# Studies on the Constituents of *Gueldenstaedtia multiflora*

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**From the whole plants and the roots of *Gueldenstaedtia multiflora*, which has been used in traditional Chinese medicine, five new oleanane glycosides and one lupane glycoside were isolated together with eight known oleanane glycosides and a medicarpin derivative. These structures were determined based on MS and 2D-NMR spectra.**

**Key words** *Gueldenstaedtia multiflora*; oleanane glycoside; lupane glycoside

In North China and Mongolia, *Gueldenstaedtia multiflora* BGE. (Leguminosae) is used as an internal or external antiphlogistic, analgesics, and antiicterus agent. Only one reference[1] describing the isolation of soyasapogenols B and E, and flavonoids from *G. multiflora* was found. Therefore, since details are required for our systematic search for constituents of leguminous plants to discover new compounds,[2] we have started to isolate the constituents in this plant and obtained 15 compounds (GM-1—GM-15) including six new triterpene glycosides from the whole plants and roots.

## Results and Discussion

The MeOH extract of the whole plants of *G. mulutiflora* (1.27 kg) was separated using Diaion HP-20 to give fr. 1 (60% MeOH eluate) and 2 (80% MeOH eluate). The 60% eluate was subjected to HPLC (ODS) to afford GM-11. The 80% MeOH was chromatographed on a Sephadex LH 20 column with 80% MeOH to provide the total isoflavonoid fraction and total saponin fraction, the latter of which was then separated by using MCI gel (60% MeOH–80% MeOH), ODS, and silica gel chromatography to give GM-1—GM-10. The MeOH extract (111.35 g) of the roots of this plant (1.5 kg) was passed through Diaion HP-20 (eluted first with water and next MeOH). A part (10 g) of the MeOH eluate (43.35 g) was subjected to MCI gel chromatography (eluted successively with 40% MeOH–50% MeOH–60% MeOH–70% MeOH–80% MeOH). The 60% MeOH eluate was further separated with ODS, silica gel and Sephadex LH-20 chromatography to afford GM-3, GM-12, GM-13, and GM-14. The 70% MeOH eluate gave GM-1 and GM-3 upon ODS separation. From the 80% MeOH eluate, GM-1 and GM-15 were obtained by using silica gel separation. GM-1, GM-2, GM-3, GM-4, GM-6, GM-7, GM-12, GM-13, and GM-15 were identified as soyasaponin I, azukisaponin V, comploside II, kudzusaponin $SB_1$, 22-dehydroazukisaponin V, dehydrosoyasaponin I, medicalpin 3-*O*-$\beta$-D-glucopyranoside, subproside V, and soyasaponin Eg, respectively, by comparison with the various data including the $^{13}$C-NMR spectral data.[2—8]

GM-5 was obtained as an amorphous powder showing $[\alpha]_D$+48.9° (pyridine) and a peak at *m*/*z* 1219 due to $[M-H]^-$ in the negative FAB-MS. The $^1$H-NMR spectrum showed five singlet signals at $\delta$ 0.86, 0.97, 0.98, 1.12, 1.73 (each 3H, s, 5×*tert*-Me), one exomethylene signal at $\delta$ 4.73, 4.86 (each 1H, br s), five sugar-anomeric proton signals at $\delta$ 4.89 (1H, d, *J*=7.3 Hz), 5.14 (1H, d, *J*=5.5 Hz), 5.67 (1H, s), 5.98 (1H, s), and 6.24 (1H, d, *J*=7.3 Hz). The sugar mixture of the acid hydrolysate was derived into the corresponding trimethylsilyl ethers of methyl 2-(polyhydroxyalkyl)-thiazolidine-4*R*-carboxylates, and their absolute configurations were determined using GCL.[9] This method was also adopted for the other glycosides. The $^{13}$C-NMR spectrum exhibited two terminal $\alpha$-L-rhamnopyranosyl moieties at $\delta$ 102.5, 72.1, 72.2, 73.5, 70.3, 18.3, 101.5, 72.3, 73.5, 73.7, 69.8, and 18.3; a 2-*O*-sugar-substituted $\alpha$-L-arabinopyranosyl moiety at $\delta$ 103.7, 76.0, 73.7, 63.5, and 64.5; a 4-*O*-sugar-substituted $\beta$-D-glucopyranosyl moiety at $\delta$ 104.5, 74.9, 76.7, 76.2, 78.6, and 61.2; and a 6-*O*-sugar-substituted $\beta$-D-glucoyranosyl moiety at $\delta$ 95.1, 73.7, 78.2, 70.5, 77.7, and 69.2. When these sugar-originating signals were deducted, the remainder was composed of 30 carbon signals due to triterpene sapogenols at $\delta$ 13.5, 14.9, 16.4, 16.9, 18.1, 19.4, 21.2, 26.1, 26.3, 30.1, 30.8, 32.2, 34.2, 36.8, 36.9, 38.3, 39.2, 41.1, 42.8, 43.5, 47.4, 47.7, 49.8, 50.9, 57.0, 63.9, 81.0, 110.0, 150.9, and 175.2; and five anomeric-carbon signals at $\delta$ 95.1, 101.5, 102.5, 103.7, and 104.5. The HMBC (Fig. 1) between $H_3$-24 at $\delta$ 0.97 and C-23 at $\delta$ 63.9, between $H_3$-30 at $\delta$ 1.73 and C-29 at $\delta$ 110.0, and between H-18 at $\delta$ 1.70 and C-28 at $\delta$ 175.2 led to the structural assignment of 23-hydroxybetulic acid.[10]

Moreover, in the sugar region, the HMBC between the terminal rhamnosyl H-1 at $\delta$ 5.98 and the glucosyl C-4 at $\delta$ 76.4, the glucosyl H-1 at $\delta$ 4.89 between the inner glucosyl C-6 at $\delta$ 69.2, and between the inner glucosyl H-1 at $\delta$ 6.16 and the C-28 of the sapogenol at $\delta$ 175.2, another terminal rhamnosyl H-1 at $\delta$ 5.67 and the arbinosyl C-2 at $\delta$ 76.0, and between the arabinosyl H-1 at $\delta$ 5.14 and the C-3 of the sapogenol at $\delta$ 81.0 were observed. Therefore the structure of GM-5 was represented as 3-*O*-$\alpha$-L-rhamnopyranosyl-(1→2)-$\alpha$-L-arabinopyranosyl 23-hydroxybeturic acid 28-*O*-$\alpha$-L-rhamnopyranosyl-(1→4)-glucopyranosyl-(1→6)-glucopyranosyl ester.

GM-8 was obtained as an amorphous powder showing $[\alpha]_D$ −17.3° (pyridine) and a peak at *m*/*z* 1121 due to $[M+H]^+$ in the positive FAB-MS. The $^1$H-NMR spectrum displayed seven singlet signals at $\delta$ 0.70, 0.90, 1.16, 1.26, 1.29, 1.41, and 1.44 (each 3H, s, 6×*tert*-Me), characteristic tof an oleanane-type triterpene, a methylpentosyl methyl signal at $\delta$ 1.81 (3H, d, *J*=6.1 Hz), and four sugar-anomeric proton sig-

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nals at $\delta$ 5.23 (1H, d, $J$=7.9 Hz), 5.44 (1H, br s), 5.69 (1H, d, $J$=7.3 Hz), and 6.19 (1H, s). Meanwhile, the $^{13}$C-NMR signals indicated the occurrence of one $\beta$-fabatriosyl moiety [$\alpha$-L-rhamnopyranosyl-(1→2)-$\beta$-D-galactopyranosyl-(1→2)-$\beta$-D-glucuronopyranosyl moiety at $\delta$ 102.2, 72.1, 72.3. 74.2, 69.3, 18.8, 101.8, 77.3, 76.3, 70.9, 76.3, 61.5, 105.3, 78.1, 76.8, 73.5, 77.6, 172.4] and one terminal $\beta$-D-glucopyranosyl moiety at $\delta$ 104.8, 76.2, 78.8, 70.1, 78.3, and 62.7. The 30 remaining signals were due to triterpene sapogenols at $\delta$ 15.7, 16.8, 18.5, 22.0, 22.5, 23.0, 24.0, 26.2, 26.3, 26.6, 28.2, 31.2, 33.0, 36.1, 36.4, 38.6, 39.4, 40.1, 41.9, 43.9, 44.5, 47.3, 47.8, 56.0, 63.5, 73.5, 91.0, 91.3, 122.7, and 141.6. This sapogenol moiety was regarded as soyasapogenol A by comparing its $^1$H- and $^{13}$C-NMR spectra. The HMBC between glcA H-1 at $\delta$ 5.23 and C-3 at $\delta$ 91.0, and the chemical shift at C-22 was downshifted to $\delta$ 91.3 in comparison with that of soyasapogenol A. Therefore the structure of GM-8 was represented as 3-*O*-$\alpha$-L-rhamnopyranosyl-(1→2)-$\beta$-D-galactopyranosyl-(1→2)-$\beta$-D-glucurono-pyranosyl soyasapogenol A 22-*O*-$\beta$-D-glucopyranoside.

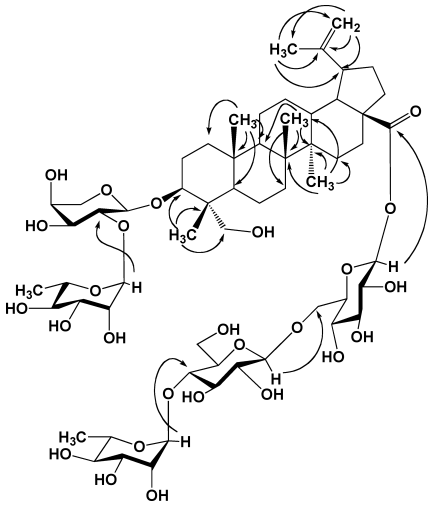


Fig. 1. Key HMBC of GM-5

GM-9 was obtained as an amorphous powder showing $[\alpha]_D$ −13.5° (pyridine) and a peak at $m/z$ 1107 due to $[M+H]^+$ in the positive FAB-MS. The $^1$H-NMR spectrum showed six singlet signals at $\delta$ 0.69, 0.93, 2×1.34, 1.38, and 1.42 (each 3H, s, 6×*tert*-Me); an olefinic proton at $\delta$ 5.32 (1H, br s); methylpentosyl methyl signals at $\delta$ 1.78 (3H, d, $J$=6.1 Hz), four sugar-anomeric proton signals at $\delta$ 4.85 (1H, d, $J$=7.3 Hz), 4.95 (1H, d, $J$=7.1 Hz), 5.62 (1H, d, $J$=7.3 Hz), and 6.12 (1H, s). The $^{13}$C-NMR spectrum displayed 30 signals due to triterpene sapogenols at $\delta$ 15.7, 16.8, 17.3, 18.5, 22.9, 23.0, 24.1, 26.5, 26.5, 26.7, 27.6, 33.0, 36.1, 38.7, 39.2, 40.2, 40.8, 41.3, 41.8, 43.5, 43.9, 47.7, 56.1, 63.4, 69.6, 70.3, 91.3, 92.8, 122.5, and 144.5, which suggested an oleanene skeleton possessing two hydroxymethyl groups and three secondary hydroxyl groups, reminiscent of kudzusapogenol A.[11,12] A comparative study of its $^1$H- and $^{13}$C-NMR data with those of kudzusaponin A3[11] previously obtained from Puerariae Radix indicated both to be almost identical except for the occurrence of an $\alpha$-L-arabinopyranosyl moiety in GM-9. The arabinopyranosyl anomeric proton signal at $\delta$ 4.85 (1H, d, $J$=7.3 Hz) correlated with the C-22 at $\delta$ 92.8 of the sapogenol in the HMBC spectrum. Therefore this structure could be represented as 3-*O*-$\alpha$-L-rhamnopyranosyl-$\beta$-D-

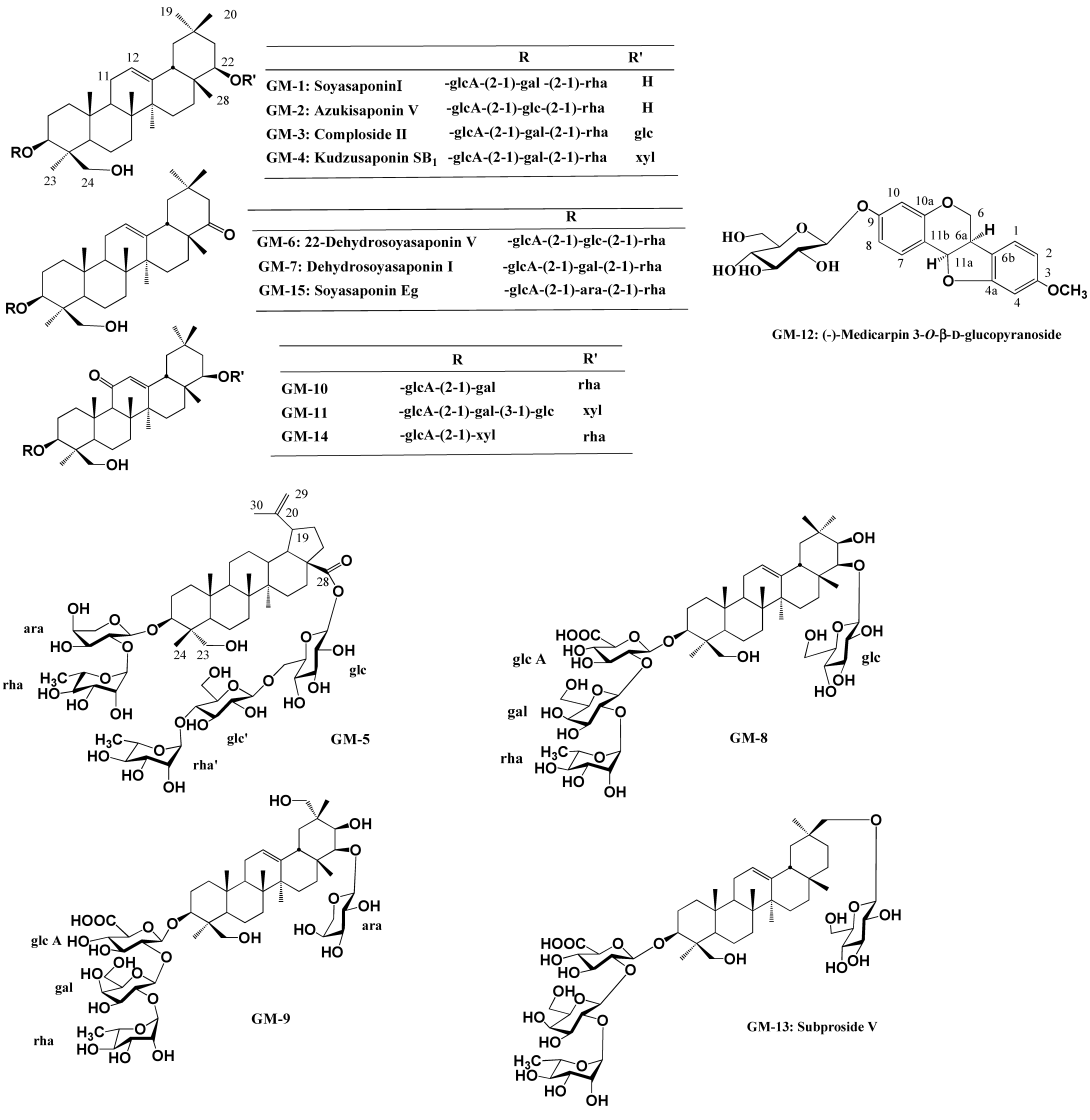
Table 1. $^{13}$C-NMR Data for Sapogenols of GM-1—11 and GM-13—15 (in pyridine-$d_5$)

| | GM-1 | GM-2 | GM-3 | GM-4 | GM-5 | GM-6 | GM-7 | GM-8 | GM-9 | GM-10 | GM-11 | GM-13 | GM-14 | GM-15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C-1 | 38.7 | 38.7 | 38.7 | 38.5 | 39.2 | 38.6 | 38.6 | 38.6 | 38.7 | 39.0 | 39.5 | 38.5 | 39.4 | 38.6 |
| 2 | 26.3 | 26.3 | 26.1 | 25.0 | 26.1 | 26.6 | 26.6 | 26.6 | 26.5 | 26.5 | 26.8 | 26.2 | 26.5 | 26.1 |
| 3 | 91.3 | 91.3 | 91.3 | 90.8 | 81.0 | 91.7 | 91.0 | 91.0 | 91.3 | 90.5 | 90.3 | 90.9 | 90.1 | 90.8 |
| 4 | 43.9 | 43.9 | 43.9 | 43.6 | 43.5 | 43.8 | 43.9 | 43.9 | 43.9 | 43.5 | 44.0 | 43.6 | 43.6 | 43.7 |
| 5 | 56.3 | 56.3 | 56.2 | 55.9 | 47.7 | 56.3 | 56.0 | 56.0 | 56.1 | 55.6 | 56.0 | 55.9 | 55.8 | 56.0 |
| 6 | 18.5 | 18.5 | 18.5 | 18.3 | 18.1 | 18.6 | 18.5 | 18.5 | 18.5 | 17.7 | 18.0 | 18.2 | 17.8 | 18.3 |
| 7 | 33.3 | 33.3 | 33.3 | 33.1 | 34.2 | 33.1 | 33.0 | 33.0 | 33.0 | 32.8 | 33.4 | 33.1 | 32.9 | 33.1 |
| 8 | 39.9 | 39.9 | 39.8 | 39.5 | 42.8 | 39.9 | 39.8 | 40.1 | 40.2 | 43.8 | 43.8 | 39.5 | 43.8 | 39.7 |
| 9 | 47.8 | 47.8 | 47.8 | 47.5 | 50.9 | 48.0 | 47.9 | 47.8 | 47.7 | 61.5 | 61.8 | 47.5 | 62.1 | 47.6 |
| 10 | 36.4 | 36.4 | 36.4 | 36.2 | 36.9 | 36.5 | 36.4 | 36.1 | 36.1 | 36.5 | 37.0 | 36.1 | 36.7 | 36.2 |
| 11 | 24.0 | 24.0 | 24.0 | 23.7 | 21.2 | 24.0 | 24.0 | 24.0 | 24.1 | 199.8 | 199.3 | 23.7 | 199.8 | 23.8 |
| 12 | 122.4 | 122.4 | 122.5 | 122.3 | 26.3 | 124.0 | 123.6 | 122.7 | 122.5 | 128.0 | 128.6 | 122.7 | 128.4 | 122.3 |
| 13 | 144.7 | 144.7 | 144.5 | 144.2 | 38.3 | 141.9 | 141.6 | 141.6 | 144.5 | 169.8 | 169.3 | 144.1 | 169.6 | 144.5 |
| 14 | 42.4 | 42.4 | 42.3 | 42.0 | 41.1 | 42.1 | 42.0 | 41.9 | 41.8 | 44.5 | 45.3 | 42.0 | 45.7 | 42.2 |
| 15 | 26.5 | 26.5 | 26.6 | 26.3 | 30.1 | 25.3 | 25.4 | 26.3 | 26.5 | 26.7 | 26.4 | 26.2 | 26.5 | 26.2 |
| 16 | 28.8 | 28.8 | 28.6 | 28.3 | 32.2 | 27.3 | 27.3 | 28.2 | 27.6 | 27.3 | 27.3 | 28.3 | 27.9 | 28.6 |
| 17 | 37.9 | 37.9 | 37.4 | 37.1 | 57.0 | 47.8 | 47.7 | 39.4 | 39.2 | 37.0 | 37.9 | 38.5 | 37.3 | 47.4 |
| 18 | 45.5 | 45.5 | 45.9 | 45.6 | 49.8 | 47.7 | 47.6 | 44.5 | 43.5 | 45.2 | 45.3 | 45.3 | 45.4 | 47.6 |
| 19 | 46.8 | 46.8 | 46.6 | 46.3 | 47.4 | 46.8 | 46.6 | 47.3 | 40.8 | 46.7 | 45.1 | 42.0 | 45.5 | 46.6 |
| 20 | 30.8 | 30.8 | 30.5 | 30.2 | 150.9 | 34.1 | 34.0 | 36.4 | 41.3 | 30.2 | 30.7 | 36.1 | 36.5 | 33.9 |
| 21 | 42.0 | 42.0 | 37.5 | 36.2 | 30.8 | 51.0 | 50.8 | 73.5 | 69.6 | 35.1 | 37.3 | 38.5 | 34.8 | 50.7 |
| 22 | 75.6 | 75.6 | 82.7 | 82.4 | 36.8 | 215.5 | 214.9 | 91.3 | 92.8 | 78.7 | 81.4 | 75.7 | 78.9 | 216.5 |
| 23 | 22.9 | 22.9 | 22.9 | 22.6 | 63.9 | 22.9 | 23.0 | 23.0 | 23.0 | 22.3 | 22.8 | 22.7 | 22.6 | 22.7 |
| 24 | 63.3 | 63.3 | 63.4 | 63.1 | 13.5 | 63.5 | 63.5 | 63.5 | 63.4 | 63.0 | 63.3 | 63.2 | 63.2 | 63.2 |
| 25 | 15.7 | 15.7 | 15.8 | 15.5 | 16.9 | 15.6 | 15.8 | 15.7 | 15.7 | 16.4 | 16.8 | 15.6 | 16.6 | 15.6 |
| 26 | 17.0 | 17.0 | 17.0 | 16.7 | 16.4 | 16.8 | 15.8 | 16.8 | 16.8 | 18.3 | 18.7 | 16.7 | 18.5 | 16.8 |
| 27 | 25.5 | 25.5 | 25.3 | 25.1 | 14.9 | 25.3 | 25.3 | 26.2 | 26.7 | 23.0 | 22.9 | 26.2 | 22.6 | 25.3 |
| 28 | 28.7 | 28.7 | 28.7 | 28.4 | 175.2 | 21.0 | 20.9 | 22.5 | 22.9 | 21.7 | 21.7 | 20.8 | 21.1 | 20.7 |
| 29 | 32.9 | 32.9 | 32.4 | 32.1 | 110.0 | 31.9 | 31.8 | 22.0 | 70.3 | 32.5 | 32.4 | 28.3 | 33.0 | 31.6 |
| 30 | 20.9 | 20.9 | 21.0 | 20.8 | 19.4 | 25.3 | 25.4 | 31.2 | 17.3 | 27.0 | 28.3 | 77.7 | 28.7 | 25.1 |

galactopyranosyl-(1→2)-$\beta$-D-glucuronopyranosyl kudzusapogenol A 22-*O*-$\alpha$-L-arabinopyranoside.

GM-10 was isolated as an amorphous powder showing $[\alpha]_D$+4.5° (pyridine) and a peak at *m*/*z* 955 due to $[M-H]^-$ in the negative FAB-MS. The $^1$H-NMR spectrum showed seven singlet signals at $\delta$ 0.86, 0.96, 0.97, 1.09, 1.12, 1.39, and 1.41 (each 3H, d, s, 7×*tert*-Me), one methylpentosyl methyl signal at $\delta$ 1.70 (3H, d, $J$=6.1 Hz); three sugar-anometic proton signals at $\delta$ 4.91 (1H, d, $J$=7.9 Hz), 5.34 (1H, s), and 5.51 (1H, d, $J$=7.9 Hz); and one olefinic proton at $\delta$ 5.72 (1H, s). On the other hand, the $^{13}$C-NMR spectrum exhibited 30 signals due to triterpene sapogenols at $\delta$ 16.4, 17.7, 18.3, 21.7, 22.3, 23.0, 26.5, 26.7, 27.0, 27.3, 30.2, 32.5, 32.8, 35.1, 36.5, 37.0, 39.0, 43.5, 43.8, 44.5, 45.2, 46.7, 55.6, 61.5, 63.0, 78.7, 90.5, 128.0, 169.8, and 199.8. The above olefinic proton correlated with a carbonyl carbon at $\delta$ 199.8, a quaternary $sp^2$ carbon at $\delta$ 169.8, a quaternary carbon at $\delta$ 44.5, and a methine carbon at $\delta$ 36.5. Taking this HMBC into consideration, it was revealed that the location of this olefinic proton was restricted to C-12, the carbonyl group located at C-11, and the double bond lied between C-12 and C-13 on the oleanane slkeleton. Regarding to the sugar moieties, three anomeric-carbon signals were observed at $\delta$ 97.6, 104.0, and 104.3, and the terminal galactosyl anomeric proton at $\delta$ 5.51 correlated with the C-2 of the inner glucuronic acid at $\delta$ 80.7, the glucuronosyl anomeric proton at $\delta$ 4.91 correlted with the C-3 of the sapogenol at $\delta$ 90.5, and the terminal rhamnosyl anomeric proton at $\delta$ 5.34 correlated with the C-22 of the sapogenol at $\delta$ 78.7 in the HMBC. The HMBC also revealed that C-22 was hydroxylated, and therefore this sapogenol was characterized as complogenin,[8] which is a characteristic sapogenol similar to glycyrrhetinic acid because it carries an $\alpha,\beta$-unsaturated carbonyl system on the C-ring. Consequently the structure of GM-10 was characterized as 3-*O*-$\beta$-D-galactopyranosyl-(1→2)-$\beta$-D-glucuronopyranosyl complogenin 22-*O*-$\alpha$-L-rhamnopyranoside.

GM-11 was obtained as an amorphous powder showing $[\alpha]_D$ +13.2° (pyridine) and a peak at *m*/*z* 1105 $[M+H]^+$ in the positive FAB-MS. The $^1$H-NMR spectrum showed seven singlet signals at $\delta$ 0.95, 1.03 1.08, 1.15, 1.17, 1.37, and 1.44; an olefinic proton at $\delta$ 5.69 (1H, s); and four sugar-anomeric proton signals at $\delta$ 4.87 (1H, d, $J$=7.6 Hz), 5.09 (1H, d, $J$=7.7 Hz), 5.22 (1H, d, $J$=7.7 Hz), and 5.55 (1H, d, $J$=7.0 Hz). On the other hand, the $^{13}$C-NMR spectrum exhibited 30 signals due to triterpene sapogenols at $\delta$ 16.8, 18.0, 18.7, 21.7, 22.8, 22.9, 26.4, 27.3, 28.3, 30.7, 32.4, 33.4, 37.0, 32.4, 33.4, 37.0, 37.3, 37.9, 39.5, 43.8, 44.0, 45.1, 45.3, 56.0, 61.8, 63.3, 81.4, 90.3, 128.6, 169.3, and 199.3, which were



identified with those of complogenin. The sugar moieties displayed four anomeric-carbon signals at $\delta$ 102.6, 102.8, 105.0, and 106.5. The HMBC suggested that the terminal xylosyl anomeric proton at $\delta$ 4.87 (1H, d, $J$=7.6 Hz) correlated to the C-22 of the sapogenol at $\delta$ 81.4, the terminal glucosyl anomeric proton signal at $\delta$ 5.55 (1H, d, $J$=7.0 Hz) correlated with the C-2 of the galactosyl moiety at $\delta$ 83.9, and this galactosyl anomeric proton at $\delta$ 5.22 (1H, d, $J$=7.7 Hz) correlated with the C-2 of glucuronosyl moiety at $\delta$ 80.3. Moreover, the glucuronosyl anomeric proton at $\delta$ 5.09 (1H, d, $J$=7.7 Hz) corelated with the C-3 of the sapogenol at $\delta$ 90.3. Therefore this structure could be represented as 3-*O*-$\beta$-D-glucopyranosyl-(1→2)-$\alpha$-D-galactopyranosyl-(1→2)-$\beta$-D-glucuronopyranosyl complogenin 22-*O*-$\beta$-D-xylopyranoside.

GM-14 was obtained as an amorphous powder showing $[\alpha]_D$+21.0° (pyridine) and a peak at *m/z* 925 $[M+H]^-$ in the negative ESI-MS. The $^1$H-NMR spectrum showed seven singlet signals at $\delta$ 0.95, 1.03, 1.09, 1.13, 1.16, 1.35, and 1.37 (each 3H, s, *tert*-Me); a methylpentosyl methyl signal at $\delta$ 1.70 (3H, d, $J$=5.5 Hz); one olefinic proton at $\delta$ 5.76 (1H, s); and three sugar-anomeric signals at $\delta$ 4.82 (1H, d, $J$=7.9 Hz), 5.13 (1H, d, $J$=7.7 Hz), and 5.37 (1H, s). On the other hand, the $^{13}$C-NMR spectrum exhibited 30 signals due to complogenin at $\delta$ 16.6, 17.8, 18.5, 21.1, 22.6, 22.6, 26.5, 26.5, 27.9, 28.7, 32.9, 33.0, 34.8, 36.5, 36.7, 37.3, 39.4, 43.6, 43.8, 45.4, 45.5, 45.7, 55.8, 62.1, 63.2, 78.9, 90.1, 128.4, 169.6, and 199.8, and three anomeric-carbon signals at $\delta$ 98.0, 104.6, and 104.8. The $^{13}$C-NMR data also suggested the presence of one terminal rhamnopyranosyl and one terminal xylopyranosyl moiety. The rhamnosyl anomeric proton at $\delta$ 5.37 (1H, s) correlated to the C-22 of the sapogenol at $\delta$ 78.9 in the HMBC. The terminal xylosyl anomeric proton signal at $\delta$ 4.82 (1H, d, $J$=7.9 Hz) correlated with the C-2 of the glucuronosyl moiety at $\delta$ 78.4, moreover, this glucuronosyl anomeric proton at $\delta$ 5.13 (1H, d, $J$=7.7 Hz) correlated with the C-3 of the sapogenol moiety at $\delta$ 90.1. Therefore this structure was characterized as 3-*O*-$\beta$-D-xylopyranosyl-(1→2)-$\beta$-D-glucuronopyranosyl complogenin 22-*O*-$\alpha$-L-rhamnopyranoside.

Here, we isolated one lupane-type triterpene glycoside and 13 oleanane-type triterpene glycosides from the whole plants and the roots of *G. multiflora*, among which the six triterpene glycosides GM-5, GM-8, GM-9, GM-10, GM-11, and GM-14 are regarded as new. The glycosides GM-10, GM-11, and GM-14 are rare naturally occurring triterpene glycosides of complogenin. These oleanane glycosides are expected to exhibit antiinflammatory activity.

## Experimental

The optical rotations were measured with a JASCO DIP-1000 ($l$=0.5) automatic digital polarimeter. $^1$H- and $^{13}$C-NMR spectra were recorded on JEOL-$\alpha$-500 and JMX-GX 400 NMR spectrometers, and chemical shifts are given on a $\delta$ (ppm) scale with tetramethylsilane as an internal standard. The FAB-MS were measured with a JEOL JMS-DX303HF spectrometer and recorded in a glycerol matrix containing NaI. HR FAB-MS were measured with a JEOL JMS T-100LP spectrometer. TLC was performed on silica gel plates (Kieselgel 60 F254, Merck) and RP $C_{18}$ silica gel plates (Merck). The spots on TLC were visualized under UV light (254/366 nm) and spraying with 10% $H_2SO_4$, followed by heating. HPLC was carried out using a pL-6200 ump (Hitachi), L-4000 UV detector (Hitachi), and L-5020 column heater: L-5020 (Hitachi). The HPLC conditions for the preparative experiment were as follows: column, Mightysil RP-18 GP (5 mm, 250—4.6 mm); and solvent, 30% $CH_3CN$. Column chromatography was carried out on Diaion HP-20, MCI gel CHP 20P (Mitsubishi Chemical Industries), Sephadex LH-20 (Pharmacia), Bondapak ODS (Waster), and silica gel 60 (spherical, 40—100 mm, and 230—400 mesh ASTM, Kanto Chemical Co., Inc.).

**Extraction and Isolation** The MeOH extract (142.8 g) of the whole plants (1.27 kg) of *G. multiflora* was separated on a Diaion HP-20 column to give fra. 1 (60% MeOH eluate) and 2 (80% MeOH eluate). The 60% eluate was subjected to HPLC (ODS) to afford GM-11 (17 mg). The 80% MeOH eluate was chromatographed on a Sephadex LH 20 column with 80% MeOH to provide the total isoflavonoid fraction and total saponin fraction, the latter of which was then separated by using MCI gel (60% MeOH–80% MeOH) ODS, and silica gel to give GM-1 (2 mg), GM-2 (5 mg), GM-3 (20 mg), GM-4 (26 mg), GM-5 (108 mg), GM-6 (9 mg), GM-7 (5 mg), GM-8 (17 mg), GM-9 (7 mg), and GM-10 (5 mg). On the other hand, the MeOH extract (111.35 g) of the roots of this plant (1.5 kg) was passed through a Diaion HP-20 column (elutted first with water and next MeOH). A part (10 g) of the MeOH eluate (43.35 g) was subjected to MCI gel (eluted successively with 40% MeOH–50% MeOH–60% MeOH–70% MeOH–80% MeOH). The 60% MeOH eluate was further separated with ODS, silica gel, and Sephadex LH-20 chromatography to afford GM-3 (3.8 mg), GM-12 (13.8 mg), GM-13 (64.4 mg), and GM-14 (9.5 mg). The 70% MeOH eluate gave GM-1 (6 mg) and GM-3 (18.7 mg) upon ODS separation. From the 80% MeOH eluate, GM-1 (44.4 mg) and GM-15 (69.4 mg) were obtained after silica gel separation.

**GM-1 (Soyasaponin I)** An amorphous powder, $[\alpha]_D$ −16.7° ($c$=0.1 MeOH). Negative FAB-MS: *m/z* 941 $[M-H]^-$, 795 $[M-H-rha]^-$, 633 $[M-H-rha-gal]^-$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.71, 0.95, 1.00, 1.22, 2× 1.28, 1.45 (each 3H, s, *tert*-Me), 1.79 (3H, d, $J$=5.5 Hz, rha $H_3$-6), 4.96 (1H, d, $J$=6.7 Hz, glc A H-1), 5.31 (1H, s, H-12), 5.71 (1H, d, $J$=7.3 Hz, gal H-1), 6.35 (1H, s, rha H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc A part, 105.2 (C-1), 78.1 (C-2), 76.3 (C-3), 73.5 (C-4), 77.7 (C-5), 172.8 (C-6), gal part; 101.7 (C-1), 76.8 (C-2), 76.7 (C-3), 70.9 (C-4), 77.5 (C-5), 61.5 (C-6), rha part; 102.1 (C-1), 72.1 (C-2), 72.3 (C-3), 74.1 (C-4), 69.2 (C-5), 18.7 (C-6).

**GM-2 (Azukisaponin V)** An amorphous powder, $[\alpha]_D$−17.2° ($c$=0.1, MeOH). Negative FAB-MS: *m/z* 941 $[M+H]^-$, 794 $[M-H-rha]^-$, 633 $[M-H-rha-glc]^-$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.87, 089, 0.99, 1.07, 1.12, 1.17, 1.30 (each 3H, s, *tert*-Me), 1.70 (3H, d, $J$=6.1 Hz, rha $H_3$-6), 4.56 (1H, d, $J$=7.3 Hz, glc H-1), 4.98 (1H, d, $J$=7.9, glc A H-1), 5.12 (1H, s, H-12), 6.21 (1H, s, rha H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc part; 101.8 (C-1), 78.7 (C-2), 76.1 (C-3), 69.9 (C-4), 78.1 (C-5), 61.3 (C-6), rha part; 101.9 (C-1), 72.1 (C-2), 72.3 (C-3), 74.0 (C-4), 69.3 (C-5), 18.7 (C-6).

**GM-3 (Comploside II)** An amorphous powder, $[\alpha]_D$ −6.2° ($c$=0.1 MeOH). Negative FAB-MS: *m/z* 1126 $[M+Na-H]^-$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.70, 0.90, 0.99, 1.17, 1.22, 1.24, 1.44 (each 3H, s, *tert*-Me), 1.08 (3H, d, $J$=6.1 Hz, rha $H_3$-6), 4.85 (1H, d, $J$=7.9 Hz, glc A H-1), 5.25 (1H, s, H-12), 5.74 (1H, d, $J$=7.9 Hz, gal H-1), 6.15 (1H, s, rha H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc A part, 105.3 (C-1), 78.1 (C-2), 76.3 (C-3), 73.5 (C-4), 77.7 (C-5), 172.8 (C-6); gal part, 101.7 (C-1), 76.8 (C-2), 76.7 (C-3), 70.9 (C-4), 77.5 (C-5), 61.5 (C-6); rha part, 102.1 (C-1), 72.1 (C-2), 72.3 (C-3), 74.1 (C-4), 69.2 (C-5), 18.7 (C-6); Glc part, 102.3 (C-1), 75.0 (C-2), 78.3 (C-3), 71.8 (C-3), 71.8 (C-4), 78.3 (C-5), 62.8 (C-6).

**GM-4 (Kuszusaponin SB$_1$)** An amorphous powder, $[\alpha]_D$ −4.0° ($c$=0.1 MeOH). Negative FAB-MS: *m/z* 1096 $[M+Na-H]^-$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.73, 0.90, 0.99, 1.15, 1.20, 1.23, 1.44 (each 3H, s, *tert*-Me), 1.77 (3H, d, $J$=6.1 Hz, rha $H_3$-6), 4.85 (1H, d, $J$=7.9 Hz, glc A H-1), 4.99 (1H, d, $J$=7.3 Hz, xyl H-1), 5.25 (1H, s, H-12), 5.38 (1H, d, $J$=7.3 Hz, gal H-1), 6.15 (1H, s, rha H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc A part, 105.3 (C-1), 78.0 (C-2), 76.3 (C-3), 73.5 (C-4), 77.7 (C-5), 172.8 (C-6); gal part, 101.7 (C-1), 76.8 (C-2), 76.7 (C-3), 70.9 (C-4), 77.5 (C-5), 61.5 (C-6); rha part, 102.1 (C-1), 72.1 (C-2), 72.3 (C-3), 74.0 (C-4), 69.2 (C-5), 18.7 (C-6); xyl part, 101.8 (C-1), 75.1 (C-2), 78.1 (C-3), 70.0 (C-4), 66.5 (C-5).

**GM-5 (23-Hydroxybeturic acid)** An amorphous powder, $[\alpha]_D$+48.9° ($c$=0.1 MeOH). Negative FAB-MS: *m/z* 1219 $[M+H]^-$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.86, 0.97, 0.98, 1.12, 1.73 (each 3H, s, *tert*-Me), 1.63 (6H, d, $J$=6.1 Hz, rha $H_3$-6×2), 4.73, 4.86 (each 1H, br s, $H_2$-29), 4.89 (1H, d, $J$=7.3 Hz, glc′ H-1), 5.14 (1H, d, $J$=5.5 Hz, ara H-1), 5.67 (1H, s, rha H-1), 5.98 (1H, s, rha′ H-1), 6.15 (1H, d, $J$=7.3 Hz, glc H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: rha part, 102.5 (C-1), 72.1 (C-2), 72.2 (C-3), 73.5 (C-4), 70.3 (C-5), 18.3 (C-6); rha′ part, 101.5 (C-1), 72.3 (C-2), 73.5 (C-3), 73.7 (C-4), 69.8 (C-5), 18.3 (C-6); glc part, 95.1 (C-1), 73.7 (C-2), 78.2 (C-3), 70.5 (C-4), 77.7 (C-5), 69.2 (C-6); glc′ part, 104.5 (C-1), 74.9 (C-2), 76.7 (C-3), 76.2 (C-4), 78.2 (C-5), 61.2 (C-6); ara part, 103.7 (C-1), 76.0 (C-2), 73.7 (C-3), 68.5 (C-4), 64.5 (C-5). A small amount of GM-5 was hydrolyzed with 2 N HCl in a hot bath (80 °C) for 1.5 h. Its filtrate was passed through Amberlite IRA400 and the eluate was concentrated to dryness *in vacuo* to give a residue, which was dissolved in dry pyridine, and then L-cysteine methyl

ester hydrochloride was added to the solution. The reaction mixture was heated at 60 °C for 2 h and concentrated to dryness using $N_2$. To the residue was added trimethylsilylimidazole, and the mixture was heated at 60 °C for 1 h. The reaction mixture was concentrated to dryness, and the residue was extracted with a mixture of *n*-hexane and $H_2O$, and the organic layer was analyzed using GLC under the following conditions: column, OV-17 (0.32 mm×30 m); detector, FID; column temperature, 230 °C; injector temperature, 270 °C; carrier gas, He (2.2 kg/cm$^2$). Each peak was observed at $t_R$ (min): 17′16″ (D-glc), 16′54″ (D-gal), 11′71″ (L-rha), 9′82″ (D-xyl), 8′32″ (L-ara). Other glycosides of GM-8—11 and GM-14 were also analogously examined.

**GM-6 (22-Dehydroazukisaponin V)** An amorphous powder, $[\alpha]_D$ −48.3° (*c*=0.5 pyridine). Positive FAB-MS: *m/z* 941 $[M+H]^+$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.69, 0.85, 0.86, 0.96, 1.17, 1.29, 1.48 (each 3H, s, *tert*-Me), 1.79 (3H, d, *J*=6.1 Hz, rha $H_3$-6), 5.00 (1H, d, *J*=7.9 Hz, glc A H-1), 5.24 (1H, br s, H-12), 6.41 (1H, s, rha H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc A part, 105.2 (C-1), 78.3 (C-2), 77.3 (C-3), 73.7 (C-4), 77.9 (C-5), 172.5 (C-6); rha part, 102.0 (C-1), 72.3 (C-2), 72.8 (C-3), 74.4 (C-4), 69.5 (C-5), 19.0 (C-6).

**GM-7 (Dehydrosoyasaponin I)** An amorphous powder, $[\alpha]_D$ −98.3° (*c*=0.5 pyridine). Positive FAB-MS: *m/z* 941 $[M+H]^+$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.70, 0.86, 0.87, 0.97, 1.17, 1.31, 1.45 (each 3H, s, *tert*-Me), 1.79 (3H, d, *J*=6.1 Hz, rha $H_3$-6), 4.62 (1H, d, *J*=7.3 Hz, glc A H-1), 5.25 (1H, br s, H-12), 5.80 (1H, d, *J*=6.7 Hz, gal H-1), 6.30 (1H, s, rha H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc A part, 105.2 (C-1), 78.3 (C-2), 76.4 (C-3), 73.6 (C-4), 77.6 (C-5), 173.4 (C-6); gal part, 101.6 (C-1), 77.6 (C-2), 76.4 (C-3), 71.1 (C-4), 76.8 (C-5), 61.7 (C-6); rha part, 102.1 (C-1), 72.2 (C-2), 72.6 (C-3), 74.3 (C-4), 69.3 (C-5), 18.9 (C-6).

**GM-8** An amorphous powder, $[\alpha]_D$−17.3° (*c*=0.5 pyridine). Positive FAB-MS: *m/z* 1121 $[M+H]^+$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.70, 0.90, 1.16, 1.26, 1.29, 1.41, 1.44 (each 3H, s, *tert*-Me), 1.81 (3H, d, *J*=6.1 Hz, rha $H_3$-6), 5.23 (1H, d, *J*=7.9 Hz, glc A H-1), 5.44 (1H, br s, H-12), 5.69 (1H, d, *J*=7.3 Hz, gal H-1), 6.19 (1H, s, rha H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc A part, 105.3 (C-1), 78.1 (C-2), 76.8 (C-3), 73.5 (C-4), 77.6 (C-5), 172.4 (C-6); gal part, 101.8 (C-1), 77.3 (C-2), 76.3 (C-3), 70.9 (C-4), 76.3 (C-5), 61.5 (C-6); rha part, 102.2 (C-1), 72.1 (C-2), 72.3 (C-3), 74.2 (C-4), 69.3 (C-5), 18.8 (C-6); glc part, 104.8 (C-1), 76.2 (C-2), 78.8 (C-3), 70.1 (C-4), 78.3 (C-5), 62.7 (C-6).

**GM-9** An amorphous powder, $[\alpha]_D$−13.5° (*c*=0.5 pyridine). Positive FAB-MS: *m/z* 1107 $[M+H]^+$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.69, 0.93, 2×1.34, 1.38, 1.42 (each 3H, s, *tert*-Me), 1.78 (3H, d, *J*=6.1 Hz, rha $H_3$-6), 4.85 (1H, d, *J*=7.3 Hz, ara H-1), 4.95 (1H, d, *J*=7.1 Hz, glc A H-1), 5.32 (1H, br s, H-12), 5.62 (1H, d, *J*=7.3 Hz, gal H-1), 6.12 (1H, s, rha H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc A part, 105.2 (C-1), 78.3 (C-2), 76.3 (C-3), 73.6 (C-4), 77.5 (C-5), 172.5 (C-6); gal part, 101.9 (C-1), 77.5 (C-2), 76.8 (C-3), 70.9 (C-4), 76.8 (C-5), 61.6 (C-6); rha part, 102.0 (C-1), 72.1 (C-2), 72.3 (C-3), 74.1 (C-4), 69.3 (C-5), 18.8 (C-6); ara part, 108.4 (C-1), 73.6 (C-2), 75.5 (C-3), 69.0 (C-4), 69.6 (C-5).

**GM-10** An amorphous powder, $[\alpha]_D$ +4.5° (*c*=0.5 pyridine). Negative FAB-MS: *m/z* 955 $[M+H]^-$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.86, 0.96, 0.97, 1.09, 1.12, 1.39, 1.41 (each 3H, s, *tert*-Me), 1.70 (3H, d, *J*=6.1 Hz, rha $H_3$-6), 4.91 (1H, d, *J*=7.9Hz, glc A H-1), 5.34 (1H, s, rha H-1), 5.51 (1H, d, *J*=7.9 Hz, gal H-1), 5.72 (1H, s, H-12). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc A part, 104.3 (C-1), 80.7 (C-2), 75.3 (C-3), 73.3 (C-4), 77.9 (C-5), 172.5 (C-6); gal part, 104.0 (C-1), 73.3 (C-2), 75.3 (C-3), 69.7 (C-4), 77.7 (C-5), 61.4 (C-6); rha part, 97.6 (C-1), 72.0 (C-2), 72.3 (C-3), 73.4 (C-4), 70.0 (C-5), 18.1 (C-6).

**GM-11** An amorphous powder, $[\alpha]_D$ +13.2° (*c*=0.5 pyridine). Positive FAB-MS: *m/z* 1105 $[M+H]^+$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.95, 1.03, 1.08, 1.15, 1.17, 1.37, 1.44 (each 3H, d, *tert*-Me), 4.87 (1H, d, *J*=7.6 Hz, xyl H-1), 5.09 (1H, d, *J*=7.7 Hz, glc A H-1), 5.22 (1H, d, *J*=7.7 Hz, gal H-1), 5.55 (1H, d, *J*=7.0 Hz, glc H-1), 5,69 (1H, s, H-12). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: sapogenol part, 39.5 (C-1), 26.8 (C-2), 90.3 (C-3), 44.0 (C-4), 56.0 (C-5), 18.0 (C-6), 33.4 (C-7), 43.8 (C-8), 61.8 (C-9), 37.0 (C-10), 199.3 (C-11), 128.6 (C-12), 169.3 (C-13), 45.3 (C-14), 26.4 (C-15), 27.3 (C-16), 37.9 (C-17), 45.3 (C-18), 45.1 (C-19), 30.7 (C-20), 37.3 (C-21), 81.4 (C-22), 22.8 (C-23), 63.3 (C-24), 16.8 (C-25), 18.7 (C-26), 22.9 (C-27), 21.7 (C-28), 32.4 (C-29), 28.3 (C-30); glc A part, 105.0 (C-1), 80.3 (C-2), 77.6 (C-3), 72.4 (C-4), 77.8 (C-5), 172.3 (C-6); gal part, 102.8 (C-1), 83.9 (C-2), 74.4 (C-3), 69.4 (C-4), 76.5 (C-5), 63.0 (C-6); glc part, 106.5 (C-1), 76.5 (C-2), 78.4 (C-3), 71.7 (C-4), 78.9 (C-5), 63.2 (C-6); xyl part, 102.6, 75.3, 77.8, 72.1, 67.0.

**GM-12 (Medicarpin 3-*O*-$\beta$-D-Glucopyranoside)** Colorless needles, $[\alpha]_D$ −73.8° (*c*=0.05 pyridine). Negative ESI-MS: *m/z* 431.13 $[M-H]^-$ and HR negative ESI-MS: *m/z* 431.1342 $[M+H]^-$ (Calcd for $C_{22}H_{24}O_4$: 431.1344). $^1$H-NMR (pyridine-$d_5$) $\delta$: 3.74 (1H, m, H-6a), 3.75 (1H, d, *J*=7.3 Hz, $H_3$-6), 3.75 (3H, s, –$OCH_3$), 4.37 (1H, d, *J*=4.2 Hz, H-11a), 6.62 (1H, dd, *J*=2.4 Hz, H-10), 6.68 (1H, s, H-8), 7.03 (1H, s, H-4), 7.12 (1H, dd, *J*=2.4 Hz, H-2), 7.33 (1H, d, *J*=8.5 Hz, H-7), 7.55 (1H, d, *J*=8.6 Hz, H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: 132.3 (C-1), 111.0 (C-2), 156.8 (C-3), 105.0 (C-4), 156.8 (C-4a), 66.6 (C-6), 39.7 (C-6a), 119.6 (C-6b), 125.3 (C-7), 97.0 (C-8), 161.3 (C-9), 106.5 (C-10), 160.9 (C-10a), 78.6 (C-11a), 111.0 (C-11b), 55.3 (OMe), 101.6 (glc C-1), 74.3 (glc C-2), 78.2 (glc C-3), 70.7 (glc C-4), 78.2 (glc C-5), 61.7 (glc C-6).

**GM-13 (Subproside V)** An amorphous powder, $[\alpha]_D$ −8.9° (*c*=0.05 pyridine). Negative FAB-MS: *m/z* 1119 $[M+H]^-$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.68, 0.89, 1.00, 1.17, 1.23, 1.24 (each 3H, s, *tert*-Me), 1.60 (3H, d, *J*=6.1 Hz, rha $H_3$-6), 5.24 (1H, s, H-12), 4.87 (1H, d, *J*=7.3 Hz, glc A H-1), 5.70 (1H, d, gal H-1), 6.16 (1H, s, rha H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc A part, 104.8 (C-1), 78.0 (C-2), 77.3 (C-3), 73.7 (C-4), 77.7 (C-5), 175.0 (C-6); gal part, 101.9 (C-1), 77.3 (C-2), 76.1 (C-3), 70.8 (C-4), 76.1 (C-5), 61.4 (C-6); rha part, 102.1 (C-1), 72.0 (C-2), 72.0 (C-3), 73.0 (C-4), 69.0 (C-5), 18.5 (C-6); glc part, 104.8 (C-1), 75.7 (C-2), 77.7 (C-3), 71.5 (C-4), 77.7 (C-5), 62.5 (C-6).

**GM-14** An amorphous powder, $[\alpha]_D$ +21.0° (*c*=0.05 pyridine). Negative ESI-MS: *m/z* 925 $[M+H]^-$, 794 $[M-H-xyl]^-$, 780 $[M-H-rha]^-$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.95, 1.03, 1.09, 1.13, 1.16, 1.35, 1.37 (each 3H, s, *tert*-Me), 1.70 (3H, d, *J*=5.5 Hz, rha $H_3$-6), 4.82 (1H, d, *J*=7.9 Hz, xyl H-1), 5.13 (1H, d, *J*=7.7 Hz, glc A H-1), 5.37 (1H, s, rha H-1), 5.76 (1H, s, H-12). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc A part, 104.8 (C-1), 78.4 (C-2), 75.5 (C-3), 73.3 (C-4), 79.9 (C-5), 172.3 (C-6); rha part, 98.0 (C-1), 72.1 (C-2), 72.3 (C-3), 73.3 (C-4), 69.9 (C-5), 18.7 (C-6); xyl part, 104.6 (C-1), 75.5 (C-2), 77.9 (C-3), 70.7 (C-4), 67.3 (C-5).

**GM-15 (Soyasaponin Eg)** An amorphous powder, $[\alpha]_D$ −4.8° (*c*=0.5 pyridine). Negative ESI-MS: *m/z* 909 $[M+H]^-$. $^1$H-NMR (pyridine-$d_5$) $\delta$: 0.69, 0.89, 0.94, 1.01, 1.23, 1.28, 1.42 (each 3H, s, *tert*-Me), 1.78 (3H, d, *J*=5.5 Hz, rha $H_3$-6), 4.89 (1H, d, *J*=7.9 Hz, glc A H-1), 5.31 (1H, s, H-12), 5.46 (1H, d, *J*=7.3 Hz, ara H-1), 6.13 (1H, s, rha H-1). $^{13}$C-NMR (in pyridine-$d_5$) $\delta$: glc A part, 104.8 (C-1), 77.8 (C-2), 77.1 (C-3), 75.2 (C-4), 77.3 (C-5), 175.3 (C-6); rha part, 101.9 (C-1), 72.2 (C-2), 71.9 (C-3), 73.7 (C-4), 70.0 (C-5), 18.5 (C-6).

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