Acyclic Diterpene Glycosides, Capsianosides VIII, IX, X, XIII, XV and XVI from the Fruits of Paprika *Capsicum annuum* L. var. *grossum* Bailey and Jalapeño *Capsicum annuum* L. var. *annuum*

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Paprika and Jalapeño are used as vegetables and spices. We have obtained six new acyclic diterpene glycosides, called capsianosides XIII (2), XV (3), IX (4), XVI (5), X (6) and VIII (7) together with known capsianoside II (1) from the fruits of the Paprika and Jalapeño. The structures of these compounds have been elucidated by the ^{1}H- and ^{13}C-NMR spectra and two-dimensional NMR methods.

Key words Paprika; Jalapeño; capsianoside; acyclic diterpene glycoside; Solanaceae; *Capsicum annuum*

Paprika is known for its high vitamin C content and has been isolated from Hungarian paprika in large amounts.[1] Jalapeño is a stimulating spice which contains capsaicin and related compounds in its fruits and veins. Carotenoids,[2,3] lipids and capsaicin[4] have been well studied in the *Capsicum* species. Now our study has focused on the water-soluble constituents of Paprika and Jalapeño fruits. Previous studies in this laboratory led to the isolation of novel acyclic diterpene glycosides, capsianoside A—H and I—VI from *Capsicum* plants.[5] In this study, we isolated six new acyclic diterpene glycosides termed capsianosides XIII (**2**), XV (**3**), IX (**4**), XVI (**5**), X (**6**) and VIII (**7**) along with one known compound.[5] Since the known compound, capsianoside II[5] had an error in sugar sequence, we revised it. Distribution of these new compounds is summarized in Table 1.

Capsianoside II (**1**), an amorphous powder, $[\alpha]_D$ −31.2°, showed peaks due to $[M+Na]^+$ at *m/z* 1108, [*m/z* 1108-deoxyhexose]$^+$ at 962 and [*m/z* 962-hexose-deoxyhexose]$^+$ at 654 in positive FAB-MS and gave a molecular formula $C_{50}H_{84}O_{25}Na$ at *m/z* 1107.5374 by HR-FAB-MS. Moreover, the ^{1}H-NMR spectrum of **1** disclosed the presence of four methyl groups at δ 1.39 (3H, s), 1.61 (6H, s) and 1.77 (3H, s), three olefinic protons at δ 5.22 (1H, br d, J=11.0 Hz), 5.23 (1H, br d, J=18.3 Hz) and 6.12 (1H, dd, J=11.0, 18.3 Hz) arising from a mono-substituted double bond, three olefinic protons at δ 5.12 (2H, m) and 5.40 (1H, t) adjacent to methylene group and seven methylene groups at δ 1.61 (2H, m), 1.95—2.20 (10H, m), 4.13 (1H, d, J=11.6 Hz) and 4.32 (1H, d, J=11.6 Hz). The ^{13}C-NMR spectrum of **1** as listed in Table 2 showed total twenty carbon signals composed of three tri-substituted double bonds at δ 125.8, 125.9, 131.2, 132.4, 135.5 and 136.0, a mono-substituted double bond at δ 116.0 and 144.4, three methyl groups at δ 16.3 (2×C), 23.4 and seven methylene groups. Since all the signals due to the aglycone moiety of capsianoside II (**1**) in the ^{1}H- and ^{13}C-NMR spectra were identical with those of capsianoside A reported previously,[5] the configuration at C-3 was characterized as *S*. The above NMR signals were identical with those of the aglycone moiety, 17-hydroxy-6*E*,10*E*,14*Z*-(3*S*)-geranyl-linalool, of capsianoside II previously reported.[5] Other sapogenols of capsianosides XIII (**2**), IX (**4**), XVI (**5**), X (**6**) and VIII (**7**) were also coincident with that of **1**. The ^{1}H-NMR spectrum due to the sugar part of **1** showed signals ascribable to 3 mol of hexosyl and 2 mol of deoxyhexosyl moieties from the evidence of signals ascribable to five anomeric protons at δ 4.21 (1H, d, J=7.3 Hz), 4.47 (1H, d, J=7.3 Hz), 4.56 (1H, d, J=7.3 Hz), 4.71 (1H, s) and 4.83 (1H, s). The ^{13}C-NMR spectra also exhibited five anomeric carbon signals at δ 105.9, 102.7, 102.2, 101.6 and 98.3. The following HMBC correlations shown in Fig. 1 revealed the sugar connections respectively: correlations between the signal at δ_H 4.47 (1H, d, J=7.3 Hz) and the signal at δ_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 δ_H 4.56 (1H, d, J=7.3 Hz) and the signal at δ_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 δ_H 4.21 (1H, d, J=7.3 Hz) and the signal at δ_C 67.8 (aglycone C-17) exhibiting that the Glc IV H-1 was linked to the C-17 of the aglycone; the signal at δ_H 4.83 (1H, s) and the signal at δ_C 79.3 (Glc IV C-4) indicating that the Rha I H-1 was bound to the Glc IV C-4; the signal at δ_H 4.71 (1H, s) and the signal at δ_C 66.9 (Glc IV C-6) showing the Rha II H-1 to be linked to the Glc IV C-6. The sugar structure of **1** previously reported should be revised. The structure of **1** was determined to be 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl 17-hydroxy-6*E*,10*E*,14*Z*-(3*S*)-geranyllinalool 17-*O*-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside.

Capsianoside XIII (**2**), an amorphous powder, $[\alpha]_D$ −38.9°, showed a peak due to $[M+Na]^+$ at *m/z* 1108 in positive FAB-MS and gave a molecular formula $C_{50}H_{84}O_{25}Na$ at *m/z* 1107.5350 by HR-FAB-MS. Compound **2** was constituted of 3 mol of hexosyl and 2 mol of deoxyhexosyl moieties based on the signals of anomeric protons at δ 4.20 (1H,

Table 1. Distribution of Capsianosides in Paprika and Jalapeño

Capsianoside	II (**1**)	VIII (**7**)	IX (**4**)	X (**6**)	XIII (**2**)	XV (**3**)	XVI (**5**)
C. annuum L. var. *grossum* (Paprika)	○		○	○	○	○	○
C. annuum L. var. *annuum* (Jalapeño)	○	○	○	○	○		

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d, J=7.3 Hz), 4.39 (1H, d, J=7.3 Hz), 4.41 (1H, d, J=7.3 Hz), 4.71 (1H, s) and 4.82 (1H, s). Moreover, the ^{13}C-NMR spectra exhibited five anomeric carbon signals at δ 104.6, 102.7, 102.2, 101.6 and 99.4. Compared with the NMR signals of **1**, the signal due to the C-4 of Glc I appeared at δ_C 81.0 (+9.6 ppm shift), while the signals due to C-3 and C-5 shifted by −1.5 and −1.6 ppm, respectively. No glycosylation shift at C-2 in Glc I was observed, however. The signals due to the sugar moiety bound to C-17-OH were superimposable on those of compound **1**. The HMBC correlations between the signal at δ_H 4.39 (1H, d, J=7.3 Hz) and the signal at δ_C 81.5 (aglycone C-3), and between the signal at δ_H 4.41 (1H, d, J=7.3 Hz) and that at δ_C 81.0 (Glc I C-4) clarified its sugar connections to be clear. Thus, it was suggested that the sugar part is constituted of 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl residues.

Capsianoside XV (**3**), an amorphous powder, $[\alpha]_D$ −36.9°, showed peaks due to $[M+Na]^+$ at m/z 1123, [m/z 1123-hexose]$^+$ at 961, [m/z 961-deoxyhexose]$^+$ at 815, [m/z 815-deoxyhexose]$^+$ at 669 and [m/z 669-hexose]$^+$ at 507 in positive FAB-MS and gave a molecular formula $C_{50}H_{84}O_{26}Na$ at m/z 1123.5298 by HR-FAB-MS. Compound **3** displayed the signals from three hexosyl and two deoxyhexosyl anomeric protons [δ 4.21 (1H, d, J=7.3 Hz), 4.39 (1H, d, J=7.9 Hz), 4.41 (1H, d, J=7.9 Hz), 4.71 (1H, s) and 4.82 (1H, s)] in the ^{1}H-NMR spectrum. The ^{13}C-NMR spectrum also exhibited five anomeric carbon signals at δ 104.4, 102.5, 102.0, 101.4 and 99.2. In a comparative study of the NMR signals with those of capsianoside II,[5] the signal due to Glc I C-4 to appear at δ 80.8 (+9.5 ppm shift), while the signals due to C-3 and C-5 shifted −0.2 and −1.4 ppm, respectively. But no glycosylation shift at C-2 was observed, suggesting that the sugar part is constituted with 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl residue. The signals ascribable to the sugar moiety were superimposable on those of **2**, however, the signals due to the aglycone moiety were different. In **3**, the signal due to one hydroxymethyl group appeared at δ 4.09 (2H, s) instead of one methyl group in **2**. The signals due to C-6, C-7 and C-8 in **3** appeared at δ 129.0, 139.2 and 36.0, respectively, showing hydroxylation shifts[5] by +3.2, +3.7 and −4.7 ppm, respectively. From the above evidence, a methyl group at C-19 in **2** changed to a hydroxymethyl group in **3**.

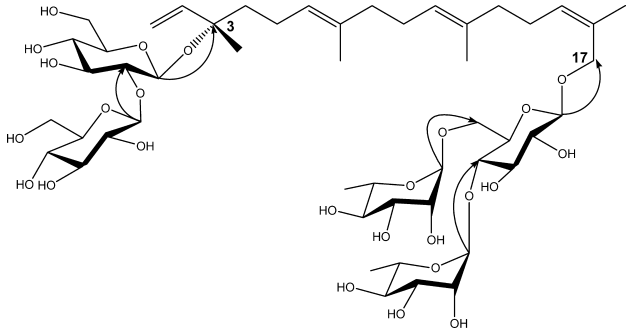


Fig. 1. Key HMBC of **1**

Capsianoside IX (**4**), an amorphous powder, $[\alpha]_D$ −32.7°, showed a peak due to $[M+Na]^+$ at m/z 1269 in positive FAB-MS and gave a molecular formula $C_{56}H_{94}O_{30}Na$ at m/z 1269.5649 by HR-FAB-MS. Compound **4** was shown to be composed of 4 mol of hexosyl and 2 mol of deoxyhexosyl moieties from evidence due to anomeric proton signals at δ 4.20 (1H, d, J=7.9 Hz), 4.41 (1H, d, J=7.9 Hz), 4.50 (1H, d, J=7.9 Hz), 4.58 (1H, d, J=7.9 Hz), 4.71 (1H, s) and 4.83 (1H, s). Moreover, the ^{13}C-NMR spectrum exhibited six anomeric carbon signals at δ 106.0, 104.6, 102.7, 102.2, 101.6 and 98.3. By comparing the ^{13}C-NMR signals with those of **1**, it was recognized that the signal of Glc I C-4 shifted to δ_C 80.8 (+9.4 ppm shift), while the signals due to C-3 and C-5 shifted by −0.2 and −1.0 ppm, respectively. The following HMBC showed the connections to the respective sugar: correlations between the signal at δ_H 4.50 (1H, d, J=7.9 Hz) and the signal at δ_C 82.1 (aglycone C-3) showing the Glc I H-1 to be linked to the C-3 of the aglycone; the signal at δ_H 4.58 (1H, d, J=7.9 Hz) and that at δ_C 82.8 (Glc I C-2) indicating the Glc II H-1 to be linked to the C-2 of the Glc I; the signal at δ_H 4.41 (1H, d, J=7.9 Hz) and that at δ_C 80.8 (Glc I C-4) showing the Glc III H-1 to be linked to C-4 of Glc I. Therefore, the 3-*O*-sugar part was constituted with β-D-glucopyranosyl-(1→4)-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl residue.

Capsianoside XVI (**5**), an amorphous powder, $[\alpha]_D$ −35.5°, showed a peak due to $[M+Na]^+$ at m/z 1431.6107 (Calcd for $C_{62}H_{104}O_{35}Na$, 1431.6256) in HR-ESI-MS. Compound **5** showed five hexosyl and two deoxyhexosyl anomeric proton signals at δ 4.20 (1H, d, J=7.3 Hz), 4.41 (1H, d, J=7.9 Hz), 4.51 (1H, d, J=7.9 Hz), 4.58 (1H, d, J=7.9 Hz), 4.58 (1H, d, J=7.9 Hz), 4.72 (1H, s) and 4.84 (1H, s). The ^{13}C-NMR spectrum also exhibited seven anomeric carbon signals at δ 106.0, 105.6, 104.6, 102.4, 102.2, 101.6 and 98.3. The HMBC spectrum revealed the respective connectivities: the Glc I H-1 at δ_H 4.51 (1H, d, J=7.9 Hz) and the C-3 at δ_C 82.1 of the aglycone; the Glc II H-1 at δ_H 4.58 (1H, d, J=7.9 Hz) and the Glc I C-2 δ_C 82.9;

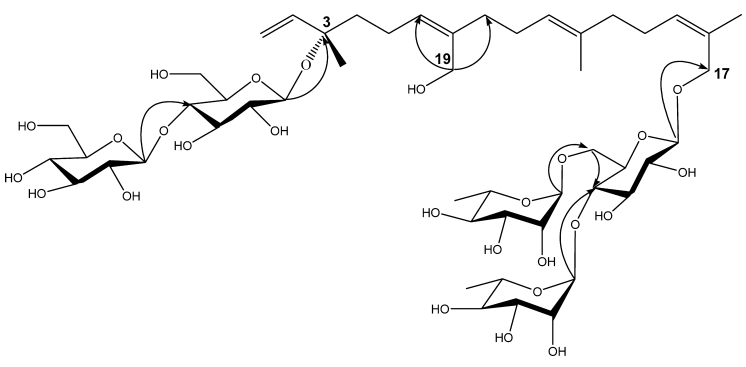


Fig. 2. Key HMBC of **3**

Table 2. ^{13}C-NMR Data of Compounds **1**, **2**, **3**[a], **4** and **5** in CD_3OD (125 MHz)

Position	1	2	3	4	5	Position	1	2	3	4	5	Position	1	2	3	4	5
1	116.0	115.8	115.6	116.0	116.0	Glc I-1	98.3	99.4	99.2	98.3	98.3	Glc V-1					105.6
2	144.4	144.4	144.1	144.4	144.4	2	83.3	74.9	74.8	82.8	82.9	2					74.9
3	82.1	81.5	81.3	82.1	82.1	3	77.5	76.6	76.4	76.5	76.8	3					78.2
4	43.0	42.6	42.8	43.0	43.1	4	71.4	81.0	80.8	80.8	80.9	4					71.4
5	23.6	23.5	23.6	23.6	23.6	5	77.7	76.1	76.1	76.7	76.7	5					77.6
6	125.9	125.8	129.0	125.8	125.8	6	62.7	62.2	62.0	62.7	62.7	6					62.8
7	135.5	135.5	139.2	135.5	135.5	Glc II-1	105.9			106.0	106.0	Rha I-1	102.7	102.7	102.5	102.7	102.4
8	40.8	40.7	36.0	40.8	40.8	2	76.5			76.0	76.6	2	72.3	71.4	71.3	72.2	72.2
9	27.7	27.6	27.9	27.7	27.7	3	78.2			78.0	78.3	3	72.5	72.4	72.3	72.4	71.6
10	125.8	125.9	125.7	125.9	125.9	4	71.7			72.3	72.3	4	73.8	74.0	73.7	73.8	83.3
11	136.0	135.9	135.3	136.0	136.0	5	78.1			77.5	78.0	5	69.8	69.8	69.7	69.8	69.3
12	40.8	40.9	40.9	40.8	40.9	6	62.7			62.4	62.4	6	17.9	17.9	17.9	17.9	18.0
13	27.3	27.3	27.4	27.3	27.3	Glc III-1		104.6	104.4	104.6	104.6	Rha II-2	101.6	101.6	101.4	101.6	101.6
14	131.2	131.2	131.1	131.2	131.3	2		75.2	75.1	74.9	75.3	2	72.2	72.2	72.2	72.3	72.4
15	132.4	132.5	132.2	132.4	132.4	3		77.9	77.8	77.9	78.3	3	72.4	72.5	72.2	72.5	72.4
16	21.9	21.9	22.0	21.9	21.9	4		72.3	72.4	71.4	72.3	4	74.0	73.8	74.0	74.0	74.0
17	67.8	67.8	67.6	67.8	67.8	5		78.1	78.0	77.5	77.9	5	70.6	70.6	70.5	70.6	69.8
18	16.3	16.3	16.4	16.3	16.3	6		62.5	62.4	62.1	62.2	6	18.2	18.2	18.3	18.2	18.2
19	16.3	16.1	59.9	16.3	16.3	Glc IV-1	102.2	102.2	102.0	102.2	102.2						
20	23.4	23.3	23.2	23.5	23.5	2	75.2	74.9	74.8	75.2	75.5						
						3	76.7	76.8	76.7	76.5	76.8						
						4	79.3	79.4	79.2	79.3	79.1						
						5	75.4	75.4	75.3	75.4	76.1						
						6	66.9	66.9	66.8	66.9	66.9						

a) Spectra recorded in CD_3OD at 100.4 MHz.

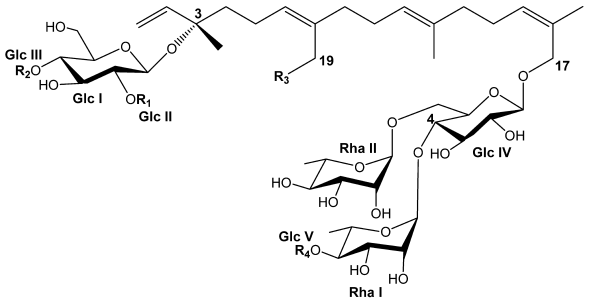
the Glc III H-1 at δ_H 4.41 (1H, d, J=7.9 Hz) and the Glc I C-4 at δ_C 80.9; the Glc IV H-1 at δ_H 4.20 (1H, d, J=7.3 Hz) and the C-17 at δ_C 67.8 of the aglycone; the Rha I H-1 at δ_H 4.84 (1H, s) and the Glc IV C-4 δ_C 79.1; the Rha II H-1 at δ_H 4.72 (1H, s) and the Glc IV C-6 δ_C 66.9; the Glc V H-1 at δ_H 4.58 (1H, d, J=7.9 Hz) and the Rha I C-4 δ_C 83.3. This suggested that the sugar part was constituted with 3-*O*-β-D-glucopyranosyl-(1→4)-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl residue and another branched sugar part was identical to 17-*O*-β-D-glucopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranosyl residue.

Capsianoside X (**6**), an amorphous powder, $[\alpha]_D$ −16.7°, showed a peak due to $[M+Na]^+$ at *m/z* 1286 in positive FAB-MS and gave a molecular formula $C_{56}H_{94}O_{31}Na$ at *m/z* 1285.5880 by HR-FAB-MS. Compound **6** displayed five hexosyl and one deoxyhexosyl anomeric proton signals at δ 4.36 (1H, d, J=7.9 Hz), 4.42 (1H, d, J=7.9 Hz), 4.50 (1H, d, J=7.3 Hz), 4.58 (1H, d, J=7.3 Hz), 4.62 (1H, d, J=7.9 Hz) and 4.75 (1H, s). The ^{13}C-NMR spectrum also exhibited six anomeric carbon signals at δ 106.1, 104.8, 104.6, 102.1, 101.1 and 98.3. The following HMBC correlations were observed between the signal at δ_H 4.50 (1H, d, J=7.3 Hz) and the signal at δ_C 82.1 (aglycone C-3): the Glc I H-1 linked to the C-3 of the aglycone; the signal at δ_H 4.58 (1H, d, J=7.3 Hz) and the signal at δ_C 82.9 (Glc I C-2): the Glc II H-1 linked to the C-2 of the Glc I; the signal at δ_H 4.42 (1H, d, J=7.9 Hz) and the signal at δ_C 80.8 (Glc I C-4): the Glc III H-1 linked to the C-4 of the Glc I; the signal at δ_H 4.36 (1H, d, J=7.9 Hz) and the signal at δ_C 68.3 (aglycone C-17): the Glc IV H-1 linked to the C-17 of the aglycone; the signal at δ_H 4.62 (1H, d, J=7.9 Hz) and the signal at δ_C 82.1 (Glc IV C-2): (1→2) linkage between the two glucoses. The linkage of rhamnose to the Glc IV C-6 was also determined by the HMBC correlation between the signal at δ_H 4.75 (1H, s) and the signal at δ_C 67.7 (Glc IV C-6). From the above evidence, **6** was determined as 3-*O*-β-D-glucopyranosyl-(1→4)-[β-D-glucopyranosyl-(1→2)]-β-D-glucopyranosyl 17-hydroxy-6*E*,10*E*,14*Z*-(3*S*)-geranyllinalool 17-*O*-β-D-glucopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside.

Capsianoside VIII (**7**), an amorphous powder, $[\alpha]_D$ −20.4°, showed a peak due to $[M+Na]^+$ at *m/z* 1124 in positive FAB-MS and gave a molecular formula $C_{50}H_{84}O_{26}Na$ at *m/z* 1123.5348 by HR-FAB-MS. Compound **7** showed 4 mol of hexosyl and one deoxyhexosyl anomeric proton signals at δ 4.35 (1H, d, J=7.9 Hz), 4.39 (1H, d, J=7.9 Hz), 4.41 (1H, d, J=7.9 Hz), 4.63 (1H, d, J=7.9 Hz) and 4.75 (1H, s). The ^{13}C-NMR spectrum exhibited five anomeric carbon signals at δ 104.8, 104.6, 102.1, 101.1 and 99.3. The sequence of the sugar part was determined by the HMBC spectrum to provide the following connections: correlations between the signal at δ_H 4.39 (1H, d, J=7.9 Hz) and the signal at δ_C 81.5 (aglycone C-3) indicating the Glc I H-1 to be linked to the C-3 of the aglycone; the signal at δ_H 4.41 (1H, d, J=7.9 Hz) and the signal at δ_C 81.0 (Glc I C-4) indicating the Glc III H-1 to be linked to the C-4 of the Glc I; the signal at δ_H 4.35 (1H, d, J=7.9 Hz) and the signal at δ_C 68.3 (aglycone C-17) indicating the Glc IV H-1 to be linked to the C-17 of the aglycone; the signal at δ_H 4.63 (1H, d, J=7.9 Hz) and the signal at δ_C 82.0 (Glc IV C-2) suggesting the two glucosyl moieties have a (1→2) linkage; the rhamnosyl H-1 to the C-6 of Glc IV was also determined by the HMBC correlation between the signal at δ_H 4.75 (1H, s) and the signal at δ_C 67.6 (Glc IV C-6). From the above evidence, **7** was determined as 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl 17-hydroxy-6*E*,10*E*,14*Z*-(3*S*)-geranyllinalool 17-*O*-β-D-glucopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→6)]-β-D-glucopyranoside.

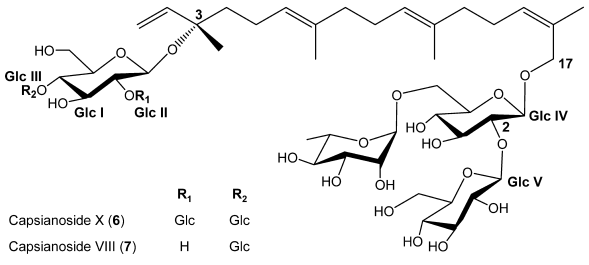
Table 3. ^{13}C-NMR Data of Compounds **6** and **7** in CD_3OD (125 MHz)

Position	6	7	Position	6	7	Position	6	7
1	116.0	115.8	Glc I-1	98.3	99.3	Glc IV-1	101.1	101.1
2	144.4	144.4	2	82.9	74.9	2	82.1	82.0
3	82.1	81.5	3	76.1	76.6	3	77.5	77.7
4	43.0	42.6	4	80.8	81.0	4	71.4	71.5
5	23.6	23.5	5	76.7	76.1	5	76.5	76.6
6	126.0	125.8	6	62.8	62.4	6	67.7	67.6
7	135.4	135.4	Glc II-1	106.1		Glc V-1	104.8	104.8
8	40.8	40.7	2	76.6		2	76.0	75.9
9	27.7	27.6	3	77.8		3	78.0	78.0
10	125.8	125.9	4	71.4		4	71.4	71.4
11	136.0	135.9	5	77.8		5	77.8	77.8
12	40.9	40.8	6	62.1		6	62.8	62.8
13	27.3	27.2	Glc III-1	104.6	104.6	Rha 1	102.1	102.1
14	131.2	131.2	2	74.9	74.9	2	72.2	72.1
15	132.4	132.4	3	78.0	78.0	3	72.4	72.4
16	21.9	22.0	4	71.5	71.4	4	74.0	74.0
17	68.3	68.3	5	78.4	78.2	5	69.7	69.7
18	16.3	16.2	6	62.4	62.2	6	18.1	18.1
19	16.3	16.1						
20	23.4	23.3						



	R_1	R_2	R_3	R_4
Capsianoside II* (**1**)	Glc	H	H	H
Capsianoside XIII (**2**)	H	Glc	H	H
Capsianoside XV (**3**)	H	Glc	**OH**	H
Capsianoside IX (**4**)	Glc	Glc	H	H
Capsianoside XVI (**5**)	Glc	Glc	H	**Glc**

* : Revised structure



	R_1	R_2
Capsianoside X (**6**)	Glc	Glc
Capsianoside VIII (**7**)	H	Glc

Fig. 3. Structures of Capsianosides

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 and JMX-GX 400 NMR spectrometers, and chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. The FAB-MS were measured with a JEOL JMS-DX303HF spectrometer and taken in a glycerol matrix containing NaI. HR-ESI-MS were measured with a 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_2SO_4, followed by heating. Column chromatography was carried out on a Diaion HP-20 (Mitsubishi Chemical Ind.), 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 mm, and 230—400 mesh ASTM, Kanto Chemical Co. Inc.).

Plant Material The fruits of Paprika *Capsicum annuum* L. var. *grossum* Bailey and Jalapeño *Capsicum annuum* L. var. *annuum* were harvested at Nagao Farm, Kumamoto prefecture in Japan.

Extraction and Isolation The fresh Paprika (3.15 kg) was extracted successively with 100% MeOH (three times). After evaporation of MeOH *in vacuo*, the residue (179.55 g) was suspended in water and subjected to Diaion HP-20 using H_2O and MeOH (100%). The fraction (5.39 g) eluted with MeOH was subjected to ODS (Wako) column chromatography (eluted with 50—80% MeOH). The fractions eluted with MeOH/H_2O were subsequently subjected to silica gel column chromatography ($CHCl_3$/MeOH/H_2O solvent system, 7 : 3 : 0.3—6 : 4 : 1), and ODS (Chromatorex) column chromatography (MeOH/H_2O solvent system, 55—80% MeOH). From the Paprika, capsianoside II (87.2 mg), IX (183.6 mg), X (25.8 mg), XIII (28.6 mg), XV (28.5 mg) and XVI (16.8 mg) were obtained.

The fresh Jalapeño (6.8 kg) was extracted with 100% MeOH. After evaporation of MeOH *in vacuo*, the residue (252 g) was suspended in water and subjected to Diaion HP-20 using H_2O, MeOH (100%) and acetone. The fraction (5 g from 19.11 g) eluted with MeOH was subjected to ODS (Wako) column chromatography (eluted with 50—100% MeOH). The fractions eluted with MeOH/H_2O were subsequently subjected to silica gel column chromatography ($CHCl_3$/MeOH/H_2O solvent system, 9 : 1 : 0.1—6 : 4 : 1). From the Jalapeño, we obtained capsianoside II (55.8 mg), VIII (42.1 mg), IX (420.5 mg), X (25.9 mg), XIII (87.8 mg).

Capsianoside II (1) An amorphous powder, $[\alpha]_D^{25}$ −31.2° (c=0.19, MeOH), positive FAB-MS m/z: 1108 $[M+Na]^+$, 962, 654; positive HR-FAB-MS $[M+Na]^+$ m/z 1107.5374 (Calcd for $C_{50}H_{84}O_{25}Na$, 1107.5199). ^{1}H-NMR (CD_3OD) δ: 1.26 (3H, d, J=5.5 Hz, Rha H_3-6), 1.27 (3H, d, J=6.1 Hz, Rha H_3-6), 1.39, 1.61×2, 1.77 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-16), 1.61 (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), 4.13, 4.32 (each 1H, d, J=11.6 Hz, H_2-17), 4.21, 4.47, 4.56 (each 1H, d, J=7.3 Hz, Glc H-1), 4.71, 4.83 (each 1H, s, Rha H-1), 5.12×2 (each 1H, m, H-6, H-10), 5.22, 5.23 (each 1H, br d, H_2-1), 5.40 (1H, t, H-14), 6.12 (1H, dd, J=11.0, 18.3 Hz, H-2).

Capsianoside XIII (2) An amorphous powder, $[\alpha]_D^{25}$ −38.9° (c=0.5, MeOH), positive FAB-MS m/z: 1108 $[M+Na]^+$; positive HR-FAB-MS $[M+Na]^+$ m/z 1107.5350 (Calcd for $C_{50}H_{84}O_{25}Na$, 1107.5199). ^{1}H-NMR (CD_3OD) δ: 1.26 (3H, d, J=6.1 Hz, Rha H_3-6), 1.27 (3H, d, J=6.7 Hz, Rha H_3-6), 1.37, 1.60×2, 1.77 (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), 4.13, 4.32 (each 1H, d, J=11.6 Hz, H_2-17), 4.20, 4.39, 4.41 (each 1H, d, J=7.9 Hz, Glc H-1), 4.71, 4.82 (each 1H, s, Rha H-1), 5.11×2 (each 1H, m, H-6, H-10), 5.20, 5.23 (each 1H, br d, H_2-1), 5.40 (1H, t, H-14), 5.93 (1H, dd, J=11.0, 17.7 Hz, H-2).

Capsianoside XV (3) An amorphous powder, $[\alpha]_D^{26}$ −36.9° (c=0.67, MeOH), positive FAB-MS m/z: 1123 $[M+Na]^-$, 961, 815, 669, 507; positive HR-FAB-MS $[M+Na]^+$ m/z 1123.5298 (Calcd for $C_{50}H_{84}O_{26}Na$, 1123.5149). ^{1}H-NMR (CD_3OD) δ: 1.26 (3H, d, J=6.8 Hz, Rha H_3-6), 1.27 (3H, d, J=5.5 Hz, Rha H_3-6), 1.38, 1.61, 1.77 (each 3H, s, H_3-20, H_3-18, H_3-16), 1.63 (2H, m, H_2-4), 1.99—2.20 (10H, m, H_2-5, H_2-8, H_2-9, H_2-12, H_2-13), 3.20—4.01 (m, sugar), 4.09 (2H, s, H_2-19), 4.13, 4.32 (each 1H, d, J=11.6 Hz, H_2-17), 4.21 (1H, d, J=7.3 Hz, Glc H-1), 4.39, 4.41 (each 1H, d, J=7.9 Hz, Glc H-1), 4.71, 4.82 (each 1H, s, Rha H-1), 5.14 (1H, m, H-10), 5.20, 5.24 (each 1H, br d, H_2-1), 5.29 (1H, t, H-6), 5.40 (1H, t, H-14), 5.94 (1H, dd, J=11.0, 17.6 Hz, H-2).

Capsianoside IX (4) An amorphous powder, $[\alpha]_D^{25}$ −32.7° (c=0.5, MeOH), positive FAB-MS m/z: 1269 $[M+Na]^+$; positive HR-FAB-MS $[M+Na]^+$ m/z 1269.5649 (Calcd for $C_{56}H_{94}O_{30}Na$, 1269.5728). ^{1}H-NMR (CD_3OD) δ: 1.26 (3H, d, J=5.5 Hz, Rha H_3-6), 1.27 (3H, d, J=6.1 Hz, Rha H_3-6), 1.38, 1.61×2, 1.77 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-16), 1.61 (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), 4.13, 4.32 (each 1H, d, J=11.6 Hz, H_2-17), 4.20, 4.41, 4.50, 4.58 (each 1H, d, J=7.9 Hz, Glc H-1), 4.71, 4.83 (each 1H, s, Rha H-1), 5.12×2 (each 1H, m, H-6, H-10), 5.21, 5.24 (each 1H, br d, H_2-1), 5.40 (1H, t, H-14), 6.13 (1H, dd, J=11.0, 18.3 Hz, H-2).

Capsianoside XVI (5) An amorphous powder, $[\alpha]_D^{26}$ −35.5° (c=0.88, MeOH), HR-ESI-MS $[M+Na]^+$ m/z 1431.6107 (Calcd for $C_{62}H_{104}O_{35}Na$, 1431.6256). ^{1}H-NMR (CD_3OD) δ: 1.27 (3H, d, J=6.1 Hz, Rha H_3-6), 1.33 (3H, d, J=6.1 Hz, Rha H_3-6), 1.38, 1.61×2, 1.77 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-16), 1.61 (2H, m, H_2-4), 1.99—2.20 (10H, m, H_2-5, H_2-8, H_2-9, H_2-12, H_2-13), 3.20—4.10 (m, sugar), 4.13, 4.33 (each 1H, d, J=11.6 Hz, H_2-17), 4.20 (1H, d, J=7.3 Hz, Glc H-1), 4.41, 4.51, 4.58×2 (each 1H, d, J=7.9 Hz, Glc H-1), 4.72, 4.84 (each 1H, s, Rha H-1), 5.12×2 (each 1H, m,

H-6, H-10), 5.21, 5.24 (each 1H, br d, H_2-1), 5.40 (1H, t, H-14), 6.13 (1H, dd, J=10.4, 17.7 Hz, H-2).

Capsianoside X (6) An amorphous powder, $[\alpha]_D^{25}$ −16.7° (c=0.18, MeOH), positive FAB-MS m/z: 1286 $[M+Na]^+$; positive HR-FAB-MS $[M+Na]^+$ m/z 1285.5880 (Calcd for $C_{56}H_{94}O_{31}Na$, 1285.5677). ^{1}H-NMR (CD_3OD) δ: 1.27 (3H, d, J=6.1 Hz, Rha H_3-6), 1.38, 1.61×2, 1.79 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-16), 1.99—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), 4.22 (1H, d, J=11.6 Hz, H-17), 4.29 (1H, d, J=11.0 Hz, H-17), 4.36, 4.42 (each 1H, d, J=7.9 Hz, Glc H-1), 4.50, 4.58 (each 1H, d, J=7.3 Hz, Glc H-1), 4.62 (each 1H, d, J=7.9 Hz, Glc H-1), 4.75 (1H, s, Rha H-1), 5.12×2 (each 1H, m, H-6, H-10), 5.21 (1H, br d, H-1), 5.24 (1H, br d, H-1), 5.39 (1H, t, H-14), 6.12 (1H, dd, J=11.0, 18.3 Hz, H-2).

Capsianoside VIII (7) An amorphous powder, $[\alpha]_D^{25}$ −20.4° (c=0.19, MeOH), positive FAB-MS m/z: 1124 $[M+Na]^+$; positive HR-FAB-MS $[M+Na]^+$ m/z 1123.5348 (Calcd for $C_{50}H_{84}O_{26}Na$, 1123.5149). ^{1}H-NMR (CD_3OD) δ: 1.26 (3H, d, J=6.1 Hz, Rha H_3-6), 1.37, 1.60, 1.61, 1.79 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-16), 1.60 (2H, m, H_2-4), 1.99—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 (1H, d, J=11.6 Hz, H-17), 4.29 (1H, d, J=11.0 Hz, H-17), 4.35, 4.39, 4.41, 4.63 (each 1H, d, J=7.9 Hz, Glc H-1), 4.75 (1H, s, Rha H-1), 5.12×2 (each 1H, m, H-6, H-10), 5.21 (1H, br d, H-1), 5.25 (1H, br d, H-1), 5.38 (1H, t, H-14), 5.93 (1H, dd, J=11.0, 17.7 Hz, H-2).

Acid Hydrolysis of 2 and 3 with 1 N HCl A solution of **2** (4.4 mg) and **3** (2.5 mg) in 1 N HCl was heated under reflux for 2 h. The reaction mixture eluted with H_2O and MeOH successively was subjected to Amberlite IRA-400. The aqueous layer was subjected to HPLC analysis under the following conditions: HPLC column, COSMOSIL Sugar-D, 4.6 mm i.d.×250 mm (Nacalai Tesque, Inc., Tokyo, Japan); detector, JASCO OR-2090; pump, JASCO PU-2080; solvent, 80% CH_3CN; column oven, Co-2060 plus; column temperature, 30 °C. Identification of D-glucose and L-rhamnose in the aqueous layer was carried out by comparison of retention time with those of an authentic sample: D-glucose, t_R 12.30 min; L-rhamnose, t_R 6.27 min.

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