HHDP C-3,3′), 115.4, 115.9 (HHDP C-1,1′), 125.2, 125.4 (HHDP C-2,2′), 136.7, 137.2 (HHDP C-5,5′), 145.0, 145.4 (each 2C, HHDP C-4,4′, 6,6′), 110.6 (6C) (galloyl C-2,6), 120.2, 120.5, 120.7 (galloyl C-1), 139.5, 139.8 (2C) (galloyl C-4), 146.1 (6C) (galloyl C-3,5), 109.9, 127.7, 132.4, 151.4 (*p*-dipside galloyl C), 116.4, 117.9, 120.2, 139.8, 144.3, 146.9 (*m*-depside galloyl C), 165.2, 165.4, 165.6, 166.0, 166.5, 168.3 (COO).

**Methanolysis of 24** A solution of **24** (12.7 mg) in a mixture of 0.1 M acetate buffer (0.75 ml, pH 5.4) and MeOH (1.5 ml) was kept at 80 °C for 2 h. The reaction mixture was concentrated *in vacuo*, and the aqueous solution was shaken successively with ether and ethyl acetate. The ether layer was examined by silica gel TLC [benzene–ethyl formate–formic acid (5:4:1)] and the spot (*Rf*: 0.41) of methyl gallate was detected. The ethyl acetate layer was concentrated under reduced pressure, and the residue was crystallized from $H_2O$ to afford punicafolin (**16**) (5.7 mg).

**Compound 25** A tan amorphous powder, $[\alpha]_D^{21}$ −104.4° ($c$=0.6, MeOH). Negative FAB-MS *m/z*: 1103 $[M-H]^-$, 951 $[M-\text{galloyl}]^-$. *Anal.* Calcd for $C_{48}H_{32}O_{31} \cdot 5H_2O$: C, 48.25; H, 3.54. Found: C, 48.45; H, 3.47. $^1$H-NMR (acetone-$d_6$ + $D_2O$) $\delta$: 4.25—4.50 (1H, m, H-5), 4.70—4.93 (2H, m, H-3,6), 4.93 (1/2H, d, $J$=2 Hz, DHHDP H-1), 5.23 (1/2H, s, DHHDP H-1), 5.38—5.65 (3H, m, H-2,4,6), 6.26 (1/2H, d, $J$=2 Hz, DHHDP-H-3), 6.53 (1/2H, s, DHHDP H-3), 6.54 (H, br s, H-1), 6.67, 6.69 (1H, in total, each s, HHDP-H), 7.00, 7.06, 7.09, 7.14 (3/2H in total, each s, HHDP-H, *p*-depside galloyl H), 7.24, 7.26 (1H in total, each 1H, s, DHHDP H-3′), 7.29, 7.30 (2H in total, galloyl H), 7.46—7.51 (3/2H in total, m, *m*-depside galloyl H).

**Preparation of Phenazine Derivative (25a)** A solution of **25** (70 mg) and *o*-phenylenediamine (10 mg) in 20% AcOH–EtOH (3 ml) was stirred at room temperature for 1 h. After removal of EtOH under reduced pressure, the aqueous solution was subjected to MCI-gel CHP 20P chromatography to give **25a** as a tan amorphous powder, *Anal.* Calcd for $C_{54}H_{34}N_2O_{28} \cdot 7H_2O$: C, 50.47; H, 3.77; N, 2.19. Found: C, 50.74; H, 3.56; N, 2.43. $^1$H-NMR (acetone-$d_6$ + $D_2O$) $\delta$: 4.07—4.15 (1H, m, H-6), 4.71—5.05 (2H, m, H-5,6), 5.49 (2H, br s, H-3,4), 5.70 (1H, d, $J$=6 Hz, H-2), 6.19 (1H, d, $J$=6 Hz, H-1), 6.71 (1H, s, HHDP-H), 6.97, 6.99, 7.00 (1H, in total, HHDP-H), 7.06 (1/2H, s, *p*-depside galloyl H), 7.24 (2H, s, terminal galloyl H), 7.25, 7.31 (each 3/4H, d, $J$=2 Hz, *m*-depside galloyl H), 7.47, 7.48 [1H in total, each s, phenazine (ph.) H-3′], 8.32 (1H, s, ph. H-3), 7.97—8.08, 8.26—8.36 (each 2H, m, ph. H-3″, 4″,5″,6″). $^{13}$C-NMR (270 MHz, acetone-$d_6$ + $D_2O$) $\delta$: 91.6 (glc C-1), 77.0 (glc C-5), 76.6 (glc C-2), 68.8 (glc C-3), 67.7 (glc C-4), 65.4 (glc C-6), 110.5 (2C, galloyl C-2,6), 120.0 (galloyl C-1), 139.8 (galloyl C-4), 146.2 (2C, galloyl C-3,5), 108.1, 109.7 (HHDP C-3,3′), 113.2 (ph. C-3′), 114.8, 115.1, 116.6, 117.4 (HHDP C-1,1′; Ph. C-1,1′), 119.6 (ph. C-3), 120.1 (ph. C-1′), 124.2, 125.2 (HHDP C-2,2′), 130.2, 130.3, 132.5, 132.7 (ph. C-3″,4″,5″,6″), 136.1, 136.2 (ph. C-2,5), 137.3 (ph. C-5′), 139.1, 139.6 (HHDP C-5,5′), 142.8, 143.0 (ph. C-1″, 2″), 144.7 (ph C-4), 145.0, 145.1, 145.2, 145.3 (HHDP C-4,4′,6,6′), 145.9, 146.1 (ph. C-4′,6′), 152.5 (ph. C-6), 110.1, 126.9, 132.8, 151.5 (*p*-depside galloyl C), 116.8, 117.6, 120.1, 139.8, 144.2, 147.0 (*m*-depside galloyl C).

**Methanolysis of 25** A solution of **25** (27 mg) in a mixture of 0.1 M acetate buffer (1 ml, pH 5.4) and MeOH (1 ml) was kept at 65 °C for 1.5 h. The reaction mixture was concentrated to dryness under reduced pressure, and the residue was partitioned between $H_2O$ and ether. From the ether layer, methyl gallate was detected by silica gel TLC. The $H_2O$ layer was chromatographed over Sephadex LH-20 with 60% MeOH to afford geraniin (**19**) (9.7 mg).

**Compound 26** A white amorphous powder, $[\alpha]_D^{18}$ −23.1° ($c$=0.7, MeOH). Negative FAB-MS *m/z*: 605 $[M-H]^-$. *Anal.* Calcd for $C_{26}H_{22}O_{17} \cdot 3H_2O$: C, 47.28; H, 4.27. Found: C, 46.78; H, 4.05. $^1$H-NMR (270 MHz, acetone-$d_6$) $\delta$: 2.73 (1H, dd, $J$=2, 19 Hz, H-3′), 3.13 (1H, dd, $J$=19, 8 Hz H-3′), 3.64 (2H, d like, $J$=6 Hz, H-4,5), 3.71 (1H, dd, $J$=12, 5 Hz, H-6), 3.79 (1H, dd, $J$=8, 9 Hz, H-2), 3.86 (1H, d, $J$=12 Hz, H-6), 4.72 (1H, dd, $J$=8, 2 Hz, H-2′), 5.15 (1H, t, $J$=9 Hz, H-3), 5.78 (1H, d, $J$=8 Hz, H-1), 7.19 (2H, s, galloyl H), 7.45 (1H, H-3′′). $^{13}$C-NMR (acetone-$d_6$) $\delta$: 61.2 (glc C-1), 68.7, 71.6, 77.6, 78.8 (glc C-2, 3, 4, 5), 95.2 (glc C-1), 119.8 (galloyl C-1), 110.5 (2C, galloyl C-2, 6), 145.8 (2C, galloyl C-3, 5), 139.9 (galloyl C-4), 150.4 [brevifolincarboxyl (brev.) C-1], 42.3 (brev. C-2), 38.3 (brev. C-3), 196.0 (brev. C-4), 140.6 (brev. C-5), 114.4 (brev. C-1′′), 116.2 (brev. C-2′′), 109.6 (brev. C-3′′), 144.3 (brev. C-4′′), 141.3 (brev. C-5′′), 146.9 (brev. C-6′′), 162.4, 166.6, 173.7 (–COO–).

**Acid Hydrolysis of 26** A solution of **26** (2 mg) in 1 N $H_2SO_4$ (0.2 ml) was heated at 95 °C for 10 h. After cooling, the reaction mixture was neutralized with Amberlite MB-3. Spots corresponding to glucose, gallic acid and brevifolincaboxylic acid [silica gel/benzene–ethyl formate–formic acid (1:7:1.5), *Rf*: 0.63] were detected by TLC examination.

**Enzymatic Hydrolysis of 26** A solution of **26** (7 mg) in MeOH–$H_2O$ (1:1, 2 ml) was incubated with tannase at room temperature for 2 h. The reaction mixture was directly subjected to Sephadex LH-20 chromatography with EtOH to yield methyl gallate and compound **25a** (2.8 mg) as a white amorphous powder, negative FAB-MS *m/z*: 453 $[M-H]^-$. $^1$H-NMR (270 MHz, acetone-$d_6$ + $D_2O$) $\delta$: 2.68 (H-3′, $\beta$-form), 2.69 (H-3′, $\alpha$-form) (1H, in total each, dd, $J$=2, 19 Hz), 3.07 (1H, dd, $J$=8, 19 Hz, H-3′), 4.64 (1/2H, d, $J$=8 Hz, ($\beta$) (H-1), 4.67 (1H, dd, $J$=2, 8 Hz, H-2′), 4.99 (1/2H, t, $J$=9 Hz, ($\beta$) H-3), 5.20 (1/2H, d, $J$=4 Hz, ($\alpha$) H-1), 5.23 (1/2H, t, $J$=10 Hz, ($\alpha$) H-3), 7.43 (1H, s, H-3′′).

**Compound 27** An off-white amorphous powder, $[\alpha]_D^{21}$ −96.0° ($c$=0.5, MeOH). Negative FAB-MS *m/z*: 937 $[M-H]^-$. *Anal.* Calcd for $C_{41}H_{30}O_{26} \cdot 4H_2O$: C, 48.72; H, 3.79. Found: C, 49.02; H, 3.88. $^1$H-NMR (acetone-$d_6$ + $D_2O$) $\delta$: 4.13 (1H, dd, $J$=4, 12 Hz, H-6), 4.48 (1H, br s, $J_{1/2w}$=4 Hz, H-5), 5.07 (1H, br s, H-4), 5.19 (1H, d, $J$=12 Hz, H-6), 5.68—5.46 (2h, m, H-2, 3), 6.48 (1H, d, $J$=9 Hz, H-1), 7.00, 7.14, 7.26 (each 2H, s, galloyl H), 7.18, 7.20 (each 1H, HHDP-H). $^{13}$C-NMR: (acetone-$d_6$) $\delta$: 63.3 (glc C-1), 71.4, 74.3, 76.1, 78.4 (glc C-2,3,4,5), 90.3 (glc C-1), 110.1 (2C), 110.2 (4C) (galloyl C-2, 6), 120.1, 120.3, 120.6, 121.2, 125.8 (galloyl C-1, HHDP C-2,2′), 145.8, 146.0, 146.3 (each 2C, galloyl C-3,5), 139.1, 139.7, 139.8 (galloyl C-4), 116.2, 117.2 (HHDP C-1,1′), 109.5, 112.3 (HHDP C-3, 3′), 144.7 (2C, HHDP C-4,4′), 137.1, 138.4 (HHDP C-5,5′), 145.0 (2C, HHDP C-6,6′), 164.9, 165.2, 165.6, 167.4, 167.8 (–COO–).

**Methylation of 27** A mixture of **27** (40 mg), dimethyl sulfate (0.4 ml) and anhydrous potassium carbonate (375 mg) in dry acetone (4 ml) was heated under reflux for 1.5 h. After removal of the inorganic precipitates by filtration, the filtrate was concentrated to dryness under reduced pressure. The residue was chromatographed over silica gel, and elution with benzene–acetone (9:1) afforded the pentadecamethylate (**27a**) as a white amorphous powder (44 mg), $[\alpha]_D^{22}$ 69.1° ($c$=1.1, acetone). FD-MS *m/z*: 1148 ($M^+$). $^1$H-NMR ($CDCl_3$) $\delta$: 3.50, 3.66 (each 3H, s), 3.77 (6H, s), 3.81, 3.83, 3.89 (each 3H, s), 3.91, 3.95, 3.97 (each 6H, s), 4.00, 4.10 (each 3H, s) ($OCH_3 \times 15$), 4.16 (1H, dd, $J$=4, 12 Hz, H-6), 4.56 (1H, d, $J$=4 Hz, H-5), 5.26 (1H, d, $J$=12 Hz, H-6), 5.27 (1H, s, H-4), 5.55 (1H, d, $J$=8 Hz, H-3), 5.67 (1H, dd, $J$=8,9 Hz, H-2), 6.57 (1H, d, $J$=9 Hz, H-1), 7.01, 7.28 (each 2H, s, galloyl H), 7.36 (1H, s, HHDP-H), 7.43 (3H, s, galloyl H and HHDP-H).

**Alkaline Methanolysis of 27a** A solution of **27a** (44 mg) in MeOH (2 ml) and 10% aqueous NaOH (2 ml) was refluxed for 1 h. After removal of MeOH *in vacuo*, the aqueous solution was acidified with 10% HCl and then extracted with ether. The organic layer was treated with ethereal $CH_2N_2$ for 1 h. The reaction mixture was concentrated and applied to a column of silica gel. Elution with benzene–acetone (19:1) furnished methyl 3,4,5-trimethoxybenzoate (**27b**) (11.2 mg) as colorless needles and (*S*)-dimethyl hexamethoxydiphenoate (**27c**) (6.9 mg) as a colorless syrup, $[\alpha]_D^{22}$ −32.9° ($c$=0.6, acetone).

**Partial Hydrolysis of 27** A solution of **27** (12.5 mg) in $H_2O$ (1 ml) was heated at 95 °C for 6 h. After cooling, the reaction mixture was subjected to MCI-gel CHP 20P chromatography with MeOH–$H_2O$ to yield ellagic acid and a hydrolysate (**27d**) as an off-white amorphous powder, $[\alpha]_D^{22}$ −57.2° ($c$=0.4, acetone). $^1$H-NMR (acetone-$d_6$) $\delta$: 3.68 (2H, br s, H-6), 3.92 (1H, m, H-5), 4.33 (1H, t, $J$=8 Hz, H-3), 5.22 (1H, t, $J$=8 Hz, H-4),

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5.34 (1H, t, $J$=8 Hz, H-2), 6.05 (1H, d, $J$=8 Hz, H-1), 7.11 (4H, s, galloyl H) 7.18 (2H, s, galloyl H).

**Compound 28** A yellow amorphous powder, $[\alpha]_D^{22}$ −83.7° ($c$=0.5, MeOH). Negative FAB-MS $m/z$: 953 $[M-H]^-$. *Anal.* Calcd for $C_{41}H_{30}O_{27}\cdot 4H_2O$: C, 47.96; H, 3.73. Found: C, 47.76, H, 3.64. $^1$H-NMR (270 MHz, acetone-$d_6$+$D_2O$) $\delta$: 4.46 (1H, d, $J$=12 Hz, H-6), 4.70 (1H, br s, H-5), 4.92 (1/4H, d, $J$=2 Hz, DHHDP H-1), 5.31 (1H, dd, $J$=12,3 Hz, H-6), 5.33 (3/4H, s, DHHDP H-1), 5.42 (1H, d, $J$=3 Hz, H-3), 5.58 (1H, $J$=3 Hz, H-4), 5.61 (1H, $J$=7 Hz, H-2), 6.32 (1H, d, $J$=7 Hz, H-1), 6.33 (1/4H, d, $J$=2 Hz, DHHDP H-3), 6.71 (3/4H, s, DHHDP H-3), 7.28 (1H, s, DHHDP H-3′), 7.13, 7.18, 7.31 (each 1/2H, s, galloyl H), 7.16, 7.20, 7.32 (each 3/2H, s, galloyl H). $^{13}$C-NMR (acetone-$d_6$) $\delta$: 66.2 (glc C-6), 67.6, 72.3, 73.2, 80.6 (glc C-2, 3, 4, 5), 92.1 (glc C-1), 119.8, 120.0 (2C), 120.2 (galloyl C-1, HHDP C-2′), 110.2 (4C), 110.4 (2C) (galloyl C-2,6), 146.0 (5C), 146.2 (2C) (galloyl C-3,5, DHHDP C-4′), 139.7, 140.0, 140.1 (galloyl C-4), 144.8 (DHHDP C-1), 152.3 (DHHDP C-2), 129.2 (DHHDP C-3), 191.2 (DHHDP C-4), 96.6 (DHHDP C-5), 94.1 (DHHDP C-6), 114.0, 114.8 (DHHDP C-1′,3′), 138.5 (DHHDP C-5′), 143.0 (DHHDP C-6′), 164.7, 165.3, 165.5, 165.7, 168.3 (–COO–).

**Reduction of 28** A solution of **28** (40 mg) in 10% aqueous $Na_2S_2O_4$ (7 ml) was stirred at room temperature for 1 h. The reaction mixture was directly subjected to MCI-gel CHP 20P chromatography to afford punicafolin (**16**) (20 mg).

**Preparation of Phenazine Derivative (28a)** A solution of **28** (50 mg) in EtOH (3 ml) was treated with *o*-phenylenediamine (10 mg) in 20% AcOH–EtOH (3.5 ml). The mixture was stirred at room temperature for 1.5 h. After removal of EtOH under reduced puressure, the product was separated by MCI-gel CHP 20P chromatography to give **28a** as a tan amorphous powder, $[\alpha]_D^{18}$ −57.7° ($c$=0.4, acetone). *Anal.* Calcd for $C_{47}H_{32}N_2O_{24}\cdot 3H_2O$: C, 53.11; H, 3.60; N, 2.65. Found: C, 53.01; H, 3.79; N, 2.53. $^1$H-NMR (acetone-$d_6$+$D_2O$) $\delta$: 4.40—4.90 (3H, in total, m, H-5,6,6′), 5.29 (1H, d, $J$=3 Hz, H-3), 5.82 (1H, d, $J$=3 Hz, H-4), 6.61 (1H, d, $J$=4 Hz, H-1), 7.06 (1H, s, ph. H-3′), 7.18, 7.23, 7.28 (each 2H, s, galloyl H), 8.25 (1H, s, ph. H-3), 7.90—8.04, 8.30—8.40 (each 2H, m, ph. H-3″, 4″, 5″, 6″). $^{13}$C- NMR (acetone-$d_6$) $\delta$: 64.1 (glc C-6), 64.6 (glc C-4), 71.1 (glc C-2), 71.7 (glc C-3), 75.5 (glc C-5), 91.9 (glc C-1), 119.7, 119.8, 120.2 (2C) (galloyl C-1, ph. C-3), 110.4 (3C), 110.5 (3C) (galloyl C-2,6), 146.0 (3C), 146.1 (3C) (galloyl C-3,5), 139.9 (2C), 140.0 (galloyl C-4), 117.1 (ph. C-1), 133.8 (ph. C-2), 144.8 (ph. C-4), 138.6 ph. C-5), 152.5 (ph. C-6), 115.9 (ph. C-1′), 123.1 (ph. C-2′), 109.4 (ph. C-3′), 145.7 (ph. C-4′), 137.8 (ph. C-5′), 145.6 (ph. C-6′), 143.1 (ph. C-1″), 143.0 (ph, C-2″), 132.4 (ph. C-3″), 130.1 (ph. C-4″), 129.8 (ph. C-5″), 132.3 (ph. C-6″), 165.7, 165.9, 166.3, 166.4, 168.2 (–COO–).

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