# Structures of Anagallosaponins I—V and Their Companion Substances from *Anagallis arvensis* L.

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**From the herb of *Anagallis arvensis* L., we have isolated five novel oleanane glycosides, anagallosaponins I—V and the artifact, methyl anagallosaponin I, besides anagallosides A, B, C, and desglucoanagallosides A and B. The structures of isolates were identified by the use of 2D-NMR techniques ($^1$H–$^1$H correlation spectroscopy (COSY), $^1$H-detected heteronuclear multiple quantum coherence (HMQC), heteronuclear multiple quantum coherence (HMBC), rotating frame Overhauser enhancement spectroscopy (ROESY), total correlation spectroscopy (TOCSY). The structures of anagallosaponins I and II were characterized as anagallogenin A 3-*O*-{*β*-D-glucopyranosyl (1→4)-[*β*-D-xylopyranosyl (1→2)-]*β*-D-glucopyranosyl (1→4)-[*β*-D-glucopyranosyl (1→2)]-α-L-arabinopyranoside} and anagallogenin A 22-acetate 3-*O*-{*β*-D-xylopyranosyl (1→2)-*O*-*β*-D-glucopyranosyl (1→4)-[*β*-D-glucopyranosyl (1→2)]-α-L-arabinopyranoside}, respectively. The structures of anagallosaponins III, IV and V were characterized as priverogenin B 22-acetate 3-*O*-*β*-D-xylopyranosyl (1→2)-*β*-D-glucopyranosyl (1→4)-α-L-arabinopyranoside, 3-*O*-{*β*-D-xylopyranosyl (1→2)-*β*-D-glucopyranosyl (1→4)-[*β*-D-glucopyranosyl (1→2)]-α-L-arabinopyranoside}, 3-*O*-{*β*-D-glucopyranosyl (1→4)-[*β*-D-xylopyranosyl (1→2)]-*β*-D-glucopyranosyl (1→4)-α-L-arabinopyranoside}, respectively. Methyl anagallosaponin I, the methylacetal of anagallosaponin I might be derived from anagallosaponin I during the isolation procedure.**

**Keywords** *Anagallis arvensis*; Primuraceae; oleanane glycoside; anagallosaponin; anagalloside; 23-hydroxyanagalligenin

*Anagallis arvensis* L., an annual plant distributed from the tropics to the temperate regions, is used as a diuretic in Europe,[1] and as a remedy for snake or mad dog bite.[2] The saponin fraction has been investigated by several researchers.[3-6] In this paper, we report the isolation and structural elucidation of six novel saponins, anagallosaponins I—V (**1**—**5**) and methylanagallosaponin I (**6**), besides anagallosides A (**7**), B (**8**) and C (**9**), and desglucoanagallosides A (**10**) and B (**11**).[5] Their structures were elucidated by chemical and spectral methods, especially 2D-NMR techniques.

The 50% MeOH extract of *Anagallis arvensis*, was partitioned between $H_2O$ and EtOAc, the water layer was extracted with *n*-BuOH afford a saponin fraction. Repeated separation of the saponin fraction by ordinary-phase $SiO_2$ and reversed-phase $SiO_2$ furnished five novel saponins anagallosaponins I—V (**1**—**5**) and an artifact, methylanagallosaponin I (**6**), besides anagallosides A (**7**), B (**8**), C (**9**), and desglucoanagallosides A (**10**), and B (**11**).

Anagallosaponin III (**3**), $[\alpha]_D^{20}$ −17.3° (MeOH), obtained as colorless needles, was deduced to have the molecular formula $C_{48}H_{78}O_{18}\cdot 3H_2O$ based on the elementary analysis. The negative FAB-MS of **3** showed ion peaks at *m/z* 941 $[M-H]^-$, 809 $[M-\text{pentose}-H]^-$, 779 $[M-\text{hexose}-H]^-$ and 647 $[M-\text{pentose}-\text{hexose}-H]^-$. On acid hydrolysis, **3** afforded L-arabinose, D-glucose and D-xylose in the ratio of 1 : 1 : 1 (confirmed by chiral detection in HPLC). The $^1$H- and $^{13}$C-NMR spectra of **3** indicated the presence of one acetyl unit [*δ* 2.04, 21.1, 170.6], one α-arabinopyranosyl unit [H-1: *δ* 4.67 (d, *J* = 7.3 Hz), C-1: *δ* 107.6], one *β*-glucopyranosyl unit [H-1: *δ* 5.03 (d, *J* = 8.0 Hz), C-1: *δ* 105.4], and one *β*-xylopyranosyl unit [H-1: *δ* 4.90 (d, *J* = 7.8 Hz), C-1: *δ* 108.1]. $^1$H–$^1$H correlation spectroscopy ($^1$H–$^1$H COSY), $^1$H–$^{13}$C COSY and $^1$H-detected multiple-bond heteronuclear multiple quantum coherence (HMBC) (Fig. 1), as well as rotating frame Overhauser enhancement spectroscopy (ROESY) experiments enabled us to identify the aglycone of **3** as priverogenin B 22-acetate.[7] A $^{13}$C-NMR spectral comparison of **3** with anagalloside C(**9**) showed that **3** varies structurally from **9** only in its saccharide moieties, though these sugar units are also affixed to the C-3 position.

The sugar sequence of **3** was determined as follows. In the HMBC spectrum of **3**, long-range correlations were seen between C-3 (*δ* 88.9) of the aglycone and H-1 (*δ* 4.67) of the arabinose, C-4 (*δ* 81.3) of the arabinose and H-1 (*δ* 5.03) of the glucose, and C-2 (*δ* 86.3) of the glucose and H-1 (*δ* 4.90) of the xylose. Further, nuclear Overhauser effects (NOE)s were also observed between C-3-H (*δ* 3.33) and H-1 (*δ* 4.67) of the arabinose, H-4 (*δ* 4.14) of the arabinose and H-1 (*δ* 5.03) of the glucose, and H-2 (*δ* 4.24) of glucose and H-1 (*δ* 4.90) of the xylose in the ROESY experiment. Hence, **3** was formulated as privero-

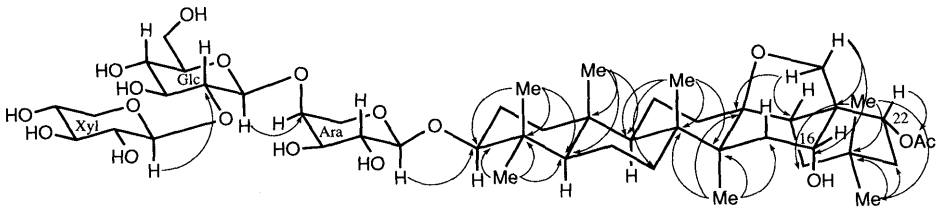



Fig. 1. The Main HMBC Correlations for Agallosaponin III (**3**)

genin B 22-acetate 3-*O*-*β*-D-xylopyranosyl (1→2)-*β*-D-glucopyranosyl (1→4)-*α*-L-arabinopyranoside.

Anagallosaponin IV (**4**), was obtained as colorless needles. The negative FAB-MS of **4** showed ion peaks at *m/z* 1103 $[M-H]^-$, 971 $[M-\text{pentose}-H]^-$, 941 $[M-\text{hexose}-H]^-$, 809 $[M-\text{pentose}-\text{hexose}-H]^-$ and 647 $[M-\text{pentose}-2\text{hexose}-H]^-$, *i.e.*, 162 mass units higher than that of **3** suggesting the molecular formula $C_{54}H_{88}O_{23}$. Acid hydrolysis of **4** afforded L-arabinose, D-glucose and D-xylose in the ratio of 1 : 2 : 1. The $^1$H- and $^{13}$C-NMR spectra of **4** indicated the presence of one acetyl unit [*δ* 2.03, 21.1, 170.5], one *α*-arabinopyranosyl unit [H-1, *δ* 4.79 (d, *J*=5.6 Hz); C-1, *δ* 104.8], two *β*-glucopyranosyl units [H-1, *δ* 5.00 (d, *J*=7.5 Hz), C-1, *δ* 104.2; H-1, *δ* 5.50 (d, *J*=7.5 Hz), C-1, *δ* 104.9], and one *β*-xylopyranosyl unit [H-1, *δ* 4.92 (d, *J*=7.0 Hz); C-1, *δ* 107.7]. A $^{13}$C-NMR spectral comparison of **4** with **3** showed that **4** is also a glycoside of priverogenin B 22-acetate, varying structurally from **3** only in its saccharide moieties, and that these sugar units are also affixed to the C-3 position. The arabinosyl C-2 signal of **4** appeared at lower field by +5.9 ppm than that of **3** because of the glycosylation shift,[8,9] indicating a *β*-glucopyranosyl group to be located at C-2 of arabinose. Therefore, **4** was formulated as priverogenin B 22-acetate 3-*O*-{*β*-D-xylopyranosyl (1→2)-*β*-D-glucopyranosyl (1→4)-[*β*-D-glucopyranosyl (1→2)]-*α*-L-arabinopyranoside}.

Anagallosaponin V (**5**), obtained as colorless needles, revealed the same ion peaks at *m/z* 1103 $[M-H]^-$, 971 $[M-\text{pentose}-H]^-$, 941 $[M-\text{hexose}-H]^-$, 809 $[M-\text{pentose}-\text{hexose}-H]^-$ and 647 $[M-\text{pentose}-2\text{hexose}-H]^-$ as **4** in the negative FAB-MS. On acid hydrolysis, **5** afforded L-arabinose, D-glucose and D-xylose in the ratio of 1 : 2 : 1. The $^1$H- and $^{13}$C-NMR spectra of **5** showed similar patterns to those of **4** except for those due to sugar moieties. A $^{13}$C-NMR spectral comparison of **5** with **3** showed a glycosylation shift at the C-4 signal (+9.1 ppm) of glucosyl, demonstrating a *β*-glucopyranosyl group to be located at the C-4-OH of glucose. Therefore, **5** was formulated as priverogenin B 22-acetate 3-*O*-{*β*-D-glucopyranosyl (1→4)-[*β*-D-xylopyranosyl (1→2)-]*β*-D-glucopyranosyl (1→4)-*α*-L-arabinopyranoside}.

Anagallosaponin I (**1**), $[\alpha]_D^{20}$ −11.1° (MeOH) had the molecular formula $C_{58}H_{96}O_{28}\cdot 3H_2O$ based on the elementary analysis. Its negative FAB-MS showed ion peaks at ion peak at *m/z* 1239 $[M-H]^-$, 1107 $[M-\text{pentose}-H]^-$, 1077 $[M-\text{hexose}-H]^-$, 945 $[M-\text{pentose}-\text{hexose}-H]^-$ and 783 $[M-\text{pentose}-2\text{hexose}-H]^-$, *i.e.*, 42 mass units lower than those of anagalloside A (**7**).[5] Acid hydrolysis of **1** afforded L-arabinose, D-glucose and D-xylose in the ratio of 1 : 3 : 1. The $^1$H- and $^{13}$C- NMR spectra of **1** indicated the presence of one *α*-arabinopyranosyl unit [H-1, *δ* 4.79 (d, *J*=5.7 Hz), C-1, *δ* 104.9], three *β*-glucopyranosyl units [H-1, *δ* 4.90 (d, *J*=7.2 Hz), C-1, *δ* 104.1; H-1, *δ* 5.14 (d, *J*=7.8 Hz); C-1, *δ* 105.1; H-1, *δ* 5.46 (d, *J*=8.3 Hz), C-1, *δ* 105.1], and one *β*-xylopyranosyl unit [H-1, *δ* 4.91 (d, *J*=8.0 Hz); C-1, *δ* 107.5]. $^1$H–$^1$H COSY, $^1$H–$^{13}$C COSY, HMBC and ROESY experiments (Fig. 2) enabled us to identify the aglycone as anagallogenin A.[5]

The sugar sequence of **1** was determined as follows. In the HMBC spectrum of **1**, long-range correlations were seen between C-3 (*δ* 89.4) and H-1 (*δ* 4.79) of the arabinose, C-2 (*δ* 80.0) of the arabinose and H-1 (*δ* 5.46) of the glucose (Glc-1), C-2 (*δ* 84.2) of the glucose (Glc-2) and H-1 (*δ* 5.14) of the xylose, and C-4 (*δ* 80.6) of the glucose (Glc-2) and H-1 (*δ* 5.14) of the glucose (Glc-3). Further, NOEs were also observed between C-3-H (*δ* 3.15) and H-1 (*δ* 4.79) of the arabinose, H-2 (*δ* 4.47) of the arabinose and H-1 (*δ* 5.46) of the Glc-1, H-4 (*δ* 4.45) of the arabinose and H-1 (*δ* 4.90) of the Glc-2, H-2 (*δ* 3.90) of the Glc-2 and H-1 (*δ* 4.91) of the xylose, and H-4 (*δ* 4.29) of the Glc-2 and H-1 (*δ* 5.14) of the Glc-3 in the ROESY experiment (Fig. 2). Therefore, **1** was formulated as anagallogenin A 3-*O*-{*β*-D-glucopyranosyl (1→4)-[*β*-D-xylopyranosyl (1→2)-]*β*-D-glucopyranosyl (1→4)-[*β*-D-glucopyranosyl (1→2)]-*α*-L-arabinopyranoside}.

Anagallosaponin II (**2**), obtained as colorless needles, had the molecular formula $C_{54}H_{88}O_{25}$ (negative FAB-MS, *m/z* 1135 $[M-H]^-$), *i.e.*, 16 mass units higher than that of desglucoanagalloside A (**10**).[5] On acid hydrolysis, **1** afforded L-arabinose, D-glucose and D-xylose in the ratio of 1 : 2 : 1. The $^1$H-NMR spectrum of **2** indicated the presence of six tertiary methyl groups (*δ* 0.95, 1.10, 1.10, 1.13, 1.38, and 1.53), one acetyl unit (*δ* 1.97), one *α*-arabinopyranosyl unit [H-1, *δ* 5.00 (d, *J*=5.6 Hz)], two *β*-glucopyranosyl units [H-1, *δ* 5.00 (d, *J*=7.3 Hz); H-1, *δ* 5.50 (d, *J*=8.0 Hz)], and one *β*-xylopyranosyl unit [H-1, *δ* 4.95 (d, *J*=6.0 Hz)]. A $^{13}$C-NMR spectral comparison of **2** with **10** showed that **2** differs structurally from **10** only in its C-4 substituent: a hydroxymethyl group in **2** instead of a methyl group in **10**. In the ROESY experiment on **2**, an NOE was observed between the H-25 signal (*δ* 0.95) and H-24 signal (*δ* 1.10), indicating the orientation of the hydroxymethyl group to be *α*. Hence, the aglycone of **2** was formulated as 13*β*, 28-epoxy-3*β*,16*α*,22*α*,23,28-pentahydroxyoleanane (23-hydroxyanagalligenin A), which is identical with compound **2** reported by Napoli

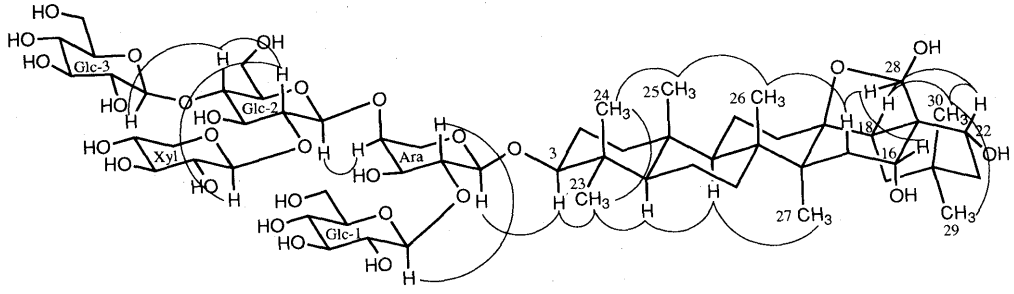
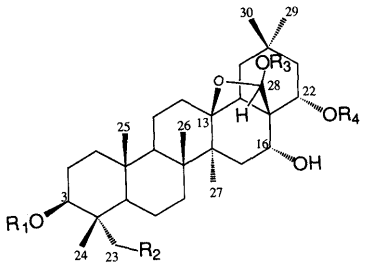
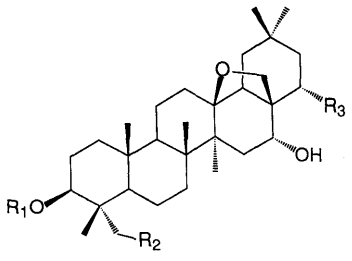


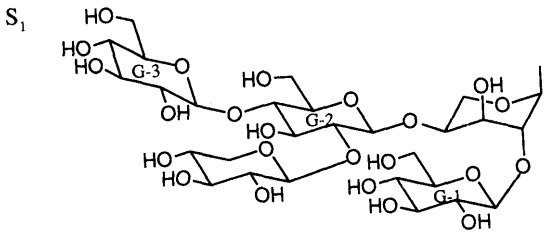

Fig. 2. The Main NOE Correlations for Agallosaponin I (**1**)

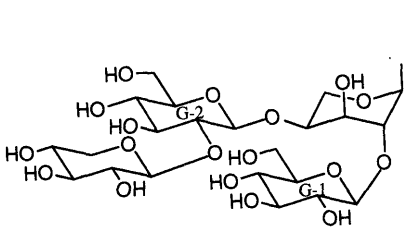


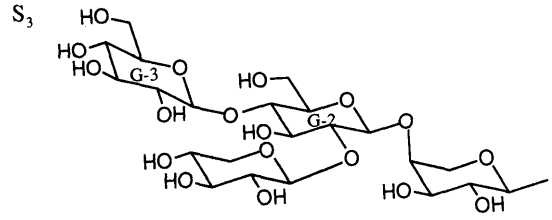
| | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|
| **1** | $S_1$ | H | H | H |
| **2** | $S_2$ | OH | H | Ac |
| **6** | $S_1$ | H | Me | H |
| **7** | $S_1$ | H | H | Ac |
| **10** | $S_2$ | H | H | Ac |

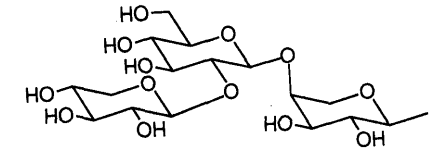


| | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| **3** | $S_4$ | H | OAc |
| **4** | $S_2$ | H | OAc |
| **5** | $S_3$ | H | OAc |
| **8** | $S_1$ | OH | H |
| **9** | $S_1$ | H | OAc |
| **11** | $S_2$ | OH | H |









*et al.*[10] The carbon signals due to the sugar moieties of **2** are superimposable on those of **10**, indicating that the sugar moieties are the same. Therefore, **2** was formulated as 23-hydroxyanagalligenin A 22-acetate 3-*O*-{*β*-D-xylopyranosyl (1→2)-*β*-D-glucopyranosyl (1→4)-[*β*-D-glucopyranosyl (1→2)]-α-L-arabinopyranoside}.

Methylnagallosaponin I (**6**), $C_{59}H_{98}O_{28}$ was obtained as colorless needles and the relative molecular mass ($M_r$) was considered to be 1254, *i.e.*, 14 mass units higher than that of **1**, as the deprotonated molecular ion was apparent at *m/z* 1253 in the negative FAB-MS. Acid hydrolysis of **6** afforded L-arabinose, D-glucose and D-xylose in the ratio of 1 : 3 : 1. The $^1$H- and $^{13}$C-NMR spectra of **6** indicated the presence of one methoxy group ($\delta$ 3.45, 54.9), one α-arabinopyranosyl unit [H-1, $\delta$ 4.78 (d, $J$=6.0 Hz), C-1, $\delta$ 104.7], three *β*-glucopyranosyl units [H-1, $\delta$ 4.90 (d, $J$=7.0 Hz), C-1, $\delta$ 103.9; H-1, $\delta$ 5.13 (d, $J$=7.8 Hz); C-1, $\delta$ 104.8; H-1, $\delta$ 5.46 (d, $J$=7.3 Hz), C-1, $\delta$ 104.8], and one *β*-xylopyranosyl unit [H-1, $\delta$ 4.90 (d, $J$=7.0 Hz); C-1, $\delta$ 107.3]. The $^1$H- and $^{13}$C-NMR spectra of **6** showed similar patterns to those of **1** except for those due to D/E rings, indicating the presence of a methoxy group in the D/E rings. A $^{13}$C-NMR spectral comparison of **6** with **1** showed an alkylation shift at the C-28 signal (+5.8 ppm), demonstrating a methoxy group to be located at the C-28. Therefore, **1** was formulated as anagallogenin A 28-*O*-methyl-3-*O*-{*β*-D-xylopyranosyl (1→2)-*O*-*β*-D-glucopyranosyl (1→4)-[*β*-D-glucopyranosyl (1→2)]-α-L-arabinopyranoside}. The occurrence of the acetal compound shows that **6** might have been derived from **1** during the extraction and/or purification procedure.

**Experimental**

Melting points were measured with a Yanagimoto micromelting point apparatus without correction. Optical rotations were taken on a JASCO DIP-140 digital polarimeter and IR spectra on JASCO FT/IR-5300. NMR spectra were recorded on a JEOL GX-400 or Varian UNITY 600 spectrometer in $C_5D_5N$ solution using tetramethylsilane as an internal standard. NMR experiments included $^1$H–$^1$H correlation spectroscopy (COSY), heteronuclear multiple quantum coherence (HMQC), insensitive nuclei enhanced by polarization transfer (INEPT), total correlation spectroscopy (TOCSY), ROESY and HMBC (512 × 1024 data matrix size, 128 scans, recycle delay = 1.16 s). Coupling constants ($J$ values) are given in hertz (Hz). The FAB-MS (Xe gun, 10 kV, *m*-nitrobenzyl alcohol as matrix) were measured on a JEOL JMS-PX303 mass spectrometer. For column chromatography, Silica gel 60 (40—63 μm, Merck) and Silica gel 60 silanised (63—200 μm, Merck) were used. TLC was carried out on Silica gel 60F-254 (Merck) with $CHCl_3$–MeOH–$H_2O$ (65 : 30 : 4), and Silica gel 60 silanised with MeOH–$H_2O$ (1 : 1).

**Isolation of Saponins** Dried whole plants (3.3 kg) were extracted with 50% MeOH. The 50% methanolic extract was partitioned between $H_2O$ and EtOAc. The water layer was further partitioned between $H_2O$ and *n*-BuOH. A part (140 g) of the butanolic layer (280 g) was chromatographed on a silica gel column and eluted with EtOAc–MeOH (4 : 1) to give saponin fractions. These saponin factions (80 g) were repeatedly chromatographed on silica gel with $CHCl_3$–MeOH–$H_2O$ (65 : 30 : 4), followed by Sephadex LH-20 (MeOH) and reversed-phase MPLC (40—80% MeOH) to afford anagallosaponins I (**1**, 0.31 g), II (**2**, 1.1 g), III (**3**, 0.085 g), IV (**4**, 0.08 g), V (**5**, 0.13 g), methylanagallosaponin I (**6**, 0.06 g), anagallosides A (**7**, 18.0 g), B (**8**, 3 g), C (**9**, 1.8 g), desglucoanagallosides A (**10**, 15.5 g) and B (**11**, 25 g).

Anagallosaponin I (**1**): mp > 300 °C (MeOH), $[\alpha]_D^{20}$ −11.1° ($c$ = 1.93, MeOH). *Anal.* Calcd for $C_{58}H_{96}O_{28}\cdot 3H_2O$: C, 53.78; H, 7.94. Found; C, 53.90; H, 8.05. FAB-MS *m/z* 1239 $[M-H]^-$, 1107 $[M-H-Xyl]^-$, 1077 $[M-H-Glc]^-$, 945 $[M-H-Xyl-Glc]^-$, 783 $[M-H-Xyl-2Glc]^-$. IR $\nu_{max}$(film) cm$^{-1}$: 3360, 1070, 1040. $^1$H-NMR (600 MHz) $\delta$: 0.85 (H-25), 1.07 (H-24), 1.14 (H-29), 1.14 (H-30), 1.20 (H-23), 1.35 (H-26), 1.62 (H-27), 2.20 (1H, br d, $J$=11.5 Hz, H-18), 2.90 (1H, dd, $J$=13.0, 11.5 Hz, $H_\alpha$-19), 2.92 (1H, dd, $J$=12.5, 12.0 Hz, $H_\alpha$-21), 3.15

TABLE I. $^{13}$C-NMR Data for Compounds **1**—**11** (Pyridine-$d_5$, $\delta$-Values)

| Carbon | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 39.5 | 39.2 | 39.3 | 39.2 | 39.3 | 39.2 | 39.3 | 39.3 | 38.2 | 39.2 | 39.3 |
| 2 | 26.9 | 26.1 | 26.9 | 26.6 | 26.9 | 26.7 | 26.6 | 26.1 | 26.8 | 26.6 | 26.1 |
| 3 | 89.4 | 82.5 | 88.9 | 89.0 | 88.9 | 89.1 | 89.1 | 82.6 | 89.4 | 89.1 | 82.5 |
| 4 | 40.0 | 43.8 | 39.8 | 39.8 | 39.8 | 39.8 | 39.8 | 43.8 | 39.9 | 39.9 | 43.8 |
| 5 | 56.0 | 47.9 | 55.8 | 55.7 | 55.8 | 55.7 | 55.8 | 47.9 | 55.9 | 55.7 | 47.9 |
| 6 | 18.2 | 17.8 | 18.0 | 18.0 | 18.0 | 18.0 | 18.1 | 17.8 | 18.2 | 18.0 | 17.8 |
| 7 | 34.7 | 34.1 | 34.4 | 34.4 | 34.4 | 34.4 | 34.4 | 34.3 | 34.6 | 34.3 | 34.2 |
| 8 | 43.0 | 42.8 | 42.7 | 42.6 | 42.7 | 42.7 | 42.8 | 42.6 | 42.8 | 42.7 | 42.6 |
| 9 | 50.7 | 50.5 | 50.5 | 50.4 | 50.5 | 50.4 | 50.4 | 50.7 | 50.6 | 50.3 | 50.7 |
| 10 | 37.2 | 36.9 | 37.0 | 36.9 | 37.0 | 36.9 | 36.9 | 37.0 | 37.1 | 36.9 | 36.9 |
| 11 | 19.7 | 19.4 | 19.3 | 19.2 | 19.2 | 19.4 | 19.3 | 19.4 | 19.4 | 19.3 | 19.4 |
| 12 | 33.6 | 33.4 | 33.0 | 33.0 | 33.0 | 33.3 | 33.3 | 33.0 | 33.1 | 33.4 | 33.0 |
| 13 | 87.7 | 87.7 | 86.4 | 86.3 | 86.3 | 88.2 | 87.6 | 86.6 | 86.5 | 87.6 | 86.6 |
| 14 | 44.4 | 44.0 | 45.1 | 45.1 | 45.1 | 44.2 | 44.0 | 44.7 | 45.2 | 43.9 | 44.7 |
| 15 | 37.0 | 36.9 | 36.6 | 36.6 | 36.6 | 36.8 | 36.8 | 37.1 | 36.7 | 36.8 | 37.1 |
| 16 | 69.9 | 69.7 | 70.7 | 70.6 | 70.7 | 69.3 | 69.7 | 77.3 | 70.8 | 69.7 | 77.3 |
| 17 | 53.1 | 51.5 | 48.9 | 48.8 | 48.9 | 47.7 | 51.5 | 44.7 | 49.0 | 51.5 | 44.7 |
| 18 | 47.6 | 47.4 | 51.3 | 51.3 | 51.3 | 53.0 | 47.3 | 51.7 | 51.5 | 47.3 | 51.7 |
| 19 | 38.9 | 38.3 | 38.2 | 38.2 | 38.1 | 38.5 | 38.4 | 39.1 | 38.2 | 38.3 | 39.1 |
| 20 | 33.5 | 33.3 | 33.3 | 33.3 | 33.3 | 33.7 | 33.3 | 31.9 | 33.4 | 33.3 | 31.9 |
| 21 | 46.9 | 41.6 | 42.1 | 42.1 | 42.1 | 46.5 | 41.7 | 37.0 | 42.2 | 41.6 | 36.9 |
| 22 | 68.4 | 73.0 | 77.4 | 77.3 | 77.4 | 67.3 | 73.0 | 31.9 | 77.5 | 72.9 | 31.9 |
| 23 | 28.4 | 65.0 | 28.1 | 28.1 | 28.1 | 28.1 | 28.1 | 64.9 | 28.2 | 28.1 | 64.9 |
| 24 | 16.9 | 13.3 | 16.8 | 16.7 | 16.8 | 16.7 | 16.7 | 13.4 | 16.8 | 16.7 | 13.3 |
| 25 | 16.7 | 17.1 | 16.5 | 16.4 | 16.5 | 16.5 | 16.5 | 17.2 | 16.6 | 16.4 | 17.1 |
| 26 | 18.9 | 18.6 | 18.6 | 18.6 | 18.6 | 18.7 | 18.7 | 18.7 | 18.8 | 18.7 | 18.7 |
| 27 | 19.7 | 19.7 | 19.8 | 19.7 | 19.8 | 19.7 | 19.7 | 19.7 | 19.9 | 19.7 | 19.7 |
| 28 | 98.9 | 97.8 | 76.9 | 76.9 | 76.9 | 104.7 | 97.8 | 78.1 | 77.0 | 97.8 | 78.1 |
| 29 | 34.1 | 33.4 | 33.3 | 33.3 | 33.3 | 33.1 | 33.4 | 33.9 | 33.5 | 33.4 | 33.9 |
| 30 | 26.3 | 25.7 | 25.5 | 25.5 | 25.5 | 26.0 | 25.7 | 24.9 | 25.7 | 25.6 | 24.9 |
| 3-*O*-Ara | | | | | | | | | | | |
| 1 | 104.9 | 104.1 | 107.6 | 104.8 | 107.6 | 104.7 | 104.7 | 103.8 | 104.8 | 104.7 | 104.1 |
| 2 | 80.0 | 80.3 | 73.8 | 79.7 | 73.8 | 79.6 | 79.6 | 80.1 | 79.6 | 79.7 | 80.2 |
| 3 | 73.4 | 73.5 | 74.5 | 73.3 | 74.5 | 73.2 | 73.2 | 73.3 | 73.5 | 73.3 | 73.4 |
| 4 | 78.9 | 78.1 | 81.3 | 78.6 | 81.4 | 78.5 | 78.5 | 78.4 | 79.0 | 78.7 | 78.5 |
| 5 | 64.3 | 64.3 | 66.5 | 64.2 | 66.4 | 64.1 | 64.1 | 64.1 | 64.5 | 64.3 | 64.3 |
| 3-*O*-Glc-1 | | | | | | | | | | | |
| 1 | 105.1 | 105.1 | | 104.9 | | 104.8 | 104.8 | 104.8 | 104.8 | 104.9 | 105.0 |
| 2 | 76.2 | 76.2 | | 76.3 | | 76.2 | 76.2 | 76.2 | 76.3 | 76.3 | 76.2 |
| 3 | 78.5 | 78.4 | | 78.3 | | 78.2 | 77.4 | 78.4 | 78.4 | 78.3 | 78.3 |
| 4 | 72.1 | 71.5 | | 71.9 | | 71.9 | 71.9 | 71.6 | 72.0 | 71.9 | 71.5 |
| 5 | 78.2 | 78.3 | | 78.0 | | 78.0 | 78.0 | 78.2 | 78.1 | 78.0 | 78.2 |
| 6 | 63.3 | 62.8 | | 63.0 | | 63.0 | 63.1 | 62.9 | 63.2 | 63.1 | 62.8 |
| 3-*O*-Glc-2 | | | | | | | | | | | |
| 1 | 104.1 | 103.7 | 105.4 | 104.2 | 104.8 | 103.9 | 103.9 | 103.8 | 104.8 | 104.2 | 103.8 |
| 2 | 84.2 | 85.5 | 86.3 | 85.5 | 84.9 | 83.9 | 83.9 | 83.9 | 84.0 | 85.5 | 85.4 |
| 3 | 75.1 | 77.7 | 77.7 | 77.6 | 74.9 | 74.8 | 74.8 | 74.9 | 75.0 | 77.6 | 77.6 |
| 4 | 80.6 | 71.1 | 71.7 | 71.1 | 80.2 | 80.4 | 80.4 | 80.3 | 80.2 | 71.1 | 71.1 |
| 5 | 76.7 | 78.4 | 78.4 | 78.4 | 76.4 | 76.4 | 76.4 | 76.5 | 76.5 | 78.4 | 78.3 |
| 6 | 61.9 | 62.4 | 62.4 | 62.3 | 61.7 | 61.7 | 61.7 | 61.6 | 61.6 | 62.3 | 62.4 |
| 3-*O*-Xyl | | | | | | | | | | | |
| 1 | 107.5 | 107.7 | 108.1 | 107.7 | 107.8 | 107.3 | 107.3 | 107.3 | 107.3 | 107.7 | 107.7 |
| 2 | 76.3 | 76.2 | 76.4 | 76.2 | 76.3 | 76.1 | 76.1 | 76.1 | 76.1 | 76.2 | 76.2 |
| 3 | 77.6 | 77.9 | 78.0 | 77.9 | 77.6 | 77.4 | 77.4 | 77.5 | 77.5 | 77.9 | 77.9 |
| 4 | 70.9 | 70.7 | 70.5 | 70.7 | 70.3 | 70.7 | 70.7 | 70.7 | 70.8 | 70.7 | 70.8 |
| 5 | 67.5 | 67.5 | 67.3 | 67.5 | 67.2 | 67.3 | 67.3 | 67.3 | 67.4 | 67.5 | 67.5 |
| 3-*O*-Glc-3 | | | | | | | | | | | |
| 1 | 105.1 | | | | 105.1 | 104.8 | 104.9 | 105.0 | 104.9 | | |
| 2 | 76.0 | | | | 75.8 | 75.8 | 75.8 | 75.8 | 75.8 | | |
| 3 | 78.6 | | | | 78.2 | 78.2 | 78.2 | 78.2 | 78.2 | | |
| 4 | 71.7 | | | | 71.5 | 71.5 | 71.5 | 71.6 | 71.6 | | |
| 5 | 78.8 | | | | 78.4 | 78.4 | 78.4 | 78.3 | 78.2 | | |
| 6 | 62.6 | | | | 62.3 | 62.3 | 62.4 | 62.4 | 62.4 | | |
| $CH_3CO$ | | 21.4 | 21.1 | 21.1 | 21.1 | | 21.4 | | 21.4 | 21.3 | |
| | | 170.4 | 170.6 | 170.5 | 170.5 | | 170.2 | | 171.0 | 170.4 | |
| $CH_3O$ | | | | | | 54.9 | | | | | |

(1H, dd, $J$=11.0, 5.0 Hz, H-3), 4.29 (1H, dd, $J$=8.5, 8.5 Hz, H-4 of Glc-2), 4.45 (1H, m, H-4 of Ara), 4.47 (1H, m, H-2 of Ara), 4.79 (1H, d, $J$=5.7 Hz, H-1 of Ara), 4.90 (1H, d, $J$=7.2 Hz, H-1 of Glc-2), 4.91 (1H, d, $J$=8.0 Hz, H-1 of Xyl), 5.04 (1H, dd, $J$=12.0, 5.0 Hz, H-22), 5.08 (1H, m, H-16), 5.14 (1H , d, $J$=7.8 Hz, H-1 of Glc-3), 5.44 (1H, s, H-28), 5.46 (1H, d, $J$=8.3 Hz, H-1 of Glc-1). For $^{13}$C-NMR data, see Table I.

Anagallosaponin II (**2**): mp 255—257 °C (MeOH), $[\alpha]_D^{20}$ −4.5° ($c$=3.55, MeOH). *Anal.* Calcd for $C_{54}H_{88}O_{25}\cdot H_2O$: C, 56.14; H, 7.85. Found: C, 56.22; H, 8.06. FAB-MS $m/z$: 1135 $[M-H]^-$, 1003 $[M-H-Xyl]^-$, 973 $[M-H-Glc]^-$, 841 $[M-H-Xyl-Glc]^-$, 679 $[M-H-Xyl-2Glc]^-$, 547 $[M-H-Xyl-Ara-2Glc]^-$. IR $\nu_{max}^{film}$ cm$^{-1}$: 3400, 1715, 1250, 1080, 1040. $^1$H-NMR (400 MHz) $\delta$: 0.95 (H-25), 1.10 (H-24), 1.10 (H-29), 1.13 (H-30), 1.38 (H-26), 1.53 (H-27), 1.97 (Ac), 2.17 (1H, br d, $J$=11.5 Hz, H-18), 2.77 (1H, dd, $J$=12.5, 11.5 Hz, $H_\alpha$-21), 2.83 (1H, dd, $J$=13.2, 11.5 Hz, $H_\alpha$-19), 3.70, 4.22 (each 1H, d, $J$=10.5 Hz, $H_2$-23), *ca.* 4.12 (1H, m, H-3), 4.75 (1H, m, H-16), 4.95 (1H, d, $J$=6.0 Hz, H-1 of Xyl), 5.00 (1H, d, $J$=5.6 Hz, H-1 of Ara), 5.00 (1H, d, $J$=7.3 Hz, H-1 of Glc-2), 5.50 (1H, d, $J$=8.0 Hz, H-1 of Glc-1), 6.04 (1H, dd, $J$=11.5, 5.5 Hz, H-22). For $^{13}$C-NMR data, see Table I.

Anagallosaponin III (**3**): mp 246—247 °C (MeOH), $[\alpha]_D^{20}$ −17.3° ($c$=2.07, MeOH). *Anal.* Calcd for $C_{48}H_{78}O_{18}\cdot 2H_2O$: C, 58.88; H, 8.44. Found; C, 59.02; H, 8.54. FAB-MS $m/z$: 941 $[M-H]^-$, 809 $[M-H-Xyl]^-$, 779 $[M-H-Glc]^-$, 647 $[M-H-Xyl-Glc]^-$. IR $\nu_{max}^{film}$ cm$^{-1}$: 3400, 1730, 1250, 1080, 1045. $^1$H-NMR (600 MHz) $\delta$: 0.89 (H-25), 1.02 (H-30), 1.03 (H-24), 1.09 (H-29), 1.29 (H-23), 1.32 (H-26), 1.59 (H-27), 1.78 (1H, dd, $J$=12.0, 4.0 Hz, H-18), 2.04 (Ac), 2.80 (1H, dd, $J$=12.0, 10.0 Hz, $H_\alpha$-21), 2.85 (1H, dd, $J$=14.0, 12.0 Hz, $H_\alpha$-19), 3.33 (1H, dd, $J$=12.0, 4.5 Hz, H-3), 3.71, 3.74 (each 1H, d, $J$=8.0 Hz, $H_2$-28), 4.14 (1H, m, H-4 of Ara), 4.56 (1H, m, H-16), 4.67 (1H, d, $J$=7.3 Hz, H-1 of Ara), 4.90 (1H, d, $J$=7.8 Hz, H-1 of Xyl), 5.03 (1H, d, $J$=8.0 Hz, H-1 of Glc), 5.27 (1H, dd, $J$=12.0, 5.0 Hz, H-22). For $^{13}$C-NMR data, see Table I.

Anagallosaponin IV (**4**): mp 237—239 °C (MeOH), $[\alpha]_D^{20}$ −19.4° ($c$=1.39, MeOH). *Anal.* Calcd for $C_{54}H_{88}O_{23}\cdot 3H_2O$: C, 55.95; H, 8.17. Found: C, 55.74; H, 8.09. FAB-MS $m/z$: 1103 $[M-H]^-$, 971 $[M-H-Xyl]^-$, 941 $[M-H-Glc]^-$, 809 $[M-H-Xyl-Glc]^-$, 647 $[M-H-Xyl-2Glc]^-$. IR $\nu_{max}^{film}$ cm$^{-1}$: 3400, 1715, 1250, 1070, 1045. $^1$H-NMR (400 MHz) $\delta$: 0.85 (H-25), 1.02 (H-30), 1.09 (H-29), 1.10 (H-24), 1.22 (H-23), 1.31 (H-26), 1.56 (H-27), 1.76 (1H, dd, $J$=12.0, 4.0 Hz, H-18), 2.03 (Ac), 2.80 (1H, dd, $J$=12.0, 12.0 Hz, $H_\alpha$-21), 2.85 (1H, dd, $J$=13.0, 12.0 Hz, $H_\alpha$-19), 3.16 (1H, dd, $J$=11.0, 5.5 Hz, H-3), 3.67, 3.70 (each 1H, d, $J$=8.0 Hz, $H_2$-28), 4.59 (1H, m, H-16), 4.79 (1H, d, $J$=5.6 Hz, H-1 of Ara), 4.92 (1H, d, $J$=7.0 Hz, H-1 of Xyl), 5.00 (1H, d, $J$=7.5 Hz, H-1 of Glc-2), 5.27 (1H, dd, $J$=12.0, 5.0 Hz, H-22), 5.50 (1H, d, $J$=7.5 Hz, H-1 of Glc-1). For $^{13}$C-NMR data, see Table I.

Anagallosaponin V (**5**): mp 253—255 °C (MeOH), $[\alpha]_D^{20}$ −26.2° ($c$=2.51, pyridine). *Anal.* Calcd for $C_{54}H_{88}O_{23}$: C, 58.68; H, 8.03. Found: C, 58.72; H, 7.97. FAB-MS $m/z$: 1103 $[M-H]^-$, 971 $[M-H-Xyl]^-$, 941 $[M-H-Glc]^-$, 809 $[M-H-Xyl-Glc]^-$, 647 $[M-H-Xyl-2Glc]^-$. IR $\nu_{max}^{film}$ cm$^{-1}$: 3390, 1730, 1250, 1070, 1045. $^1$H-NMR (400 MHz) $\delta$: 0.88 (H-25), 1.01 (H-30), 1.02 (H-24), 1.08 (H-29), 1.29 (H-23), 1.32 (H-26), 1.60 (H-27), 1.77 (1H, dd, $J$=12.0, 4.0 Hz, H-18), 2.04 (Ac), 2.80 (1H, dd, $J$=12.0, 11.5 Hz, $H_\alpha$-21), 2.85 (1H, dd, $J$=13.0, 12.0 Hz, $H_\alpha$-19), 3.42 (1H, dd, $J$=12.0, 5.0 Hz, H-3), 3.71, 3.74 (each 1H, d, $J$=8.0 Hz, $H_2$-28), 4.56 (1H, m, H-16), 4.65 (1H, d, $J$=7.8 Hz, H-1 of Ara), 4.86 (1H, d, $J$=6.5 Hz, H-1 of Glc-2), 4.93 (1H, d, $J$=7.5 Hz, H-1 of Xyl), 5.15 (1H, d, $J$=7.4 Hz, H-1 of Glc-3), 5.27 (1H, dd, $J$=11.5, 5.5 Hz, H-22). For $^{13}$C-NMR data, see Table I.

Methylanagallosaponin I (**6**): mp 256—258 °C (MeOH), $[\alpha]_D^{20}$ −13.6° ($c$=3.09, pyridine). *Anal.* Calcd for $C_{59}H_{98}O_{28}\cdot 2H_2O$: C, 54.87; H, 7.96. Found; C, 54.92; H, 8.12. FAB-MS $m/z$: 1253 $[M-H]^-$, 1121 $[M-H-Xyl]^-$, 1091 $[M-H-Glc]^-$, 959 $[M-H-Xyl-Glc]^-$, 797 $[M-H-Xyl-2Glc]^-$. IR $\nu_{max}^{film}$ cm$^{-1}$: 3410, 1115, 1080, 1040. $^1$H-NMR (400 MHz) $\delta$: 0.86 (H-25), 1.07 (H-24), 1.08 (H-29 or H-30), 1.10 (H-30 or H-29), 1.20 (H-23), 1.32 (H-26), 1.58 (H-27), 2.15 (1H, br d, $J$=11.5 Hz, H-18), 2.82 (1H, dd, $J$=12.0, 11.5 Hz, $H_\alpha$-21), 2.86 (1H, dd, $J$=13.0, 11.5 Hz, H-19), 3.15 (1H, dd, $J$=11.0, 4.5 Hz, H-3), 3.45 (O−Me), 4.66 (1H, s, H-28), 4.78 (1H, d, $J$=6.0 Hz, H-1 of Ara), 4.90 (1H, d, $J$=7.0 Hz, H-1 of Glc-2), 4.90 (1H, d, $J$=7.0 Hz, H-1 of Xyl), 5.01 (1H, m, H-16), 5.13 (1H, d, $J$=7.8 Hz, H-1 of Glc-3), 5.46 (1H, d, $J$=7.3 Hz, H-1 of Glc-1). For $^{13}$C-NMR data, see Table I.

Anagalloside A (**7**): mp 263—264 °C (MeOH), $[\alpha]_D^{20}$ −15.5° ($c$=3.87, pyridine). *Anal.* Calcd for $C_{60}H_{98}O_{29}\cdot 2H_2O$: C, 54.62; H, 7.79. Found: C, 54.75; H, 8.90. FAB-MS $m/z$ 1281 $[M-H]^-$, 1149 $[M-H-Xyl]^-$, 1119 $[M-H-Glc]^-$, 987 $[M-H-Xyl-Glc]^-$, 825 $[M-H-Xyl-2Glc]^-$, 663 $[M-H-Xyl-3Glc]^-$. IR $\nu_{max}^{film}$ cm$^{-1}$: 3400, 1715, 1255, 1070, 1040. $^1$H-NMR (400 MHz) $\delta$: 0.87 (H-25), 1.10 (H-24), 1.11 (H-29), 1.15 (H-30), 1.22 (H-23), 1.42 (H-26), 1.61 (H-27), 1.99 (Ac), 2.20 (1H, br d, $J$=11.5 Hz, H-18), 2.80 (1H, dd, $J$=11.5, 11.5 Hz, $H_\alpha$-21), 2.88 (1H, dd, $J$=12.0, 11.5 Hz, H-19), 3.17 (1H, dd, $J$=11.7, 5.0 Hz, H-3), 4.80 (1H, d, $J$=6.0 Hz, H-1 of Ara), 4.91 (1H, d, $J$=7.0 Hz, H-1 of Glc-2), 4.91 (1H, d, $J$=7.0 Hz, H-1 of Xyl), 5.10 (1H, m, H-16), 5.13 (1H, d, $J$=8.0 Hz, H-1 of Glc-3), 5.26 (1H, s, H-28), 5.47 (1H, d, $J$=7.0 Hz, H-1 of Glc-1), 6.06 (1H, dd, $J$=11.5, 6.0 Hz, H-22). For $^{13}$C-NMR data, see Table I.

Anagalloside B (**8**): mp 256—257 °C (MeOH), −0.2° ($c$=0.90, MeOH). *Anal.* Calcd for $C_{58}H_{96}O_{27}\cdot 3H_2O$: C, 54.48; H, 7.98. Found: C, 54.30; H, 8.00. FAB-MS $m/z$: 1223 $[M-H]^-$, 1091 $[M-H-Xyl]^-$, 1061 $[M-H-Glc]^-$, 929 $[M-H-Xyl-Glc]^-$, 767 $[M-H-Xyl-2Glc]^-$, 605 $[M-H-Xyl-3Glc]^-$. IR $\nu_{max}^{film}$ cm$^{-1}$: 3400, 1075, 1050. $^1$H-NMR (400 MHz) $\delta$: 0.95 (H-25), 0.96 (H-30), 1.05 (H-24), 1.05 (H-29), 1.36 (H-26), 1.46 (H-27), 2.73 (1H, dd, $J$=13.0, 12.0 Hz, $H_\alpha$-19), 3.71, 4.21 (each 1H, d, $J$=10.0 Hz, $H_2$-23), 4.90 (1H, d, $J$=8.0 Hz, H-1 of Xyl), 4.94 (1H, d, $J$=5.6 Hz, H-1 of Ara), 5.03 (1H, d, $J$=5.1 Hz, H-1 of Glc-2), 5.14 (1H, d, $J$=8.0 Hz, H-1 of Glc-3), 5.45 (1H, d, $J$=8.1 Hz, H-1 of Glc-1). For $^{13}$C-NMR data, see Table I.

Anagalloside C (**9**): mp 245—246 °C (MeOH), $[\alpha]_D^{20}$ −10.4° ($c$=0.79, MeOH). *Anal.* Calcd for $C_{60}H_{98}O_{28}\cdot 2H_2O$: C, 55.29; H, 7.89. Found; C, 55.50; H, 7.92. FAB-MS $m/z$: 1265 $[M-H]^-$, 1133 $[M-H-Xyl]^-$, 1103 $[M-H-Glc]^-$, 971 $[M-H-Xyl-Glc]^-$, 809 $[M-H-Xyl-2Glc]^-$, 647 $[M-H-Xyl-3Glc]^-$. IR $\nu_{max}^{film}$ cm$^{-1}$: 3400, 1715, 1250, 1070, 1040. $^1$H-NMR (400 MHz) $\delta$: 0.84 (H-25), 1.02 (H-30), 1.08 (H-24), 1.08 (H-29), 1.20 (H-23), 1.30 (H-26), 1.55 (H-27), 1.76 (1H, br d, $J$=11.5 Hz, H-18), 2.07 (Ac), 2.78 (1H, dd, $J$=11.5, 11.5 Hz, $H_\alpha$-21), 2.85 (1H, dd, $J$=12.0, 11.5 Hz, $H_\alpha$-19), 3.18 (1H, dd, $J$=11.0, 5.0 Hz, H-3), 3.70 (2H, s, $H_2$-28), 4.55 (1H, m, H-16), 4.76 (1H, d, $J$=6.0 Hz, H-1 of Ara), 4.82 (1H, d, $J$=7.5 Hz, H-1 of Glc-2), 4.88 (1H, d, $J$=7.5 Hz, H-1 of Xyl), 5.12 (1H, d, $J$=7.3 Hz, H-1 of Glc-3), 5.42 (1H, d, $J$=7.5 Hz, H-1 of Glc-1), 6.03 (1H, dd, $J$=11.5, 5.0 Hz, H-22). For $^{13}$C-NMR data, see Table I.

Desgluconagalloside A (**10**): mp 252—253 °C (MeOH), $[\alpha]_D^{20}$ −6.4° ($c$=1.16, MeOH). *Anal.* Calcd for $C_{54}H_{88}O_{24}\cdot 2H_2O$: C, 56.04; H, 8.01. Found; C, 56.25; H, 8.56. FAB-MS $m/z$: 1119 $[M-H]^-$, 987 $[M-H-Xyl]^-$, 957 $[M-H-Glc]^-$, 825 $[M-H-Xyl-Glc]^-$, 663 $[M-H-Xyl-2Glc]^-$. IR $\nu_{max}^{film}$ cm$^{-1}$: 3400, 1715, 1250, 1070, 1040. $^1$H-NMR $\delta$: 0.86 (H-25), 1.10 (H-24), 1.10 (H-29), 1.15 (H-30), 1.22 (H-23), 1.36 (H-26), 1.61 (H-27), 1.99 (Ac), 2.20 (1H, br d, $J$=11.5 Hz, H-18), 2.82 (1H, dd, $J$=11.5, 11.5 Hz, $H_\alpha$-21), 2.88 (1H, dd, $J$=12.5, 11.5 Hz, $H_\alpha$-19), 3.17 (1H, dd, $J$=11.5, 4.5 Hz, H-3), 4.80 (1H, d, $J$=5.5 Hz, H-1 of Ara), 4.91 (1H, d, $J$=6.1 Hz, H-1 of Xyl), 5.00 (1H, d, $J$=7.8 Hz, H-1 of Glc-2), 5.08 (1H, m, H-16), 5.26 (1H, s, H-28), 5.50 (1H, d, $J$=7.6 Hz, H-1 of Glc-1), 6.06 (1H, dd, $J$=11.5, 5.7 Hz, H-22). For $^{13}$C-NMR data, see Table I.

Desgluconagalloside B (**11**): mp 243—245 °C (MeOH), $[\alpha]_D^{20}$ −0.6° ($c$=2.5, MeOH). *Anal.* Calcd for $C_{52}H_{86}O_{22}\cdot H_2O$: C, 57.76; H, 8.20. Found: C, 57.50; H, 8.35. FAB-MS $m/z$: 1061 $[M-H]^-$, 929 $[M-H-Xyl]^-$, 899 $[M-H-Glc]^-$, 767 $[M-H-Xyl-Glc]^-$, 605 $[M-H-Xyl-2Glc]^-$. IR $\nu_{max}^{film}$ cm$^{-1}$: 3400, 1080, 1045. $^1$H-NMR (600 MHz) $\delta$: 0.95 (H-25), 0.96 (H-30), 1.05 (H-29), 1.06 (H-24), 1.36 (H-26), 1.47 (H-27), 2.73 (1H, dd, $J$=13.0, 12.0 Hz, $H_\alpha$-19), 3.70, 4.22 (2H, d, $J$=10.5 Hz, $H_2$-23), 4.95 (1H, d, $J$=6.6 Hz, H-1 of Xyl), 4.99 (1H, d, $J$=6.0 Hz, H-1 of Ara), 5.03 (1H, d, $J$=6.0 Hz, H-1 of Glc-2), 5.49 (1H, d, $J$=8.0 Hz, H-1 of Glc-1). For $^{13}$C-NMR data, see Table I.

**Acid Hydrolysis of Anagallosaponin I (1)** A solution of **1** (3 mg) in 5% $H_2SO_4$ in 5% EtOH was heated at 100 °C for 3 h. The reaction mixture was extracted with ether. The aqueous layer was neutralized with Amberlite IR-45 and evaporated *in vacuo* to dryness. The sugar was determined by using RI detection (Waters 410) and chiral detection (Shodex OR-1) in HPLC (Shodex RSpak DC-613, 75% $CH_3CN$, 1 ml/min, 70 °C) in comparison with authentic sugars (10 mM each of L-Ara, D-Glc and D-Xyl). The sugar part gave three peaks showing positive optical rotation at 5.75 min (D-Xyl, 5.73 min), 6.20 min (L-Ara, 6.18 min) and 7.38 min (D-Glc, 7.36 min).

**Acid Hydrolysis of Anagallosaponins II (2)—V (5)** Acid hydrolysis of **2**—**5** (each 3 mg) was carried out in the same way as described for **1** to give L-Ara, D-Glc and D-Xyl.

**Acid Hydrolysis of Methylanagallosaponin I (6)** Acid hydrolysis of **6**

(3 mg) was carried out in the same way as described for **1** to give L-Ara, D-Glc and D-Xyl.

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