# Acyclic Diterpene Glycosides, Capsianosides C, D, E, F and III, from the Fruits of Hot Red Pepper *Capsicum annuum* L. Used in *Kimchi* and Their Revised Structures

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Acyclic diterpene glycosides, named capsianosides I′, II, III (**1**), C (**2**), D (**3**), E (**4**) and F (**5**), have been isolated from the dried hot red pepper fruits of *Capsicum annuum* L. used in *Kimchi*. The structures of these compounds have been revised in the sugar connectivities by 1D- and 2D-NMR spectroscopic and chemical methods.

*Kimchi*, a fermented Chinese cabbage product, has been prepared and consumed in Korea traditionally. Now its consumption is expanding worldwide owing to various functional properties such as anti-carcinogenic and anti-oxidative activities.[1] *Kimchi* is made of Chinese cabbage, with different spices, garlic, ginger and hot red pepper.[2] The *Capsicum* species is a very important plant used as vegetables, spices and external medicine, and capsaicinoids are the group of compounds responsible for the 'heat' sensation. These metabolites are also used as pest repellants in agriculture, and there is interest their synergistic use with organophosphate insecticides.[3] Capsaicin, a prototypical capsaicinoid, is used to mitigate neurogenic pain; several products applied as creams and gels (*e.g.* Axsain and Zostrix) have appeared on the market as topical analgesics, but irritance severely limits the pharmacological use of capsaicinoid.[4] Peppers are also a good source of vitamins A, C, and E, which are present in high concentration in various pepper types.[5] Total flavonoid and phenolic components are important dietary antioxidants.[6] Although carotenoids, lipids and capsaicins have been studied in depth, there are few reports on the highly polar components of the *Capsicum* species. Meanwhile, a novel acyclic diterpene glycoside, capsianoside A, was obtained from the part of the polar ingredients in the fresh fruits of *Capsicum annuum* L. var. *fasciculatum* Irish.[7] Also, we isolated novel acyclic diterpene glycosides, capsianosides A—H and I—VI, VIII—X, XIII, XV and XVI, from *Capsicum* plants in the previous researches.[8—10] In this study, we have examined the chemical composition of the water-soluble fraction of dried hot red pepper fruits *C. annuum* L. used in *Kimchi*, and here we report the structure characterization of seven compounds, five of which (**1**—**5**) have been revised in the structures of the sugar connectivities.

Capsianoside III (**1**) was obtained as an amorphous powder showing $[\alpha]_D$ −28.6° (MeOH). It gave a molecular formula $C_{50}H_{84}O_{26}Na$ at *m/z* 1123.5127 by HR-ESI-MS. The $^1$H-NMR spectrum of **1** showed the presence of four methyl groups at $\delta$ 1.39 (3H, s), 1.61 (6H, s) and 1.79 (3H, s), three olefinic protons at $\delta$ 5.22 (1H, br d), 5.23 (1H, br d) and 6.13 (1H, dd, *J*=11.0, 18.3 Hz) arising from a mono-substituted double bond, three olefinic protons at $\delta$ 5.13 (2H, m) and 5.39 (1H, t) adjacent to methylene group and seven methylene groups at $\delta$ 1.60 (2H, m), 1.95—2.20 (10H, m), 4.21 (1H, d, *J*=11.6 Hz) and 4.30 (1H, d, *J*=11.6 Hz). Further-

more, the $^{13}$C-NMR spectrum of **1** as listed in Table 1 showed total twenty carbon signals composed of three tri-substituted double bonds at $\delta$ 125.8, 126.0, 131.3, 132.5, 135.5 and 136.1, mono-substituted double bond at $\delta$ 116.0 and 144.5, four methyl groups at $\delta$ 16.3 (2×C), 22.0 and 23.4 and seven methylene groups at $\delta$ 23.6, 27.3, 27.7, 40.8, 40.9, 43.1 and 68.3. Since all the signals due to the aglycone moiety of capsianoside III (**1**) in the $^1$H- and $^{13}$C-NMR spectra were identical with those of capsianoside III reported previously,[8] the configuration at C-3 was regarded as *S*, suggesting that the aglycone moiety is 17-hydroxy-6*E*,10*E*,14*Z*-(3*S*)-geranyl-linalool. Other sapogenols of capsianosides C (**2**), D (**3**), E (**4**) and F (**5**) were also coincident with that of **1**. The $^1$H-NMR spectrum **1** showed the presence of 4 mol of hexosyl and 1 mol of deoxyhexosyl moieties based on the signals ascribable to five anomeric protons at $\delta$ 4.35 (1H, d, *J*=7.3 Hz), 4.47 (1H, d, *J*=7.9 Hz), 4.56 (1H, d, *J*=7.9 Hz), 4.63 (1H, d, *J*=7.9 Hz) and 4.75 (1H, s). On the other hand,

Table 1. $^{13}$C-NMR (125 MHz) Spectroscopic Data for Compound **1** in CD$_3$OD

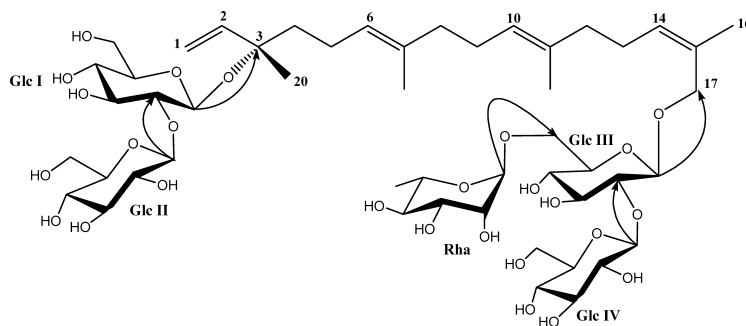| Position | $\delta_C$ | Position | $\delta_C$ | Position | $\delta_C$ |
|---|---|---|---|---|---|
| Aglycone moiety | | Sugar moiety | | | |
| 1 | 116.0 | Glc I | | Glc IV | |
| 2 | 144.5 | 1 | 98.4 | 1 | 104.9 |
| 3 | 82.1 | 2 | 83.3 | 2 | 75.9 |
| 4 | 43.1 | 3 | 77.8 | 3 | 78.2 |
| 5 | 23.6 | 4 | 71.4 | 4 | 71.7 |
| 6 | 126.0 | 5 | 77.5 | 5 | 78.1 |
| 7 | 135.5 | 6 | 62.9 | 6 | 62.8 |
| 8 | 40.8 | | | | |
| 9 | 27.7 | Glc II | | Rha | |
| 10 | 125.8 | 1 | 105.9 | 1 | 102.1 |
| 11 | 136.1 | 2 | 76.7 | 2 | 72.2 |
| 12 | 40.9 | 3 | 78.3 | 3 | 72.5 |
| 13 | 27.3 | 4 | 71.5 | 4 | 74.1 |
| 14 | 131.3 | 5 | 78.1 | 5 | 69.8 |
| 15 | 132.5 | 6 | 62.8 | 6 | 18.1 |
| 16 | 22.0 | | | | |
| 17 | 68.3 | Glc III | | | |
| 18 | 16.3 | 1 | 101.2 | | |
| 19 | 16.3 | 2 | 82.1 | | |
| 20 | 23.4 | 3 | 77.7 | | |
| | | 4 | 71.6 | | |
| | | 5 | 76.6 | | |
| | | 6 | 67.7 | | |

Fig. 1. Key HMBC of **1**

the $^{13}$C-NMR spectrum also exhibited five anomeric carbon signals at $\delta$ 105.9, 104.9, 102.1, 101.2 and 98.4. Acid hydrolysis of **1** afforded glucose and rhamnose. The HMBC correlations as shown in Fig. 1 revealed the respective sugar connectivities: correlations between the signal at $\delta_H$ 4.47 (1H, d, $J=7.9$ Hz) and the signal at $\delta_C$ 82.1 (aglycone C-3) indicating the Glc I H-1 to be linked to the C-3 of the aglycone; the signal at $\delta_H$ 4.56 (1H, d, $J=7.9$ Hz) and the signal at $\delta_C$ 83.3 (Glc I C-2) showing the Glc II H-1 to be linked to the C-2 of the Glc I; the signal at $\delta_H$ 4.35 (1H, d, $J=7.3$ Hz) and the signal at $\delta_C$ 68.3 (aglycone C-17) exhibiting the Glc III H-1 to be linked to the C-17 of the aglycone; the signal at $\delta_H$ 4.63 (1H, d, $J=7.9$ Hz) and the signal at $\delta_C$ 82.1 (Glc III C-2) indicating the Glc IV H-1 to be bound to the Glc III C-2; the signal at $\delta_H$ 4.75 (1H, s) and the signal at $\delta_C$ 67.7 (Glc III C-6) showing the Rha H-1 to be linked to the Glc III C-6. The sugar structure at the 17-*O*-part, 17-*O*-$\beta$-D-glucopyranosyl-(1→2)-$\beta$-D-glucopyranosyl-(1→6)-$\alpha$-L-rhamnopyranoside, for **1** previously reported[8] should be revised. Therefore, the structure of **1** was determined to be 3-*O*-$\beta$-D-glucopyranosyl-(1→2)-$\beta$-D-glucopyranosyl 17-hydroxy-6*E*,10*E*,14*Z*-(3*S*)-geranyllinalool 17-*O*-$\beta$-D-glucopyranosyl-(1→2)-[$\alpha$-L-rhamnopyranosyl-(1→6)]-$\beta$-D-glucopyranoside.

Capsianoside C (**2**) was obtained as an amorphous powder showing $[\alpha]_D$ −23.5° (MeOH). The molecular formula was determined to be $C_{82}H_{134}O_{38}Na$ by HR-ESI-MS (*m/z* 1749.8584). The $^1$H- and $^{13}$C-NMR signals due to the sapogenol part indicated that the sapogenol part of **2** comprised a 17-hydroxy-6*E*,10*E*,14*Z*-(3*S*)-geranyllinalool and a 6*E*,10*E*-13-hydroxy-(3*S*)-geranyllinalool-16-oic acid previously reported for dimeric ester compounds, capsianosides.[8] The $^1$H-NMR signals due to the sapogenol parts, were assigned as follows; eight methyl groups [$\delta$ 1.39 (6H, s, $H_3$-20, 20′), 1.61 (9H, s, $H_3$-18′, 19, 19′), 1.66 (3H, s, $H_3$-18), 1.77 (3H, s, $H_3$-16′) and 1.89 (3H, s, $H_3$-17)], two monosubstituted double bonds [$\delta$ 5.22 (2H, d, $J=11.6$ Hz, H-1b, 1′b), 5.23 (2H, d, $J=17.1$ Hz, H-1a, 1′a) and 6.12 (2H, dd, $J=10.7$, 18.0 Hz, H-2, 2′)], five olefinic protons [$\delta$ 5.12 (3H, m, H-6, 6′, 10′), 5.21 (1H, m, H-10) and 5.40 (1H, t, H-14′)] and one olefinic proton [$\delta$ 6.71 (1H, dd, $J=1.2$, 8.6 Hz, H-14)] coupled with an oxygenated methine proton [$\delta$ 4.53 (1H, m, H-13)], twelve methylene groups [$\delta$ 1.60 (4H, m, H-4, 4′), 1.99—2.28 (18H, m), 4.33 (1H, d, $J=11.6$ Hz, H-17′a) and 4.12 (1H, d, $J=11.6$ Hz, H-17′b)]. Also, the $^{13}$C-NMR spectrum of **2** displayed eight methyl carbons at $\delta$ 13.1, 16.3 (3×C), 16.8, 21.9, 23.5 (2×C), eleven methylene carbons at $\delta$ 43.1 (2×C), 23.6 (2×C), 40.5, 27.7, 47.9, 40.8, 27.8, 40.9, 27.3, one methine carbon at $\delta$ 68.0, two quarternary carbons

at $\delta$ 82.1 (2×C) with an oxygen function, sixteen double bond signals at $\delta$ 116.0 (2×C), 144.4 (2×C), 125.8, 135.5, 125.9 (2×C), 136.1, 131.3, 132.4, 136.0, 129.3, 131.8, 145.9, 128.9 and one methylene carbon at $\delta$ 67.7. Moreover, a signal at $\delta$ 169.2 was assigned to an ester carbonyl group. All the above carbon signals were also assigned by the aid of FGCOSY, HMQC and HMBC as in Table 2. The $^1$H-NMR signals originated from the sugar part of **2** showed seven anomeric proton signals [$\delta$ 4.21 (1H, d, $J=7.9$ Hz), 4.47 (2H, d, $J=7.3$ Hz), 4.56 (2H, d, $J=7.3$ Hz), 4.81 (1H, s) and 4.90 (1H, s)]. The $^{13}$C-NMR spectrum also showed seven anomeric carbon signals at $\delta$ 105.9 (2×C), 102.3, 101.1, 99.3 and 98.4 (2×C) together with two methyl carbons ($\delta$ 18.0, 18.2) arising from deoxyhexosyl moieties. Acid hydrolysis of **2** afforded glucose and rhamnose. The HMBC correlations revealed the respective sugar connectivities: correlations between the signal at $\delta_H$ 4.47 (2H, d, $J=7.3$ Hz) and the signal at $\delta_C$ 82.1 (aglycone C-3, 3′) indicating the Glc I H-1 and Glc III H-1 to be linked to the C-3, 3′ of the aglycone individually; the signal at $\delta_H$ 4.56 (2H, d, $J=7.3$ Hz) and the signal at $\delta_C$ 83.3 (C-2 of Glc I and Glc III) showing the Glc II H-1 and Glc IV H-1 to be linked to the C-2 of the Glc I and Glc III separately; the signal at $\delta_H$ 4.21 (1H, d, $J=7.9$ Hz) and the signal at $\delta_C$ 67.7 (aglycone C-17′) exhibiting the Glc V H-1 to be linked to the C-17′ of the aglycone; the signal at $\delta_H$ 4.90 (1H, s) and the signal at $\delta_C$ 78.6 (Glc V C-4) indicating the Rha I H-1 to be bound to the Glc V C-4; the signal at $\delta_H$ 4.81 (1H, s) and the signal at $\delta_C$ 66.2 (Glc V C-6) showing the Rha II H-1 to be linked to the Glc V C-6. The sugar structure previously reported[8] should be revised. Next, in order to determine the location of the ester bond, the $^1$H-NMR spectra of **2** and capsianoside II[8] were compared. The correlations were observed between an anomeric proton signal at $\delta$ 4.90 and a carbon signal at $\delta$ 99.3, between the signal $\delta$ 4.98 of H-2 in Rha I and a carbon signal at $\delta$ 75.0, and between the signal $\delta$ 3.89 of H-3 in Rha I and a carbon signal at $\delta$ 70.4 in the HMQC. A proton signal at $\delta$ 4.98 (1H, d, $J=3.1$ Hz) being geminal to the acyl group was observed in **2**. This signal correlated with the signals of anomeric proton [$\delta$ 4.90 (1H, s)] and $\delta_{H-3}$ 3.89 of the rhamnosyl moiety in the TOCSY. Therefore, it was found that the hydroxyl group at C-2 of the Rha I is concerned with the ester bond. The absolute configurations at C-3 and C-3′ in the aglycone part were suggested to be 3*S* as in other capsianosides isolated, on the basis of optical rotation. Consequently, the structure of capsianoside C (**2**) could be represented as 3′-*O*-$\beta$-D-glucopyranosyl-(1→2)-$\beta$-D-glucopyranosyl 6′*E*,10′*E*,14′*Z*-(3′*S*)-17′-hydroxygeranyllinalool 17′-
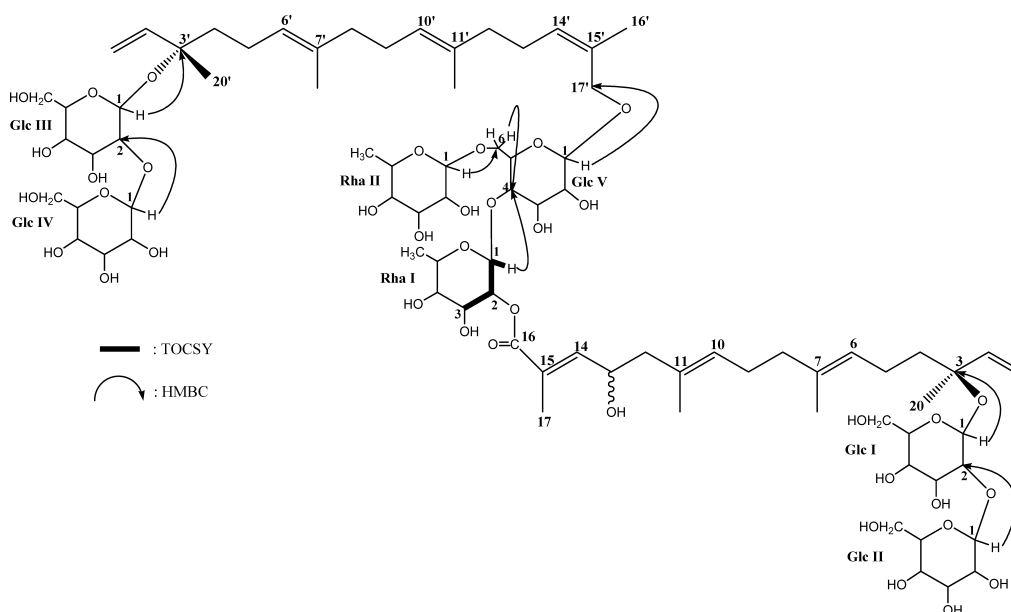
Fig. 2. Key HMBC and TOCSY of **2**

*O*-[3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl 6*E*,10*E*,14*E*-(3*S*)-13-hydroxygeranyllinalool-16-oyl(16→2)]-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside.

Capsianoside D (**3**), $[\alpha]_D$ −27.4° (MeOH), was obtained as an amorphous powder. The molecular formula was determined to be $C_{82}H_{134}O_{38}Na$ by HR-ESI-MS (*m/z* 1749.8251). Comparison of ¹H-, ¹³C-NMR and mass spectrum data of **3** with those of **2** showed clearly their structural similarity. However, in the ¹³C-NMR spectrum of **3**, the signals assignable to the Rha I appeared at $\delta$ 102.7, 70.2, 75.8, 71.7, 70.8 and 18.2, suggesting that the hydroxyl group at C-3 of Rha I participated in the ester bonding. Moreover, in comparing the ¹H-NMR spectrum of **3** with those of **2**, the H-3 of the Rha I in **3** showed acylation shifts into $\delta$ 4.99 (1H, dd, *J*=3.1, 9.8 Hz) together with the chemical shifts of $\delta$ 4.84 (1H, s, Rha I H-1) and $\delta$ 4.03 (1H, d, *J*=3.1 Hz, Rha I H-2). The signal of H-3 correlated with the signal at $\delta_H$ 4.03 (1H, d, *J*=3.1Hz), and the anomeric proton signal [$\delta$ 4.84 (1H, s)] correlated with the signal at $\delta_H$ 4.03 (1H, d, *J*=3.1 Hz) of the rhamnosyl moiety in the ¹H–¹H COSY. Consequently, it was found that the hydroxyl group at C-3 of the Rha I is concerned with the ester bond. The structure of **3** was represented as 3′-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl 6′*E*,10′*E*,14′*Z*-(3′*S*)-17′-hydroxygeranyllinalool 17′-*O*-[3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl 6*E*,10*E*,14*E*-(3*S*)-13-hydroxygeranyllinalool-16-oyl(16→3)]-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside.

Capsianoside E (**4**) was obtained as an amorphous powder showing $[\alpha]_D$ −33.4° (MeOH). The molecular formula was determined to be $C_{82}H_{134}O_{37}Na$ by HR-ESI-MS (*m/z* 1733.8426). Since compound **4** indicated the presence of an ester carbonyl group at $\delta$ 169.3 in the ¹³C-NMR spectrum, **4** was regarded as an analogous compound such as **2** and **3**. However, a signal [$\delta$ 4.53 (1H, m)] assignable to H-13, as well as appeared in **2** and **3**, vanished, and a signal due to H-14 occurred at $\delta$ 6.85 (1H, t, H-14) in **4**, thus suggesting the

occurrence of the methylene group at C-13 in **4**. This was also supported by the evidence of the ¹³C-NMR spectrum that the methine carbon due to C-13 at $\delta$ 68.0 in **2** appeared at $\delta$ 28.6 as methylene carbon in **4**. The location of the ester bond was determined by HMQC and TOCSY. The signals due to the H-1, H-2 and H-3 of Rha I showed acylation shifts to appear at $\delta$ 4.90 (1H, s), 4.97 (1H, d, *J*=3.7 Hz) and 3.88 (1H, dd, *J*=3.1, 9.2 Hz), which were coincident with those of **2** having an ester bond at C-2–OH of the Rha I. The correlations were observed between an anomeric proton signal ($\delta$ 4.90) and a carbon signal at $\delta$ 99.4, between the signal $\delta$ 4.97 of H-2 in Rha I and a carbon signal at $\delta$ 74.7, and between the signal $\delta$ 3.88 of H-3 in Rha I and a carbon signal at $\delta$ 70.4 in the HMQC. A proton signal at $\delta$ 4.97 (1H, d, *J*=3.7 Hz) geminal to the acyl group was observed in **4**. This signal was correlated with the anomeric proton [$\delta$ 4.90 (1H, s)] and $\delta_{H-3}$ 3.88 of the rhamnosyl moiety in the TOCSY. So, it was found that the hydroxyl group at C-2 of the Rha I is concerned with the ester bond. Therefore, the structure of **4** was characterized as 3′-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl 6′*E*,10′*E*,14′*Z*-(3′*S*)-17′-hydroxygeranyllinalool 17′-*O*-[3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl 6*E*,10*E*,14*Z*-(3*S*)-geranyllinalool-16-oyl(16→2)]-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside.

Capsianoside F (**5**), $[\alpha]_D$ −33.2° (MeOH), was obtained as an amorphous powder. The molecular formula was determined to be $C_{82}H_{134}O_{37}Na$ by HR-ESI-MS (*m/z* 1733.8427). The ¹H-NMR spectrum of **5** was very similar with that of **4**, signals due to the H-1, H-2 and H-3 of the Rha I appeared at $\delta$ 4.84 (1H, s), 4.02 (1H, d, *J*=3.1 Hz) and 4.98 (1H, dd, *J*=3.1, 9.8 Hz) as in the case of **3**. This fact indicated that the hydroxyl group at C-3 of the Rha I is concerned with the ester bond in **5**. Besides, a proton signal at $\delta$ 4.98 (1H, dd, *J*=3.1, 9.8 Hz) geminal to the acyl group was observed in **5**. This signal was correlated with $\delta_H$ 4.02 (1H, d, *J*=3.1 Hz) and the anomeric proton [$\delta$ 4.84 (1H, s)] was correlated with $\delta_H$ 4.02 (1H, d, *J*=3.1 Hz) of the Rha I
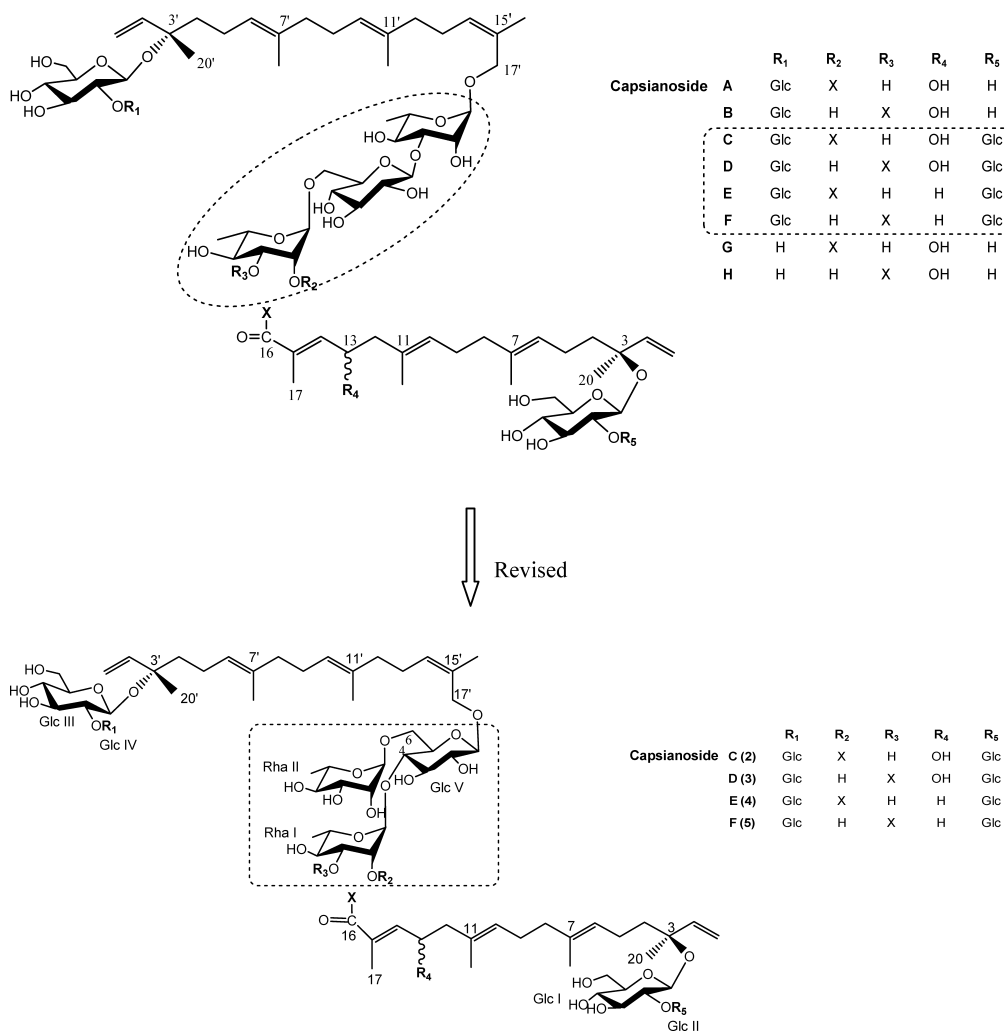
Fig. 3. Structures of **2**—**5**

Table 2. $^{13}$C-NMR (125 MHz) Spectroscopic Data for Aglycone of Compounds **2**—**5** in CD$_3$OD

| Position | **2** | Position | **2** | Position | **3** | Position | **3** | Position | **4** | Position | **4** | Position | **5** | Position | **5** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 116.0 | 1′ | 116.0 | 1 | 116.0 | 1′ | 116.0 | 1 | 116.0 | 1′ | 116.0 | 1 | 116.0 | 1′ | 116.0 |
| 2 | 144.4 | 2′ | 144.4 | 2 | 144.4 | 2′ | 144.4 | 2 | 144.4 | 2′ | 144.4 | 2 | 144.4 | 2′ | 144.4 |
| 3 | 82.1 | 3′ | 82.1 | 3 | 82.1 | 3′ | 82.1 | 3 | 82.1 | 3′ | 82.1 | 3 | 82.0 | 3′ | 82.0 |
| 4 | 43.1 | 4′ | 43.1 | 4 | 43.0 | 4′ | 43.0 | 4 | 43.1 | 4′ | 43.1 | 4 | 43.1 | 4′ | 43.1 |
| 5 | 23.6 | 5′ | 23.6 | 5 | 23.6 | 5′ | 23.6 | 5 | 23.6 | 5′ | 23.6 | 5 | 23.6 | 5′ | 23.6 |
| 6 | 125.9 | 6′ | 125.8 | 6 | 125.9 | 6′ | 125.8 | 6 | 125.9 | 6′ | 125.8 | 6 | 125.8 | 6′ | 125.9 |
| 7 | 136.0 | 7′ | 135.5 | 7 | 135.9 | 7′ | 135.5 | 7 | 136.0 | 7′ | 135.5 | 7 | 135.9 | 7′ | 135.5 |
| 8 | 40.5 | 8′ | 40.8 | 8 | 40.8 | 8′ | 40.9 | 8 | 40.7 | 8′ | 40.8 | 8 | 40.7 | 8′ | 40.8 |
| 9 | 27.7 | 9′ | 27.8 | 9 | 27.7 | 9′ | 27.7 | 9 | 27.7 | 9′ | 27.7 | 9 | 27.6 | 9′ | 27.7 |
| 10 | 129.3 | 10′ | 125.9 | 10 | 129.2 | 10′ | 125.9 | 10 | 126.3 | 10′ | 125.9 | 10 | 126.2 | 10′ | 125.9 |
| 11 | 131.8 | 11′ | 136.1 | 11 | 131.9 | 11′ | 136.0 | 11 | 135.2 | 11′ | 136.1 | 11 | 135.2 | 11′ | 136.0 |
| 12 | 47.9 | 12′ | 40.9 | 12 | 47.9 | 12′ | 40.5 | 12 | 39.3 | 12′ | 40.9 | 12 | 39.3 | 12′ | 40.9 |
| 13 | 68.0 | 13′ | 27.3 | 13 | 68.1 | 13′ | 27.3 | 13 | 28.6 | 13′ | 27.3 | 13 | 28.6 | 13′ | 27.3 |
| 14 | 145.9 | 14′ | 131.3 | 14 | 145.4 | 14′ | 131.2 | 14 | 144.6 | 14′ | 131.3 | 14 | 144.1 | 14′ | 131.2 |
| 15 | 128.9 | 15′ | 132.4 | 15 | 129.0 | 15′ | 132.4 | 15 | 128.6 | 15′ | 132.4 | 15 | 128.8 | 15′ | 132.4 |
| 16 | 169.2 | 16′ | 21.9 | 16 | 169.3 | 16′ | 21.9 | 16 | 169.3 | 16′ | 21.9 | 16 | 169.5 | 16′ | 21.9 |
| 17 | 13.1 | 17′ | 67.7 | 17 | 13.1 | 17′ | 67.9 | 17 | 12.6 | 17′ | 67.8 | 17 | 12.6 | 17′ | 67.9 |
| 18 | 16.8 | 18′ | 16.3 | 18 | 16.7 | 18′ | 16.3 | 18 | 16.3 | 18′ | 16.2 | 18 | 16.3 | 18′ | 16.3 |
| 19 | 16.3 | 19′ | 16.3 | 19 | 16.2 | 19′ | 16.3 | 19 | 16.2 | 19′ | 16.2 | 19 | 16.2 | 19′ | 16.3 |
| 20 | 23.5 | 20′ | 23.5 | 20 | 23.5 | 20′ | 23.5 | 20 | 23.4 | 20′ | 23.4 | 20 | 23.4 | 20′ | 23.4 |

Table 3. $^{13}$C-NMR (125 MHz) Spectroscopic Data for Sugar Moiety of Compounds **2**—**5** in CD$_3$OD

| Position | **2** | Position | **2** | Position | **3** | Position | **3** | Position | **4** | Position | **4** | Position | **5** | Position | **5** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Glc I-1 | 98.4 | Glc V-1 | 102.3 | Glc I-1 | 98.3 | Glc V-1 | 102.3 | Glc I-1 | 98.4 | Glc V-1 | 102.3 | Glc I-1 | 98.3 | Glc V-1 | 102.4 |
| 2 | 83.3 | 2 | 75.4 | 2 | 83.2 | 2 | 75.4 | 2 | 83.3 | 2 | 75.5 | 2 | 83.3 | 2 | 75.5 |
| 3 | 77.7 | 3 | 76.6 | 3 | 77.7 | 3 | 76.8 | 3 | 77.7 | 3 | 76.6 | 3 | 77.7 | 3 | 75.3 |
| 4 | 71.5 | 4 | 78.6 | 4 | 71.5 | 4 | 79.2 | 4 | 71.5 | 4 | 78.6 | 4 | 71.5 | 4 | 79.3 |
| 5 | 77.5 | 5 | 75.4 | 5 | 77.5 | 5 | 75.4 | 5 | 77.5 | 5 | 75.5 | 5 | 77.5 | 5 | 75.3 |
| 6 | 62.8 | 6 | 66.2 | 6 | 62.8 | 6 | 66.9 | 6 | 62.8 | 6 | 66.2 | 6 | 62.8 | 6 | 66.9 |
| Glc II-1 | 105.9 | Rha I-1 | 99.3 | Glc II-1 | 105.9 | Rha I-1 | 102.7 | Glc II-1 | 105.9 | Rha I-1 | 99.4 | Glc II-1 | 105.9 | Rha I-1 | 102.7 |
| 2 | 76.6 | 2 | 75.0 | 2 | 76.6 | 2 | 70.2 | 2 | 76.6 | 2 | 74.7 | 2 | 76.6 | 2 | 70.3 |
| 3 | 78.3 | 3 | 70.4 | 3 | 78.3 | 3 | 75.8 | 3 | 78.3 | 3 | 70.4 | 3 | 78.3 | 3 | 75.5 |
| 4 | 71.7 | 4 | 74.1 | 4 | 71.7 | 4 | 71.7 | 4 | 71.7 | 4 | 74.1 | 4 | 71.7 | 4 | 71.7 |
| 5 | 78.1 | 5 | 70.4 | 5 | 78.1 | 5 | 70.8 | 5 | 78.1 | 5 | 70.5 | 5 | 78.1 | 5 | 70.8 |
| 6 | 62.8 | 6 | 18.2 | 6 | 62.8 | 6 | 18.2 | 6 | 62.8 | 6 | 18.2 | 6 | 62.8 | 6 | 18.2 |
| Glc III-1 | 98.4 | Rha II-1 | 101.1 | Glc III-1 | 98.3 | Rha II-1 | 101.5 | Glc III-1 | 98.4 | Rha II-1 | 101.1 | Glc III-1 | 98.3 | Rha II-1 | 101.5 |
| 2 | 83.3 | 2 | 72.3 | 2 | 83.3 | 2 | 72.2 | 2 | 83.3 | 2 | 72.3 | 2 | 83.3 | 2 | 72.2 |
| 3 | 77.7 | 3 | 72.5 | 3 | 77.7 | 3 | 72.4 | 3 | 77.7 | 3 | 72.5 | 3 | 76.8 | 3 | 72.4 |
| 4 | 71.7 | 4 | 74.4 | 4 | 71.1 | 4 | 74.0 | 4 | 71.7 | 4 | 74.4 | 4 | 71.2 | 4 | 74.0 |
| 5 | 77.5 | 5 | 69.6 | 5 | 77.5 | 5 | 69.8 | 5 | 77.5 | 5 | 69.6 | 5 | 77.5 | 5 | 69.8 |
| 6 | 62.8 | 6 | 18.0 | 6 | 62.8 | 6 | 17.9 | 6 | 62.8 | 6 | 18.0 | 6 | 62.8 | 6 | 17.9 |
| Glc IV-1 | 105.9 | | | Glc IV-1 | 105.8 | | | Glc IV-1 | 105.9 | | | Glc IV-1 | 105.9 | | |
| 2 | 76.6 | | | 2 | 76.6 | | | 2 | 76.6 | | | 2 | 76.6 | | |
| 3 | 78.1 | | | 3 | 78.1 | | | 3 | 78.1 | | | 3 | 78.1 | | |
| 4 | 71.5 | | | 4 | 71.5 | | | 4 | 71.5 | | | 4 | 71.7 | | |
| 5 | 78.3 | | | 5 | 78.3 | | | 5 | 78.3 | | | 5 | 77.7 | | |
| 6 | 62.8 | | | 6 | 62.8 | | | 6 | 62.8 | | | 6 | 62.8 | | |

Table 4. Distribution of Capsianosides in Previous Study of *Capsicum* Plants

| Capsianoside | A | B | C | D | E | F | G | H |
|---|---|---|---|---|---|---|---|---|
| *C. annuum* var. *fasciculatum* (Yatsubusa) | ○ | ○ | ○ | ○ | | | | |
| *C. annuum* var. *conoides* (Takanotsume) | | | ○ | ○ | | | | |
| *C. annuum* var. *grossum* (Shishitougarashi) | ○ | ○ | ○ | ○ | | | | |
| *C. annuum* var. *grossum* (Pimiento) | | | ○ | ○ | ○ | ○ | | |
| *C. annuum* var. *fasciculatum* (Yatsubusa, aerial parts) | ○ | ○ | ○ | ○ | | | ○ | ○ |
| *C. annuum* var. *conoides* (Takanotsume, aerial parts) | ○ | ○ | ○ | ○ | | | ○ | ○ |

in the TOCSY. The evidence from the $^{13}$C-NMR spectrum of **5** was also consistent with that of the $^1$H-NMR spectrum. Hence, the structure of **5** could be determined to be 3′-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl 6′*E*,10′*E*,14′*Z*-(3′*S*)-17′-hydroxygeranyllinalool 17′-*O*-[3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl 6*E*,10*E*,14*Z*-(3*S*)-geranyllinalool-16-oyl(16→3)]-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside.

Since previous study committed the mistake at the sugar combination owing to ambiguous assignments in the $^1$H–$^1$H COSY without HMBC technique, here, we have proposed the corrected structures as shown in Fig. 3 including previous *Capsicum* investigations.

Capsianosides II, I, A, and D *in vitro* inhibited angiotensin converting enzyme 3.6% at 0.77 mg, 22.1% at 1.97 mg, 31.1% at 1.15 mg and 32.8% at 2.47 mg, individually. Capsianoside D *in vitro* inhibited renin 49.7% at 20 mg/ml and 23.4% at 2 mg/ml. So, capsianosides are useful for the improvement and prevention of hypertension.[11] These acyclic diterpenes have been revealed rarely in nature. For efficient utilization of natural resources, we plan research of aerial parts and perform various pharmacological tests.

### 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 measured with JEOL-*α*-500 NMR spectrometers, and chemical shifts are given on a $\delta$ (ppm) scale with tetramethylsilane as an internal standard. The HR-ESI-MS were measured with JEOL JMS T-100LP spectrometer. 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$_2$SO$_4$, followed by heating. Column chromatography was carried out on Diaion HP-20 (Mitsubishi Chemical Ind.), MCI, ODS (Wako Pure Chemical Industries, Ltd., Fuji Silysia Chemical, Ltd., Japan), and silica gel 60 (spherical, 40—100 mm, and 230—400 mesh ASTM; crushed, 40—63 *μ*m, and 230—400 mesh ASTM, Kanto Chemical Co. Inc.).

**Plant Material** The dried fruits of hot red pepper *Capsicum annuum* L. were purchased in Kumamoto city, Japan.

**Extraction and Isolation** The dried hot red pepper (800 g) was extracted successively with 100% MeOH (three times). After evaporation of MeOH *in vacuo*, residue (225.77 g) was suspended in water to subjected to Diaion HP-20 using H$_2$O and MeOH (100%). The fraction (23.58 g) eluted with MeOH was subjected to MCI column chromatography (eluted with 50—100% MeOH). The fractions eluted with MeOH/H$_2$O were subsequently subjected to silica gel column chromatography (CHCl$_3$/MeOH/H$_2$O solvent system, 8:2:0.2—6:4:1), and ODS (Chromatorex) column chromatography (MeOH/H$_2$O solvent system, 55—85% MeOH). From the dried hot pepper, capsianosides I′ (19.7 mg), II (672.3 mg), III (200.5 mg), C (15.2 mg), D (40.4 mg), E (60.2 mg) and F (56.2 mg) were obtained.

Capsianoside III (**1**): An amorphous powder, $[\alpha]_D^{25}$ −28.6° (*c*=0.65, MeOH), HR-ESI-MS [M+Na]$^+$ *m/z* 1123.5127 (Calcd for C$_{50}$H$_{84}$O$_{26}$Na, 1123.5149). $^1$H-NMR (CD$_3$OD) $\delta$: 1.26 (3H, d, *J*=6.1 Hz, Rha H$_3$-6), 1.39, 1.61×2, 1.79 (each 3H, s, H$_3$-20, H$_3$-19, H$_3$-18, H$_3$-16), 1.60 (2H, m, H$_2$-4), 1.95—2.20 (10H, m, H$_2$-5, H$_2$-8, H$_2$-9, H$_2$-12, H$_2$-13), 3.20—4.00 (m, sugar), 4.21, 4.30 (each 1H, d, *J*=11.6 Hz, H$_2$-17), 4.35 (1H, d, *J*=7.3 Hz, Glc III H-1), 4.47, 4.56, 4.63 (each 1H, d, *J*=7.9 Hz, Glc I H-1, Glc II H-1, Glc IV H-1), 4.75 (1H, s, Rha H-1), 5.13×2 (each 1H, m, H-6, H-10), 5.22 (1H, br d, H-1b), 5.23 (1H, br d, H-1a), 5.39 (1H, t, H-14), 6.13 (1H, dd,

$J$=11.0, 18.3 Hz, H-2).

Capsianoside C (**2**): An amorphous powder, $[\alpha]_D^{25}$ −23.5° ($c$=0.41, MeOH), HR-ESI-MS $m/z$ 1749.8584 [M+Na]$^+$ (Calcd for C$_{82}$H$_{134}$O$_{38}$Na, 1749.8451). $^1$H-NMR (CD$_3$OD) $\delta$: 1.27 (3H, d, $J$=6.1 Hz, Rha H$_3$-6), 1.30 (3H, d, $J$=6.1 Hz, Rha H$_3$-6), 1.39×2, 1.61×3, 1.66, 1.77, 1.89 (each 3H, s, H$_3$-20, H$_3$-20′, H$_3$-18′, H$_3$-19, H$_3$-19′, H$_3$-18, H$_3$-16′, H$_3$-17), 1.95—2.20 (10H, m, H$_2$-5, H$_2$-8, H$_2$-9, H$_2$-12, H$_2$-13), 3.20—4.00 (m, sugar), 3.89 (1H, dd, $J$=3.1, 7.8 Hz, Rha I H-3), 4.12, 4.33 (each 1H, d, $J$=11.6 Hz, H-17′b, H-17′a), 4.21 (1H, d, $J$=7.9 Hz, Glc V H-1), 4.47×2, 4.56×2 (each 1H, d, $J$=7.9 Hz, Glc I H-1, Glc II H-1, Glc III H-1, Glc IV H-1), 4.53 (1H, m, H-13), 4.81 (1H, s, Rha II H-1), 4.90 (1H, s, Rha I H-1), 4.98 (1H, d, $J$=3.1 Hz, Rha I H-2), 5.12×3 (each 1H, m, H-6, H-6′, H-10′), 5.21 (1H, m, H-10), 5.22×2 (each 1H, d, $J$=11.6 Hz, H-1b, H-1′b), 5.23×2 (each 1H, d, $J$=17.1 Hz, H-1a, H-1′a), 5.40 (1H, t, H-14′), 6.12 (each 1H, dd, $J$=10.7, 18.0 Hz, H-2, H-2′), 6.71 (1H, dd, $J$=1.2, 8.6 Hz, H-14).

Capsianoside D (**3**): An amorphous powder, $[\alpha]_D^{25}$ −27.4° ($c$=0.19, MeOH), HR-ESI-MS $m/z$ 1749.8251 [M+Na]$^+$ (Calcd for C$_{82}$H$_{134}$O$_{38}$Na, 1749.8451). $^1$H-NMR (CD$_3$OD) $\delta$: 1.27 (3H, d, $J$=6.1 Hz, Rha H$_3$-6), 1.30 (3H, d, $J$=6.1 Hz, Rha H$_3$-6), 1.39×2, 1.60×3, 1.77, 1.89, 1.99 (each 3H, s, H$_3$-20, H$_3$-20′, H$_3$-18′, H$_3$-19, H$_3$-19′, H$_3$-18, H$_3$-16′, H$_3$-17), 1.95—2.20 (10H, m, H$_2$-5, H$_2$-8, H$_2$-9, H$_2$-12, H$_2$-13), 3.20—4.00 (m, sugar), 4.15, 4.32 (each 1H, d, $J$=11.6 Hz, H-17′b, H-17′a), 4.03 (1H, d, $J$=3.1 Hz, Rha I H-2), 4.23 (1H, d, $J$=7.9 Hz, Glc V H-1), 4.47×2, 4.56×2 (each 1H, d, $J$=7.3 Hz, Glc I H-1, Glc III H-1, Glc II H-1, Glc IV H-1), 4.53 (1H, m, H-13), 4.71 (1H, s, Rha II H-1), 4.84 (1H, s, Rha I H-1), 4.99 (1H, d, $J$=3.1, 9.8 Hz, Rha I H-3), 5.12×3 (each 1H, m, H-6, H-6′, H-10′), 5.21 (1H, m, H-10), 5.22×2 (each 1H, d, $J$=11.6 Hz, H-1b, H-1′b), 5.23×2 (each 1H, d, $J$=17.1 Hz, H-1a, H-1′a), 5.40 (1H, t, H-14′), 6.12×2 (each 1H, dd, $J$=10.7, 18.0 Hz, H-2, H-2′), 6.74 (1H, dd, $J$=1.2, 8.6 Hz, H-14).

Capsianoside E (**4**): An amorphous powder, $[\alpha]_D^{25}$ −33.4° ($c$=0.23, MeOH), HR-ESI-MS $m/z$ 1733.8426 [M+Na]$^+$ (Calcd for C$_{82}$H$_{134}$O$_{37}$Na, 1733.8502). $^1$H-NMR (CD$_3$OD) $\delta$: 1.27 (3H, d, $J$=6.1 Hz, Rha H$_3$-6), 1.27 (3H, d, $J$=6.1 Hz, Rha H$_3$-6), 1.39×2, 1.61×3, 1.63, 1.77, 1.86 (each 3H, s, H$_3$-20, H$_3$-20′, H$_3$-18′, H$_3$-19, H$_3$-19′, H$_3$-18, H$_3$-16′, H$_3$-17), 1.95—2.20 (10H, m, H$_2$-5, H$_2$-8, H$_2$-9, H$_2$-12, H$_2$-13), 3.20—4.00 (m, sugar), 3.88 (1H, dd, $J$=3.1, 9.2 Hz, Rha I H-3), 4.13, 4.33 (each 1H, d, $J$=11.6 Hz, H-17′b, H-17′a), 4.21 (1H, d, $J$=7.9 Hz, Glc V H-1), 4.47×2 (each 1H, d, $J$=7.3 Hz, Glc I H-1, Glc III H-1), 4.56×2 (each 1H, d, $J$=7.9 Hz, Glc II H-1, Glc IV H-1), 4.81 (1H, s, Rha II H-1), 4.90 (1H, s, Rha I H-1), 4.97 (1H, d, $J$=3.7 Hz, Rha I H-2), 5.13×4 (each 1H, m, H-6, H-6′, H-10, H-10′), 5.22×2 (each 1H, d, $J$=11.0 Hz, H-1b, H-1′b), 5.23×2 (each 1H, d, $J$=16.5 Hz, H-1a, H-1′a), 5.40 (1H, t, H-14′), 6.12×2 (each 1H, dd, $J$=10.7, 18.0 Hz, H-2, H-2′), 6.85 (1H, t, $J$=7.3 Hz, H-14).

Capsianoside F (**5**): An amorphous powder, $[\alpha]_D^{25}$ −33.2° ($c$=0.22, MeOH), HR-ESI-MS $m/z$ 1733.8427 [M+Na]$^+$ (Calcd for C$_{82}$H$_{134}$O$_{37}$Na, 1733.8502). $^1$H-NMR (CD$_3$OD) $\delta$: 1.27 (3H, d, $J$=6.1 Hz, Rha H$_3$-6), 1.30 (3H, d, $J$=6.1 Hz, Rha H$_3$-6), 1.39×2, 1.61×3, 1.63, 1.78, 1.87 (each 3H, s, H$_3$-20, H$_3$-20′, H$_3$-18′, H$_3$-19, H$_3$-19′, H$_3$-18, H$_3$-16′, H$_3$-17), 1.95—2.20 (10H, m, H$_2$-5, H$_2$-8, H$_2$-9, H$_2$-12, H$_2$-13), 3.20—4.00 (m, sugar), 4.16, 4.31 (each 1H, d, $J$=11.6 Hz, H-17′b, H-17′a), 4.02 (1H, d, $J$=3.1 Hz, Rha I H-2), 4.23 (1H, d, $J$=7.9 Hz, Glc V H-1), 4.48×2 (each 1H, d, $J$=7.3 Hz, Glc I H-1, Glc III H-1), 4.56×2 (each 1H, d, $J$=7.9 Hz, Glc II H-1, Glc IV H-1), 4.71 (1H, s, Rha II H-1), 4.84 (1H, s, Rha I H-1), 4.98 (1H, dd, $J$=3.1, 9.8 Hz, Rha I H-3), 5.13×4 (each 1H, m, H-6, H-6′, H-10, H-10′), 5.22×2 (each 1H, d, $J$=11.0 Hz, H-1b, H-1′b), 5.22×2 (each 1H, d, $J$=18.3 Hz, H-1a, H-1′a), 5.40 (1H, t, H-14′), 6.11×2 (each 1H, dd, $J$=11.0, 17.7 Hz, H-2, H-2′), 6.89 (1H, t, $J$=7.3 Hz, H-14).

**Acid Hydrolysis of 1, 2 and 4 with 1 N HCl–H$_2$O** A solution of **1** (9.9 mg), **2** (2.1 mg) and **4** (2.1 mg) in 1 N HCl–H$_2$O were heated under reflux for 2 h. The reaction mixture eluted with H$_2$O and MeOH successively was subjected to Amberlite IRA-400. The D-glucose and L-rhamnose in the aqueous layer were detected on TLC (CHCl$_3$ : MeOH : acetone : H$_2$O= 3 : 3 : 3 : 1) by comparison of $Rf$ value with those of an authentic sample.

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