Two New Acyclic Diterpene Glycosides from Fruits of Habanero, *Capsicum chinense*

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Four acyclic diterpene glycosides were extracted from Habanero, the fruits of *Capsicum chinense* Jacq., which is known as one of the hottest peppers in existence. Two of these glycosides were identified as capsianoside XIII and capsianoside XV. The other two were new ones and were characterized as 3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-glucopyranosyl 17,19-dihydroxy-6*E*,10*E*,14*Z*-(3*S*)-geranyllinalool 17-*O*-*β*-D-glucopyranosyl-(1→4)-*α*-L-rhamnopyranosyl-[*α*-L-rhamnopyranosyl-(1→6)]-*β*-D-glucopyranoside and 3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-glucopyranosyl 6*E*,10*E*,14*Z*-(3*S*)-17-hydroxy-geranyllinalool 17-*O*-[3-*O*-*β*-D-glucopyranosyl-(1→4)-*β*-D-glucopyranosyl 6′*E*,10′*E*,14′*Z*-(3′*S*)-13′*R*,19′-dihydroxy-geranyllinalool-16′-oyl (16′→2)-[*α*-L-rhamnopyranosyl-(1→3)]-*α*-L-rhamnopyranosyl-(1→4)-[*α*-L-rhamnopyranosyl-(1→6)]-*β*-D-glucopyranoside.

Key words Habanero; *Capsicum chinense*; geranyllinalool glycoside

Previously, we had found the occurrence of novel characteristic acyclic diterpene glycosides, which are rarely present in the natural plant kingdom, from a series of *Capsicum* genera as follows: capsianosides I—III, A—D from *C. annuum* L. var. *fasciculatum* (Yatsubusa)[1—3]; capsianosides II, III, C, D from *C. annuum* L. var. *fasciculatum* (Shishitougarashi)[1—3]; capsianosides II, III, VIII—X, XIII, from *C. annuum* L. var. *annuum* (jalapeño)[4]; capsianosides I′, II, III, C—F from *C. annuum* (red hot pepper used in Kimchi, a fermented Chinese cabbage product)[5]; capsianosides II, III, IX, X, XIII, XV, XVI from *C. annuum* L. var. *grossum* (paprika)[4]; and capsianosides I′, II—IV, C—F from *C. annuum* L. *grossum* (pimento).[6] These acyclic diterpene glycosides are major, typical components of *Capsicum* plants. We are now investigating their pharmacological activities in reducing blood pressure and facilitating the combustion of fatty acids. As part of a continuing study, we have examined the acyclic diterpene glycosides in Habanero, the fruits of *Capsicum chinense* Jacq., which is known as one of the hottest peppers in existence.

The fruits of *Capsicum chinense* (768.3 g) were refluxed with MeOH to obtain a residue (42.4 g) after evaporation. The residue was then partitioned between *n*-hexane and water. The aqueous layer (35.1 g) was passed through Diaion HP-20 with 50—100% MeOH to afford the following three fractions: fr. 1 (0.66 g), fr. 2 (1.57 g), and fr. 3 (0.95 g). Fr. 2 was further chromatographed on octadecyl silica (ODS) with 60—90% MeOH to provide 5 fractions, fr. 2-1—fr. 2-5. Fr. 2-2 (205.0 mg) was chromatographed on silica gel with $CHCl_3$, MeOH and water in the ratio 7 : 3 : 0.5 and further subjected to HPLC with 75% MeOH to yield HAB-2 (17.4 mg) and HAB-1 (**1**, 17.8 mg). Fr. 2-4 (262.0 mg) was chromatographed on silica gel with $CHCl_3$, MeOH and water in the ratio 7 : 3 : 0.5→6 : 4 : 0.5 and separated with HPLC by using 70% MeOH to yield HAB-3 (11.1 mg) and HAB-4 (**2**, 18.0 mg).

HAB-2 and HAB-3 were identified in capsianoside XV, which was obtained from *C. annuum* L. var. *grossum* (paprika),[4] and capsianoside XIII, which was isolated from *C. annuum* L. var. *annuum* (jalapeño) and *C. annuum* L. var. *grossum* (paprika),[4] respectively, as shown in Fig. 1.

HAB-1 (**1**), which was obtained as an amorphous powder showing $[\alpha]_D$ −21.2° (MeOH), was found to have the molecular formula $C_{56}H_{94}O_{31}Na$ $[M+Na]^+$ at *m*/*z* 1285.5675 in the positive HR-FAB-MS. The ^{1}H-NMR spectrum showed signals due to two vinyl methyl groups at δ 1.61, 1.76 (each 3H, s); a methyl group at δ 1.37 (3H, s) adjacent to the oxygen function; two pentosyl methyl groups at δ 1.26 (3H, d, J= 5.7 Hz), 1.32 (3H, d, J=6.3 Hz); three olefinic protons at δ 5.13 (1H, m), 5.28 (1H, t, J=7.6 Hz), 5.40 (1H, t, J=6.9 Hz); a terminal vinyl group at δ 5.20 (1H, d, J=10.9 Hz), 5.24 (1H, d, J=17.8 Hz), 5.93 (1H, dd, J=10.9, 17.8 Hz); and two oxygenated methylene groups at δ 4.08 (2H, s), 4.11, 4.32

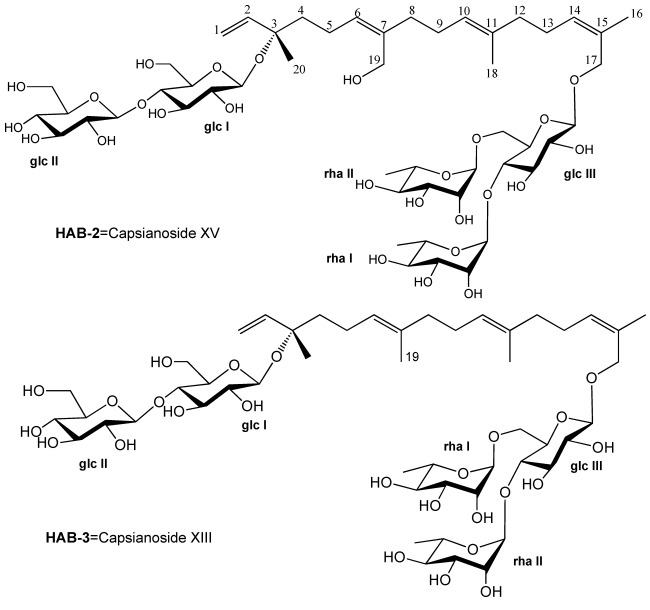

Fig. 1. Structures of HAB-2=Capsianoside XV and HAB-3=Capsianoside XIII

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(each 1H, d, J=11.4 Hz), together with six anomeric protons at δ 4.19 (1H, d, J=8.0 Hz), 4.38 (1H, d, J=8.0 Hz), 4.40 (1H, d, J=8.0 Hz), 4.58 (1H, d, J=8.1 Hz), 4.70 (1H, d, J=1.2 Hz), 4.81 (1H, d, J=1.2 Hz). Acid hydrolysis of **1** gave D-glucose and L-rhamnose. The ^{13}C-NMR spectrum of **1** showed a total of 56 carbon signals composed of two β-D-glucopyranosyl moieties at δ 106.4, 105.4, 76.8, 76.9, 78.8, 78.9, 72.1, 72.2, 78.6×2, 63.5, 62.8; a terminal α-L-rhamnopyranosyl moiety at δ 102.3, 73.0, 73.1, 74.8, 70.6, 19.0; a 4-*O*-[(β-D-glucopyranosyl)-substituted]-β-D-glucopyranosyl moiety at δ 100.1, 75.7, 77.3, 81.6, 78.9, 63.2; a 4-*O*-[β-D-(glucopyranosyl)-substituted]-α-L-rhamnopyranosyl moiety at δ 103.1, 73.0, 73.1, 84.1, 69.9, 18.2; a 4,6-di-*O*-[(α-L-rhamnopyranosyl)-substituted]-β-D-glucopyranoside moiety at δ 102.8, 76.2, 77.4, 79.7, 76.0, 67.6 in the sugar region; three tri-substituted double bonds at δ 126.7, 130.0, 140.2, 136.4, 132.1, 133.2; a mono-substituted double bond at δ 116.6 and 145.2; three methyl groups at δ 17.1, 22.7, 24.3; six methylene groups at δ 43.6, 23.9, 36.7, 28.6, 28.1, 41.7; and a hydroxymethyl group at δ 60.7 in the aglycone region. These ^{1}H and ^{13}C signals of **1** had revealed that the aglycone of HAB-1 could be identical to that of HAB-2 (capsianoside XV)[4] including the stereo-configuration at C-3,[2] that is, 17,19-dihydroxy-6*E*,10*E*,14*Z*-(3*S*)-geranyllinalool. Comparing the ^{13}C signals obtained from **1** with those from HAB-2, it was found that all the signals displayed almost identical chemical shifts, with the following exceptions: the occurrence of a terminal β-D-glucopyranosyl moiety and the difference in the chemical shifts at C-4 on the α-L-rhamnopyranosyl moiety (rha I) from those of the terminal α-L-rhamnopyranosyl moieties (rha I) in HAB-2. The molecular number of the sugar moiety was greater than that of HAB-2 by 162 atomic units, which indicates that one mole of β-D-glucopyranosyl moiety was attached to HAB-2. The anomeric proton at δ 4.58 of the newly found β-D-glucopyranosyl moiety (glc IV) correlated with the carbon signal of C-4 at δ 84.1 on the α-L-rhamnopyranosyl moiety (rha I). Therefore, the structure of **1** was characterized as 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl 17,19-dihydroxy-6*E*,10*E*,14*Z*-(3*S*)-geranyllinalool 17-*O*-β-D-glucopyranosyl-(1→4)-α-L-rhamnopyranosyl-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside, as shown in Fig. 2 and was named capsianoside XVIII.

HAB-4 (**2**), which was obtained as an amorphous powder showing $[\alpha]_D$ −28.1° (MeOH), was found to have the molecular formula $C_{88}H_{144}O_{43}Na$ $[M+Na]^+$ at *m*/*z* 1911.8942 in the positive HR-FAB-MS. Acid hydrolysis of **2** also gave D-glucose and L-rhamnose. The ^{1}H-NMR spectrum showed the signals due to five vinyl methyls at δ 1.59×2, 1.61, 1.76, 1.88 (each 3H, s); two methyls at δ 1.37 (6H, s) adjacent to

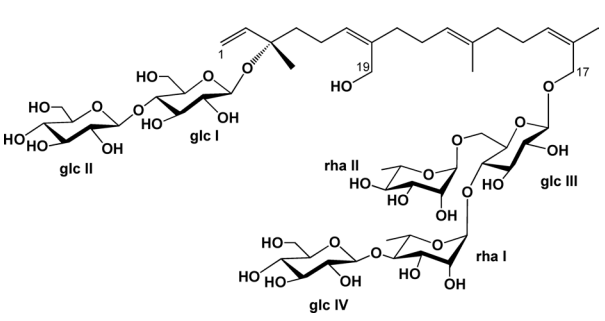

Fig. 2. Structure of HAB-1 (**1**) Capsianoside XVIII

the oxygen functions; two vinyl groups at δ 5.22 (2H, d, J=11.5 Hz), 5.23 (2H, d, J=5.2 Hz); six olefinic protons at δ 5.11 (3H, m), 5.12 (1H, t, J=8.6 Hz), 5.39 (1H, t, J=6.9 Hz), 6.70 (1H, d, J=8.6 Hz); two hydroxymethyls at δ 4.08 (2H, s), 4.11 (1H, d, J=11.5 Hz), 4.33 (1H, d, J=12.0 Hz); and a methine proton at δ 4.53 (1H, m) adjacent to the oxygen function, together with three α-L-rhamnopyranosyl anomeric protons at δ 4.82, 4.91, 4.93 (each 1H, s) and five β-D-glucopyranosyl anomeric protons at δ 4.20 (1H, d, J=8.0 Hz), 4.37 (2H, d, J=7.4 Hz), 4.40 (2H, d, J=8.0 Hz). On the other hand, the ^{13}C-NMR spectrum exhibited the following signals that can be assigned to the following groups of the aglycone part: seven methyl groups at δ 13.9, 16.9, 17.1, 17.5, 22.7, 23.9, 24.0; two hydroxymethyls at δ 60.7, 68.3; two mono-substituted vinyl groups at δ 116.7×2, 145.2×2; two oxygenated quaternary carbons at δ 82.2, 82.3; an oxygenated methine carbon at δ 68.7; 11 methylene carbons at δ 24.3×2, 28.1, 28.6×2, 36.8, 41.4, 41.7, 43.4, 43.6, 48.5; and an ester carbonyl carbon at δ 169.8. On the basis of the observation of the above ^{1}H- and ^{13}C-NMR signals due to the aglycone moiety, it was suggested that the aglycone part was composed of 6*E*,10*E*,14*Z*-(3*S*)-17-hydroxy geranyllinalool[2] and 6′*E*,10′*E*,14′*E*-(3′*S*)-13′*R*,19′-dihydroxy-geranyllinalool-16′-oic acid.[3] The ^{13}C signals arising from the sugar moiety were assigned by comparing them with those of the previously obtained acyclic diterperne glycosides.[1—6] Further, by analyzing their chemical shifts including glycosylation shifts, the signals were shown to be attributable to the occurrence of two sets of β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl moieties at δ 105.4×2, 76.9×2, 79.1×2, 72.1×2, 78.6×2, 62.8×2, 100.2×2, 75.7×2, 77.3×2, 81.5, 81.6, 78.9×2, 63.2×2 and α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranosyl moiety at δ 105.4, 73.1, 73.2, 74.9, 71.4, 18.9, 99.6, 75.7, 71.4, 73.9, 71.0 18.9, 101.7, 72.9, 73.1, 74.5, 70.4, 19.0, 102.9, 76.3, 77.3, 80.1, 76.1, 66.6. With regard to the respective connectivities of the aglycone part and each sugar moiety, the following heteronuclear multiple bond correlation (HMBC)s were observed: from glc II H-1 and glc V H-1 at δ 4.40 (each 1H, d, J=8.0 Hz) to C-4 at δ 81.5 of glc I and C-4 at δ 81.6 of glc IV, from glc I H-1 and glc IV H-1 at δ 4.37 (each 1H, d, J=7.4 Hz) to C-3 at δ 82.3 and C-3′ at δ 82.2, from rha III H-1 at δ 4.93 to C-3 at δ 71.4 of rha I, from rha I H-1 at δ 4.91 to C-4 at δ 80.1 of glc III, from H-2 at δ 5.06 (1H, m) of rha I to C-16′ at δ 169.8, from rha II H-1 at δ 4.82 to C-6 at δ 66.6 of glc III, from glc III H-1 at δ 4.20 (1H, d, J=8.0 Hz) to C-17 at δ 68.3. Consequently, the structure of **2** was characterized as 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl 6*E*,10*E*,14*Z*-(3*S*)-17-hydroxy-geranyllinalool 17-*O*-[3-*O*-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl 6′*E*,10′*E*,14′*Z*-(3′*S*)-13′*R*,19′-dihydroxy-geranyllinalool-16′-oyl (16′→2)-[α-L-rhamnopyranosyl-(1→3)]-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside, as shown in Fig. 3.

Experimental

General Procedure The optical rotations were measured with a JASCO DIP-1000 (l=0.5) automatic digital polarimeter. The ^{1}H- and ^{13}C-NMR spectra were measured with JEOL-α-500 NMR spectrometers, and the chemical shifts are given on a δ (ppm) scale with tetramethylsilane as the internal standard. The HR-FAB-MS spectra were measured with a JEOL JMS-DX303HF spectrometer and taken in a glycerol matrix containing NaI. HPLC was car-

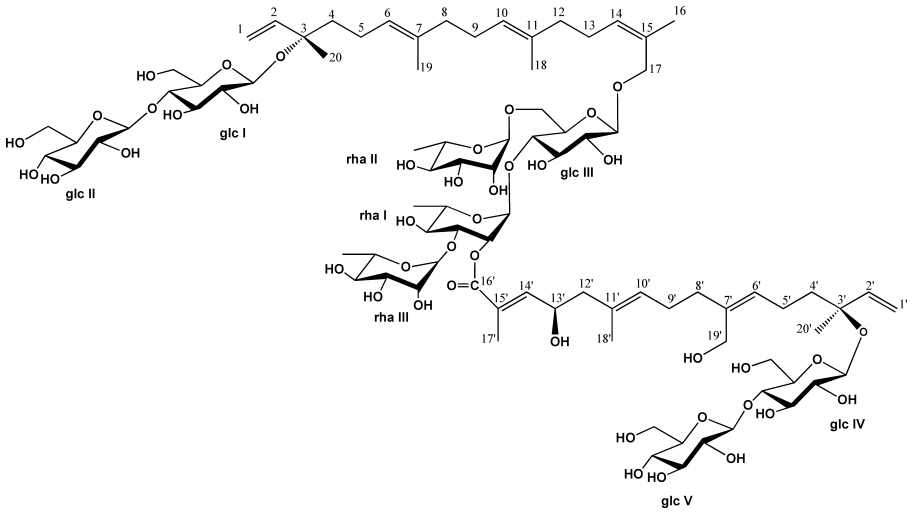

Fig. 3. Structure of HAB-4 (**2**) Capsianoside J

ried out using the Mightysil RP-18 (10.0 mm i.d.×250 mm, Kanto Chemical Co., Ltd., Tokyo, Japan); column with a Tosoh CCPM pump, Tosoh RI-8010 detector, and JASCO OR-2090 detector. TLC was performed on silica gel plates (Kieselgel 60 F_{254}, Merck) and RP C_{18} silica gel plates (Merck). The spots on TLC were visualized by UV light (254/366 nm) and sprayed with 10% H_2SO_4, followed by heating. Column chromatography was carried out on a Diaion HP-20 (Mitsubishi Chemical Ind.), ODS (Wako Pure Chemical Industries, Ltd.), and silica gel 60 (spherical, 40—100 mm, and 230—400 mesh ASTM, Kanto Chemical Co., Inc.).

Plant Material The fruits of *Capsicum chinense* JACQ. were harvested at Nagao Farm, Kumamoto Prefecture in Japan.

Extraction and Isolation The fruits of *Capsicum chinense* JACQ. (768.3 g) were extracted successively with 100% MeOH (three times). After evaporation of MeOH *in vacuo*, the residue (42.4 g) was partitioned between *n*-hexane and water. The aqueous fraction (35.1 g) was subjected to Diaion HP-20 eluted with [H_2O→(50%→70%→100% MeOH)] to afford 3 fractions (fr. 1—3). Fr. 2 [1.566 g, eluted with 70% MeOH] was subjected to ODS (Wako) column chromatography (eluted with 60—90% MeOH) to give 4 subfractions (fr. 2-1—fr. 2-4). Fr. 2-2 [205.0 mg, 60% MeOH eluate] was subsequently chromatographed on silica gel by using ($CHCl_3$–MeOH–H_2O=8 : 2 : 0.2→7 : 3 : 0.5) to provide 10 fractions (fr. 1—10). Fr. 8 (70.1 mg), which was further subjected to HPLC separation eluted with 75% MeOH to give capsianoside XV (17.4 mg). Fr. 10 (50.3 mg) was further subjected to HPLC separation eluted with 75% MeOH to give capsianoside XVIII (**1**, 17.8 mg). Fr. 2-4 [261.7 mg, 70% MeOH eluate] was subsequently chromatographed on silica gel by using silica gel ($CHCl_3$–MeOH–H_2O=7 : 3 : 0.5→6 : 4 : 0.5) to afford 8 fractions. Fr. 1 (20.4 mg) was further subjected to HPLC separation eluted with 70% MeOH to give capsianoside XIII (11.1 mg). Fr. 3 (52.7 mg) was subjected to HPLC separation eluted with 70% MeOH to give capsianoside J (**2**, 18.0 mg).

Sugar Analysis A solution of each compound (**1** or **2**) (1.0 mg) in 2 M HCl/dioxane (1 : 1, 2 ml) was heated at 100 °C for 1 h. The reaction mixture was diluted with H_2O and evaporated to remove dioxane. The solution was neutralized with Amberlite MB-3 and passed through a SEP-PAK C_{18} cartridge to give a sugar fraction. The sugar fraction was concentrated to dryness *in vacuo* to give a residue, which was dissolved in CH_3CN/H_2O (3 : 1, 250 μl). The sugar fraction was analyzed by HPLC under the following conditions: column, Shodex RS-Pac DC-613 (6.0 mm i.d.×150 mm, Showa-Denko, Tokyo, Japan); solvent, CH_3CN/H_2O (3 : 1); flow rate; 1.0 ml/min; column temperature, 70 °C; detection, refractive index (RI) and optical rotation (OR). The t_R (min) of sugars were as follow: L-rhamnose 4.4 (−), D-glucose 7.2 (+). [reference: L-rhamnose 4.4 (negative optical rotation: −), D-glucose 7.2 (positive optical rotation: +)].

HAB-1=Capsianoside XVIII (1) An amorphous powder, $[\alpha]_D^{23}$ −21.2° (*c*=1.32, MeOH), positive HR-FAB-MS $[M+Na]^+$ *m/z*: 1285.5675 (Calcd for $C_{56}H_{94}O_{31}Na$: 1285.5677). ^{1}H-NMR (CD_3OD) δ: 1.26 (3H, d, *J*=5.7 Hz, rha I H_3-6), 1.32 (3H, d, *J*=6.3 Hz, rha II H_3-6), 1.37, 1.61, 1.76 (each 3H, s, H_3-20, H_3-18, H_3-16), 4.08 (2H, s, H_2-19), 4.11 (1H, d, *J*=11.4 Hz, H-17b), 4.19 (1H, d, *J*=8.0 Hz, glc III H-1), 4.32 (1H, d, *J*=11.4 Hz, H-17a), 4.38 (1H, d, *J*=8.0 Hz, glc I H-1), 4.40 (1H, d, *J*=8.0 Hz, glc II H-1), 4.58 (1H, d, *J*=8.0 Hz, glc IV H-1), 4.70 (1H, d, *J*=1.2 Hz, rha II H-1), 4.81 (1H, d, *J*=1.2 Hz, rha I H-1), 5.13 (1H, m, H-10), 5.20 (1H, d, *J*=10.9 Hz, H-1b), 5.24 (1H, d, *J*=17.8 Hz, H-1a), 5.28 (1H, t, *J*=7.6 Hz, H-6), 5.40 (1H, t, *J*=6.9 Hz, H-14), 5.93 (1H, dd, *J*=10.9, 17.8 Hz, H-2). ^{13}C-NMR (CD_3OD) δ: aglycone moiety C-1—20, 116.6 (C-1), 145.2 (C-2), 82.2 (C-3), 43.6 (C-4), 23.9 (C-5), 130.0 (C-6), 140.2 (C-7), 36.7 (C-8), 28.6 (C-9), 126.7 (C-10), 136.4 (C-11), 41.7 (C-12), 28.1 (C-13), 132.1 (C-14), 133.2 (C-15), 22.7 (C-16), 68.4 (C-17), 17.1 (C-18), 60.7 (C-19), 24.3 (C-20); glc I moiety 100.1 (C-1), 75.7 (C-2), 77.3 (C-3), 81.6 (C-4), 78.9 (C-5), 63.2 (C-6); glc II moiety 105.4 (C-1), 76.9 (C-2) , 78.9 (C-3), 72.2 (C-4), 78.6 (C-5), 62.8 (C-6); glc III moiety 102.8 (C-1), 76.2 (C-2), 77.4 (C-3), 79.7 (C-4), 76.0 (C-5), 67.6 (C-6); glc IV moiety 106.4 (C-1), 76.8 (C-2), 78.8 (C-3), 72.1 (C-4), 78.6 (C-5), 63.5 (C-6); rha I moiety 103.1 (C-1), 73.0 (C-2), 73.1 (C-3), 84.1 (C-4), 69.9 (C-5), 18.2 (C-6); and rha II moiety 102.3 (C-1), 73.0 (C-2), 73.1 (C-3), 74.8 (C-4), 70.6 (C-5), 19.0 (C-6).

HAB-4=Capsianoside J (2) An amorphous powder, $[\alpha]_D^{23}$ −28.1° (*c*=1.42, MeOH), positive HR-FAB-MS $[M+Na]^+$ *m/z*: 1911.8942 (Calcd for $C_{88}H_{144}O_{43}Na$: 1911.8978). ^{1}H-NMR (CD_3OD) δ: 1.14 (3H, d, *J*=6.3 Hz, rha I H_3-6), 1.25 (3H, d, *J*=5.7 Hz, rha II H_3-6), 1.27 (3H, d, *J*=5.7 Hz, rha III H_3-6), 1.37 (6H, s, H_3-20, 20′), 1.59 (6H, s, H_3-18, 19), 1.61 (3H, s, H_3-18′), 1.76 (3H, s, H_3-16), 1.88 (3H, s, H_3-17′), 4.08 (2H, s, H_2-19′), 4.11 (1H, d, *J*=11.5 Hz, H-17b), 4.20 (1H, d, *J*=8.0 Hz, glc III H-1), 4.33 (1H, d, *J*=12.0 Hz, H-17a), 4.37 (2H, d, *J*=7.4 Hz, glc I, IV H-1), 4.40 (2H, d, *J*=8.0 Hz, glc II, V H-1), 4.53 (1H, m, H-13′), 4.82 (1H, s, rha II H-1), 4.91 (1H, s, rha I H-1), 4.93 (1H, s, rha III H-1), 5.06 (1H, m, rha I H-2), 5.11 (3H, m, H-6, 6′, 10), 5.12 (1H, t, *J*=8.6 Hz, H-10′), 5.22 (2H, d, *J*=11.5 Hz, H-1b, 1′b), 5.23 (2H, d, *J*=5.2 Hz, H-1a, 1′a), 5.28 (1H, t, *J*=7.5 Hz, H-6′), 5.39 (1H, t, *J*=6.9 Hz, H-14), 5.92 (2H, m, H-2, 2′), 6.70 (1H, d, *J*=8.6 Hz, H-14′). ^{13}C-NMR (CD_3OD) δ: aglycone moiety C-1—20, 116.7 (C-1), 145.2 (C-2), 82.3 (C-3), 43.6 (C-4), 24.3 (C-5), 126.6 (C-6), 136.3 (C-7), 41.4 (C-8), 28.6 (C-9), 126.7 (C-10), 136.7 (C-11), 41.7 (C-12), 28.1 (C-13), 132.1 (C-14), 133.1 (C-15), 22.7 (C-16), 68.3 (C-17), 16.9 (C-18), 17.1 (C-19), 24.0 (C-20), C-1′–20′, 116.7 (C-1′), 145.2 (C-2′), 82.2 (C-3′), 43.4 (C-4′), 24.3 (C-5′), 130.1 (C-6′), 140.2 (C-7′), 36.8 (C-8′), 28.6 (C-9′), 126.6 (C-10′), 136.3 (C-11′), 48.5 (C-12′), 68.7 (C-13′), 146.9 (C-14′), 129.6 (C-15′), 169.8 (C-16′), 13.9 (C-17′), 17.5 (C-18′), 60.7 (C-19′), 23.9 (C-20′); glc I moiety 100.2 (C-1), 75.7 (C-2), 77.3 (C-3), 81.5 (C-4), 78.9 (C-5), 63.2 (C-6); glc II moiety 105.4 (C-1), 76.9 (C-2), 79.1 (C-3), 72.1 (C-4), 78.6 (C-5), 62.8 (C-6); glc III moiety 102.9 (C-1), 76.3 (C-2), 77.3 (C-3), 80.1 (C-4), 76.1 (C-5), 66.6 (C-6); glc IV moiety 100.2 (C-1), 75.7 (C-2), 77.3 (C-3), 81.6 (C-4), 78.9 (C-5), 63.2 (C-6), glc V moiety, 105.4 (C-1), 76.9 (C-2), 79.1 (C-3), 72.1 (C-4), 78.6 (C-5), 62.8 (C-6); rha I moiety 99.6 (C-1), 75.7 (C-2), 71.4 (C-3), 73.9 (C-4), 71.0 (C-5), 18.9 (C-6); rha II moiety 101.7 (C-1), 72.9 (C-2), 73.1 (C-3), 74.5 (C-4), 70.4 (C-5), 19.0 (C-6); and rha III moiety 105.4 (C-1), 73.1 (C-2), 73.2 (C-3), 74.9 (C-4), 71.4 (C-5), 18.9 (C-6).

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