Novel Acyclic Diterpene Glycosides, Capsianosides A—F and I—V from *Capsicum* Plants (Solanaceous Studies. XVI)[1)]

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***Capsicum* species are very important plants used as vegetable foods, spices and external medicines. We obtained novel acyclic diterpene glycosides, named capsianosides A–F (1–6) and I–V (7, 1b, 10, 9, 8) from various fruits of the *Capsicum annuum* species and their structures were elucidated by spectroscopic and chemical means. Capsianosides are classified into two groups, monomeric diterpene glycosides (capsianosides I–V) and their dimeric esters (capsianosides A–F).**

Keywords red pepper; *Capsicum annuum* var. *fasciculatum*; *Capsicum annuum* var. *conoides*; *Capsicum annuum* var. *grossum*; pimiento; Solanaceae; capsianoside; acyclic diterpene glycoside; geranyllinallol derivative

Capsicum, red pepper in solanaceous plants is a very important spice. With regard to the constituents of red pepper, the less polar ones have previously been extensively studied, however, the polar ones have not been sufficiently examined. As to the water-soluble constituents in *Capsicum* plants, only a furostanol glycoside, capsicoside, from seeds and roots of *C. annuum* was known.[2)] Now our study has focused on the water-soluble constituents of *Capsicum* fruits; *Capsicum annuum* L. var. *conoides* BAILEY (takanotsume), *Capsicum annuum* L. var. *fasciculatum* BAILEY (yatsubusa) and *C. annuum* L. var. *grossum* BAILEY (shishitougarashi and pimiento), and we have isolated twelve novel acyclic diterpene glycosides, geranyllinalool derivatives, named capsianosides A—F (**1**—**6**, esters of acyclic diterpene glycosides), and capsianosides I—V (**7**, **1b**, **10**, **9** and **8**, monomeric compounds of acyclic diterpene glycoside). Distribution of these new natural products, capsianosides, within the Capsicum species is summarized in Table I. This paper deals with the structure characterization of these capsianosides.

The Dimers Capsianoside A (**1**), a white powder, $[\alpha]_D$ $-23.0°$, showed absorption bands due to the hydroxyl function ($3432\,cm^{-1}$) and α,β-unsaturated ester group (1714, $1650\,cm^{-1}$) in the infrared (IR) spectrum. The negative fast atom bombardment mass spectrum (negative FAB-MS) of **1** exhibited a molecular ion $[M-H]^-$ at m/z 1563, together with fragment ions at m/z 1083, 937 [m/z 1083 − deoxyhexose], 775 [m/z 937 − hexose], 629 [m/z 775 − deoxyhexose], 497 and 479. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum (Table II) of **1** displayed six anomeric signals at δ 105.9 ($J_{C-H}=159$ Hz), 99.2 ($J_{C-H}=171$ Hz), 99.5 ($J_{C-H}=158$ Hz), 98.4 ($J_{C-H}=158$ Hz), 101.0 ($J_{C-H}=171$ Hz) and 102.2 ($J_{C-H}=159$ Hz). Moreover, a signal at δ 169.2 was assigned to an ester carbonyl group, thus **1** was saponified with alkali to give two products, **1a** and **1b**. Compound **1a**, a white powder, $[\alpha]_D$ $-8.2°$, showed strong hydroxyl ($3452\,cm^{-1}$), and α,β-unsaturated carbonyl (1708, $1653\,cm^{-1}$) absorptions in the IR spectrum and peaks due to $[M-H]^-$ at m/z 497 and [m/z 497 − hexose]$^-$ at m/z 335 in the negative FAB-MS. Acid hydrolysis of **1a** gave glucose but no aglycone. **1a** on enzymatic hydrolysis liberated an aglycone (**1c**), an oil, $[\alpha]_D$ $+24.0°$, whose negative FAB-MS exhibited a peak due to $[M-H]^-$ at m/z 335. Moreover, the ^{1}H-NMR spectrum of **1c** disclosed the presence of four methyl groups [δ 1.24 (3H, s), 1.59 (3H, s), 1.65 (3H, s) and 1.81 (3H, d, $J=1.5$ Hz)], a mono-substituted double bond [δ 5.01 (1H, dd, $J=1.5$, 11 Hz), 5.90 (1H, dd, $J=11$, 18 Hz) and 5.19 (1H, dd, $J=1.5$, 18 Hz)], two olefinic protons [δ 5.11 (1H, t, $J=7$ Hz) and 5.18 (1H, t, $J=7$ Hz)] adjacent to the methylene group, one olefinic proton [δ 6.62 (1H, dd, $J=1.5$, 8 Hz)] coupled with an oxygenated methine proton [δ 4.53 (1H, ddd, $J=7$, 7, 9 Hz)], and five methylene groups [δ 1.50 (2H, m), 1.99 (4H, m), 2.07 (2H, m), 2.12, 2.29 (each 1H, dd, $J=7$, 13 Hz)]. Furthermore, the ^{13}C-NMR spectrum Table II of **1c** showed twenty carbon signals, which were composed of carbons due to one α,β-unsaturated carboxylic acid [δ 129.1 (s), 145.2 (d), 171.4 (s)], two tri-substituted double bonds [δ 125.9 (d), 129.1 (d), 135.7 (s), 131.7 (s)], one terminal vinyl group [δ 112.0 (t), 146.3 (d)], an oxygenated

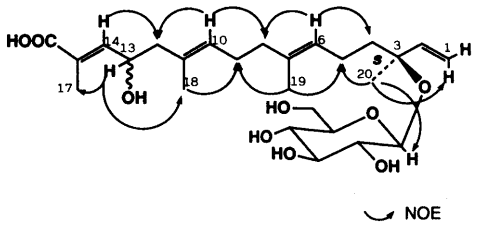


Fig. 1. NOEs of **1a**

TABLE I. Distribution of Capsianosides in Various Capsicum Plants

Capsianoside	I (7)	I′ (3a)	II (1b)	III (10)	IV (9)	V (8)	A (1)	B (2)	C (3)	D (4)	E (5)	F (6)
C. annuum var. *fasciculatum* (Yatsubusa)	○		○	○			○	○	○	○		
C. annuum var. *conoides* (Takanotsume)			○	○					○	○		
C. annuum var. *grossum* (Shishitougarashi)	○	○	○	○		○	○	○	○	○		
(Pimiento)		○	○	○	○				○	○	○	○

TABLE II. ^{13}C-NMR Data for **1**, **1a**, **1b**, **1c**, **1d**, **1e**, **2**, **3**, **3a**, **4**, **5**, **5a**, **6**, **7**, **8**, **9** and **10** (in CD_3OD)

	1	**1a**	**1c**	**1b**	**1d**	**1e**	**2**	**3**	**3a**	**4**	**5**	**5a**	**6**	**7**	**8**	**9**	**10**
C-1	115.8	115.7	112.0				115.8	116.1	116.0	116.1	115.9	116.1	116.1	116.0	115.8	116.1	
C-2	144.5	144.6	146.3				144.5	144.5	144.5	144.5	144.5	144.5	114.4	144.4	144.4	144.4	
C-3	81.5	81.5	73.9				81.5	82.1	82.1	82.1	82.1	82.8	82.1	82.1	81.2	82.1	
C-4	42.6	42.6	43.3				42.6	43.1	43.0	43.1	43.1	43.0	43.1	43.0	42.8	43.1	
C-5	23.6	23.5	23.6				23.6	23.6	23.6	23.6	23.6	23.5	23.6	23.5	23.5	23.6	
C-6	125.9	125.9	125.9				125.9	126.0	125.8	125.9	125.8	125.9	125.7	125.8	129.4	125.9	
C-7	136.0	135.8	135.7				136.0	136.0	136.0	136.0	136.0	135.9	135.9	135.9	139.3	135.9	
C-8	40.6	40.5	40.5				40.6	40.6	40.7	40.6	40.8	40.7	40.7	40.6	35.8	40.5	
C-9	27.8	27.7	27.6				27.7	27.7	27.8	27.7	27.7	27.6	27.6	27.7	28.0	27.6	
C-10	129.2	129.1	129.1				129.1	129.3	128.7	129.2	128.6	128.3	128.3	128.8	129.1	128.2	
C-11	131.8	131.8	131.7				131.9	131.8	132.3	131.9	135.2	135.0	135.2	131.8	132.1	135.0	
C-12	47.8	48.0	48.0				47.9	47.9	48.0	47.9	39.3	39.3	39.3	48.1	48.4	39.2	
C-13	68.0	68.0	68.0				68.1	68.0	68.5	68.1	28.7	28.5	28.6	68.1	68.2	28.5	
C-14	145.9	144.4	145.2				145.5	145.9	139.2	145.5	144.6	145.3	144.1	143.9	141.7	145.2	
C-15	128.9	129.5	129.1				129.0	129.0	135.1	129.0	126.3	129.2	126.1	130.2	132.1	126.4	
C-16	169.2	172.0	171.4				169.3	169.2	177.2	169.3	169.2	172.1	169.5	171.8	176.0	168.2	
C-17	13.1	13.1	13.0				13.1	13.1	14.4	13.2	12.7	12.6	12.7	13.3	13.7	12.5	
C-18	16.8	16.7	16.7				16.7	16.8	16.7	16.7	16.3	16.2	16.3	16.7	16.7	16.2	
C-19	16.2	16.0	16.0				16.1	16.3	16.2	16.2	16.2	16.2	16.2	16.2	60.0	16.1	
C-20	23.2	23.2	27.6				23.2	23.5	23.4	23.5	23.5	23.4	23.4	23.4	23.1	23.4	
C-1′	116.1			116.0	112.0	112.0	116.1	116.1		116.1	116.1		116.1				116.2
C-2′	144.5			144.3	146.3	146.3	144.4	144.5		144.5	144.5		144.4				144.3
C-3′	82.1			82.0	73.9	73.9	82.1	82.1		82.1	82.1		82.1				81.8
C-4′	43.1			42.9	43.5	43.4	43.1	43.1		43.1	43.1		43.1				43.0
C-5′	23.6			23.5	23.7	23.7	23.6	23.6		23.6	23.6		23.6				23.5
C-6′	125.8			125.7	125.7	125.9	125.8	125.8		125.8	126.0		125.8				125.7
C-7′	135.5			135.4	135.7	135.9	135.5	135.5		135.5	136.1		135.5				135.4
C-8′	40.9			40.7	40.8	40.8	40.8	40.8		40.8	40.8		40.8				40.7
C-9′	27.7			27.6	27.6	27.6	27.7	27.7		27.7	27.7		27.7				27.6
C-10′	125.9			125.9	125.8	125.8	125.9	125.9		125.9	125.9		125.9				125.9
C-11′	135.9			135.9	135.9	135.4	135.9	136.1		136.0	135.5		136.0				135.9
C-12′	40.9			40.8	41.1	40.9	40.9	40.9		41.0	41.0		40.9				40.8
C-13′	27.3			27.6	27.3	27.2	27.3	27.3		27.3	27.3		27.3				27.6
C-14′	131.1			131.1	128.5	131.2	131.1	131.4		131.3	131.2		131.3				131.2
C-15′	132.3			132.3	135.6	132.4	132.4	132.4		132.5	132.4		132.4				132.3
C-16′	21.9			21.9	21.5	21.9	21.9	21.9		22.0	21.9		21.9				22.0
C-17′	67.6			67.7	61.4	67.7	67.8	67.6		67.8	67.7		67.6				68.1
C-18′	16.3			16.3	16.0	16.0	16.3	16.3		16.3	16.3		16.3				16.3
C-19′	16.3			16.3	16.1	16.1	16.3	16.3		16.3	16.3		16.3				16.3
C-20′	23.4			23.4	27.6	27.3	23.4	23.5		23.5	23.5		23.5				23.4
Glucosyl moiety																	
C-1	99.5	99.5					99.5	98.4	98.4	98.4	98.4	98.3	98.3	98.3	99.5	98.4	
C-2	75.2	75.2					75.2	83.2	83.3	83.2	83.3	83.3	83.2	83.3	75.2	83.2	
C-3	78.1	78.2					78.0	77.7	77.6	77.7	77.7	77.5	77.6	77.5	78.2	77.5	
C-4	71.4	71.8					71.4	71.4	71.5	71.4	71.4	71.7	71.4	71.4	71.7	71.4	
C-5	77.7	77.6					77.8	77.6	77.7	77.6	77.7	77.7	77.6	77.7	77.6	77.7	
C-6	62.7	62.8					62.7	62.7	62.7	62.8	62.8	62.8	62.7	62.7	62.8	62.7	
C-1′								105.9	106.0	106.2	106.0	106.0	105.9	105.8		105.9	
C-2′								76.6	76.6	76.6	76.6	76.6	76.6	76.6		76.6	
C-3′								78.4	78.4	78.4	78.3	78.3	78.3	78.3		78.4	
C-4′								71.7	71.7	71.6	71.7	71.5	71.6	71.6		71.6	
C-5′								78.1	78.1	78.1	78.1	78.1	78.0	78.1		78.1	
C-6′								62.7	62.7	62.8	62.8	62.8	62.7	62.7		62.7	
C-1″	98.4			98.2			98.3	98.4		98.4	98.3		98.3				98.3
C-2″	83.1			83.2			83.3	83.3		83.3	83.2		83.2				83.2
C-3″	76.6			76.6			76.7	76.6		76.8	76.7		76.7				78.0
C-4″	71.7			71.3			71.1	71.7		71.2	71.4		71.4				71.2
C-5″	77.6			77.5			77.6	77.6		77.6	77.5		77.5				77.4
C-6″	62.7			62.7			62.7	62.7		62.8	62.7		62.7				62.6
C-1‴	105.9			105.7			105.9	105.9		106.2	106.0		106.1				105.8
C-2‴	76.4			76.4			76.5	76.6		76.6	76.6		76.6				76.5
C-3‴	78.2			78.1			78.2	78.1		78.1	78.0		78.0				78.1
C-4‴	71.6			71.5			71.7	71.4		71.4	71.6		71.6				71.3
C-5‴	77.6			77.3			77.5	77.7		77.7	77.6		77.6				77.5
C-6‴	62.8			62.7			62.8	62.7		62.8	62.8		62.7				62.6
Rhamnosyl moiety (or glucosyl)																	
C-1	101.0			101.4		101.6	101.4	101.0		101.5	101.1		101.4			95.9	100.9
C-2	72.4			72.0		72.2	72.2	72.4		72.3	72.3		72.3			74.0	82.1
C-3	78.5			79.2		79.2	79.1	78.5		79.1	78.5		79.1			78.8	78.0
C-4	74.4			73.7		74.0	74.0	74.1		74.0	74.0		74.0			72.2	71.4

TABLE II. (Continued)

	1	1a	1c	1b	1d	1e	2	3	3a	4	5	5a	6	7	8	9	10
C-5	70.3			70.5		70.6	70.8	70.3		70.8	70.5		70.8			78.4	77.6
C-6	18.0			17.8		17.9	17.9	18.0		17.9	18.0		17.9			62.4	62.6
Glucosyl moiety																	
C-1''''	102.2			102.1		102.2	102.2	102.2		102.3	102.2		102.2				104.7
C-2''''	75.4			75.0		75.2	75.3	75.4		75.4	75.5		75.3				75.8
C-3''''	78.3			77.9		76.7	78.3	78.4		78.4	78.3		78.3				78.2
C-4''''	72.3			72.3		72.3	72.3	72.3		72.4	72.4		71.1				71.5
C-5''''	75.5			75.3		75.4	75.3	75.5		75.4	75.5		75.3				76.3
C-6''''	66.0			66.6		66.8	66.8	66.1		66.8	66.1		66.7				67.5
Rhamnosyl moiety																	
C-1'	99.2			102.5		102.6	102.7	99.2		102.7	99.4		102.6				102.0
C-2'	75.0			72.3		72.2	70.2	75.1		70.2	74.7		70.2				72.1
C-3'	70.3			72.3		72.5	75.8	70.3		75.8	70.3		75.5				72.3
C-4'	74.4			73.8		73.7	71.7	74.4		71.7	7.44		72.2				73.9
C-5'	69.6			69.7		69.8	69.8	69.6		69.8	69.6		69.8				69.7
C-6'	18.2			18.1		18.2	18.2	18.2		18.2	18.2		18.2				18.1

methine and a carbon bearing a tertiary hydroxyl group [δ 68.0 (d) and 73.9 (s)], four methyl groups and five methylene groups. From the above evidence, **1c** was assumed to be an acyclic diterpene. Furthermore, the nuclear Overhauser effects (NOEs) of **1a** were observed as shown in Fig. 1 between each methyl group and the methylene protons or the oxygenated methine proton adjacent to the olefinic proton, and between the tri-substituted olefinic proton and the methylene protons. Thus, aglycone **1c** was deduced to be a geranyllinalool derivative. In addition, the methyl group at δ 1.24 attached to the quaternary carbon geminal to the oxygen atom has NOEs against one of the terminal vinyl protons, an anomeric proton of glucose and the methylene protons. Furthermore, the ^1H–^{13}C long range coupling two dimensional correlated (2D) NMR spectrum of **1a** showed correlations between C-3 and H_3-20, H_2-1, H-2; C-4 and H_3-20; C-6 and H_3-19; C-8 and H_3-19; C-10 and H_3-18; C-12 and H_3-18; C-13 and H_2-12; C-14 and H_3-17; C-15 and H_3-17; C-16 and H_3-17; C-17 and H-14, suggesting **1c** to be 6*E*,10*E*,14*E*-13-hydroxygeranyllinalool-16-oic acid. The ^{13}C-NMR spectrum of **1a** disclosed the presence of a β-D-glucopyranosyl residue (δ_C 99.5, 75.2, 78.2, 71.8, 77.6, 62.8) and the changes of the chemical shifts assignable to C-2, C-3 and C-20 in the aglycone part by -1.7, $+7.6$, -4.4 ppm,[3] respectively, by comparison with those of **1c**. The absolute configuration at C-3 was deduced to be 3*S* by showing a good coincidence in the chemical shifts in the C-1—11 and C-18—20 of the aglycone part on the ^{13}C-NMR spectra of **1a** and capsianoside I (**7**), whose configuration at C-3 is described later in this article. From the above evidence, **1a** could be represented as 3-*O*-β-D-glucopyranosyl 6*E*,10*E*,14*E*-13-hydroxy-(3*S*)-geranyllinalool-16-oic acid. The configuration at C-13 remained to be solved. On the other hand, **1b**, obtained by alkaline hydrolysis of **1**, a white powder, $[\alpha]_D$ $-35.5°$, showed absorptions due to hydroxyl (3436 cm^{-1}) and double bond (1638 cm^{-1}) in the IR spectrum, and a peak due to $[M-H]^-$ at *m/z* 1083 together with peaks due to [*m/z* 1083 − hexose]$^-$ at *m/z* 921, [*m/z* 921 − deoxyhexose]$^-$ at *m/z* 775 and [m/z 775 − hexose]$^-$ at *m/z* 613 in the negative FAB-MS, indicating **1b** to be a glycoside composed of at least two hexosyl and one deoxyhexosyl moieties. Enzymatic hydrolysis of **1b** yielded an aglycone (**1d**)

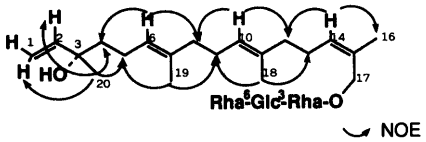


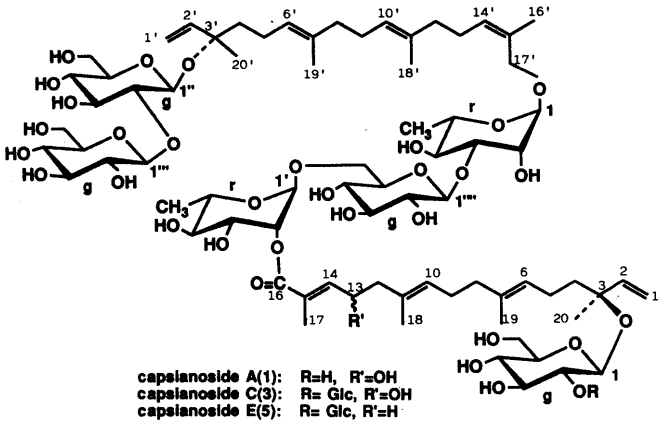
Fig. 2. NOEs of **1e**

and a partial hydrolyzed product (**1e**). Compound **1d**, a colorless oil, $[\alpha]_D$ $+6.3°$, showed a cluster ion due to $[M-H]^-$ at *m/z* 305 in the negative FAB-MS and signals due to four methyl groups [δ 1.24 (3H, s), 1.59 (6H, s), 1.75 (3H, s)], one terminal vinyl group [ABX-type, δ 5.02 (1H, dd, J=1.5, 11 Hz), 5.18 (1H, dd, J=1.5, 18 Hz), 5.91 (1H, dd, J=11, 18 Hz)], three olefinic protons [δ 5.11 (2H, t, J=7 Hz), 5.25 (1H, t, J=7 Hz)] adjacent to the methylene, one hydroxymethyl [δ 4.05 (2H, s), and six methylene groups [δ 1.51 (2H, t-like, J=7.0 Hz), 1.96—2.17 (10H, m), which were similar to those of **1c** except for signals due to protons attached to C-12—C-17. The ^{13}C-NMR spectrum (Table II) revealed the presence of twenty carbon signals including eight olefinic carbons, six methylene groups, four methyl groups, one hydroxymethyl group and one quaternary carbon bearing oxygen atom, thus indicating **1d** to be an acyclic diterpene, a geranyllinalool derivative, as well as **1c**. Ozonolysis of **1b** and subsequent reduction gave a 2ψ-hydroxypropanol glycoside (**1f**) as an epimeric mixture at C-2, whose structure was ascertained by the ^1H- and ^{13}C-NMR spectra. Since the NOE was observed between a vinyl methyl group at δ 1.75 and a hydroxymethyl group at δ 4.05, these should be located at the terminal of this molecule. In general, when a methyl group attaches in *cis* to the double bond, it is known that its chemical shift shields in a higher field owing to the *γ-gauche* effect than the corresponding *trans* one in the ^1H-NMR spectrum.[4] In comparing ^{13}C-NMR spectra of **1d** with those (δ 13.7 and 21.3) of the terminal methyl groups in 9-hydroxylinalool and 1-hydroxylinalool,[5] the chemical shift (δ 21.5) of the methyl group lying in *trans* to the γ-carbon in **1d** showed a good coincidence with that of the latter, thus suggesting **1d** to be 14*Z* configuration. Furthermore, in order to decide other configurations of the double bonds, NOE experiments for **1d** and **1e** were examined and it was revealed that **1d** could be represented as 5*E*,10*E*,14*Z*-17-hy-

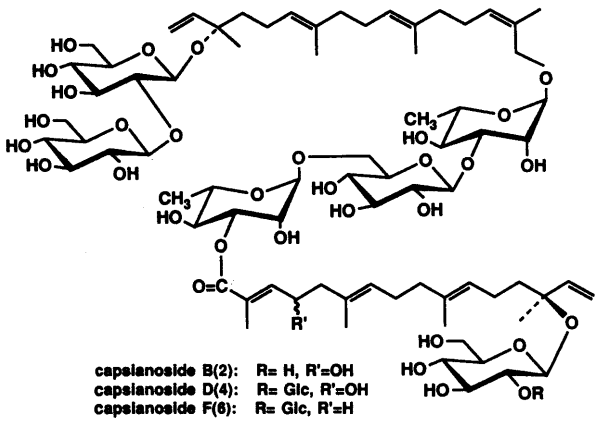
droxygeranyllinalool as shown in Fig. 2. With regard to the configuration at C-3 of **1d**, its optical rotation ($[M]_D$ +19.2°) was compared with those of (*R*)-(−)-linalool ($[M]_D$ −32°) and (*R*)-(−)-merolidol ($[M]_D$ −33°),[6] thus suggesting **1d** to be 3*S*. Consequently, **1d** was characterized as shown in the formulae 1. The ^{1}H-NMR spectrum of **1e**, a white powder, $[\alpha]_D$ −37.5°, exhibited the anomeric proton signals of one β-glucosyl moiety at δ 4.22 (1H, d, *J*=8.0 Hz) and two rhamnosyl moieties at δ 4.72 and 4.83 (each 1H, s). In addition, the ^{13}C-NMR signals (Table II) due to the anomeric carbon of a β-glucopyranose at δ 102.2 (*J*=159 Hz) and two α-rhamnopyranose at δ 102.6 (*J*=171 Hz) and 101.6 (*J*=168 Hz) were observed. Moreover, the presence of the following sugar moieties were suggested: α-rhamnopyranosyl group (δ 101.6, 72.2, 79.2, 74.0, 70.6, 17.9), possessing additional sugar linkages at its C-2 or C-3, a terminal α-rhamnopyranosyl group (δ 102.6, 72.2, 72.5, 73.7, 69.8, 18.2) and a β-glucopyranosyl group (δ 102.2, 75.2, 76.7, 72.3, 75.4, 66.8) indicating glycosylation shift[3] at its C-6. Moreover, the ^{1}H–^{1}H shift correlated spectroscopy (COSY) of the peracetate of **1e** showed signals due to the inner rhamnosyl H-1—H-3 at δ 4.81 (d, *J*=2 Hz), 5.17, 3.89 (dd, *J*=2, 9 Hz) and the terminal rhamnosyl H-1—H-3 at δ 4.85 (d, *J*=2 Hz), 5.07, 5.20, thus suggesting that the C-3–OH of the inner rhamnosyl moiety was linked to the other sugar. The electron impact mass spectrum (EI-MS) of **1e** exhibited peaks at *m/z* 273 (terminal rha·3Ac), 561 (terminal rha-glc·6Ac), 791 (terminal rha-glc-rha·8Ac). From the above evidence, the sugar part of **1e** was deduced to be α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranose. In comparing the ^{13}C-NMR spectrum of **1e** with that of **1d**, a signal assignable to C-17 deshielded by 6.3 ppm and the one due to C-15 shielded by 3.2 ppm among signals originated from aglycone. This means that the sugar residue combined with C-17. The negative FAB-MS disclosed that **1b** *m/z* 1083 $[M-H]^-$ has two more glucosyl moieties than **1e** *m/z* 759 $[M-H]^-$. When comparing the ^{13}C-NMR spectra of **1b** with those of **1e**, the C-2, C-3 and C-4 of the aglycone in **1b** were shifted by −2.0, +8.1 and −0.5 ppm, respectively, indicating a sophorosyl residue to link at C-3. Therefore, the structure of **1b** 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→6)-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranoside. Next, in order to determine the location of the ester bond, the ^{1}H-NMR spectra of **1** and **1b** were compared. A proton signal at δ 4.97 (d, *J*=3 Hz) geminal to the acyl group was observed in **1**. This signal was correlated with the anomeric proton [δ 4.90 (s)] of the rhamnosyl moiety in the ^{1}H–^{1}H COSY, thus it could be assigned to the H-2 of the rhamnosyl part. Moreover, in the ^{1}H–^{13}C COSY, correlations were observed between an anomeric proton signal (δ 4.90) and a carbon signal at δ 99.2, between the signal (δ 4.97) of H-2 in rhamnose and a carbon signal at δ 75.0, and between the signal (δ 3.89) of H-3 in rhamnose and a carbon signal at δ 70.3.[7] If the ester bond locates at C-2–OH of the inner rhamnosyl moiety, a signal at δ 3.89 due to H-3 of the rhamnosyl moiety should be correlated with the C-3 at δ 78.5 showing the glycosylation shift. However, since the proton signal of H-3 of the rhamnosyl moiety correlated with the signal at δ 70.3, not with the signal at δ 78.5, it was found that the hydroxyl group at C-2 of the terminal rhamnose unit is concerned with the ester bonding. Consequently, the structure of capsianoside A (**1**) could be 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-6*E*,10*E*,14*E*-(3*S*)-13-hydroxygeranyllinalool-16-oyl(16→2)]-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-(1→3)-α-L-rhamnopyranoside. In our preceding communication,[8] the location of the ester linkage had been deduced to be the hydroxyl group at C-2 of the inner rhamnosyl moiety, however, it should be revised as shown in this formulae **1** together with revision of the name of capsianside A into capsianoside A.

Capsianoside B (**2**), a white powder, $[\alpha]_D$ −18.0°, showed absorptions due to the hydroxyl (3432 cm^{-1}) and an α,β-unsaturated ester group (1710, 1648 cm^{-1}) in the IR spectrum. In the negative FAB-MS, the same fragment pattern (peaks at *m/z* 1563, 1083, 937, 775, 629, 497, 479) as those of **1** was obtained, thus **2** was estimated to be an isomer of **1**. The ^{13}C-NMR spectrum also suggested the presence of the ester carbonyl group at δ 169.3, therefore **1** was saponified with alkali to yield two products which were identified with **1a** and **1b** by the thin layer chromatography (TLC) and ^{1}H-NMR spectrum. To decide the location of the ester bonding between **1a** and **1b**, a comparative investigation of the ^{1}H-NMR spectra of **1** and **2** was made to reveal that the signals attributable to the H-1—H-3 of the rhamnosyl moiety possessing the acylation shifts[7] appeared at δ 4.84 (s), 4.02 (d, *J*=3 Hz) and 4.99 (dd, *J*=3, 10 Hz) in **2**, respectively. Moreover, in comparing the ^{13}C-NMR spectrum with that of **1b**, signals assingable to the terminal rhamnosyl residue appeared at δ 102.7, 70.2, 75.8, 71.7, 69.8 and 18.2 (C-1—C-6), suggesting that the hydroxyl group at C-3 of the rhamnosyl moiety participates in the ester bonding. As to whether its linkage lies in the inner rhamnosyl moiety or terminal one was spontaneously determined to be in the side of the terminal one because the glucosyl residue linked to the C-3–OH of the inner rhamnosyl residue. When a solution of **1** or **2** in dil. MeOH was heated at 70 °C for 1 h, acyl migration took place to yield a mixture of **1** and **2** in each case. Consequently, capsianoside B (**2**) could be represented as shown in the formula.

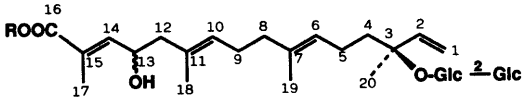
Capsianoside C (**3**), a white powder, $[\alpha]_D$ −21.0°, showed absorptions of the hydroxyl (3448 cm^{-1}) and the α,β-unsaturated ester carbonyl groups (1712, 1652 cm^{-1}) in the IR spectrum, and peaks due to molecular $[M-H]^-$ at *m/z* 1725, [*m/z* 1725−hexose]$^-$ at 1563, [*m/z* 1083−deoxyhexose]$^-$ at 937, [*m/z* 937−hexose]$^-$ at 775 and [*m/z* 659−hexose]$^-$ at 497 in the negative FAB-MS. The ^{13}C-NMR spectrum of **3** also suggested the presence of the ester carbonyl group (δ 169.2), therefore **3** was saponified with alkali to give two compounds **3a** and **1b**, the latter of which was identified with in respects with the ^{1}H-NMR and ^{13}C-NMR spectra. Compound **3a**, a white powder, $[\alpha]_D$ −1.7°, showed a cluster ion peak due to molecular ion $[M-H]^-$ at *m/z* 659 and fragment ion peaks at *m/z* 497 [*m/z* 659−hexose]$^-$ and 335 [*m/z* 497−hexose]$^-$. The ^{1}H-NMR spectrum of **3a** was similar to that of **1a**, however, the sugar moiety of **3a** exhibited signals due to two anomeric protons at δ 4.46 and 4.55 (each d, *J*=8 Hz). In the aglycone part, the following protons showed the respective shifts by



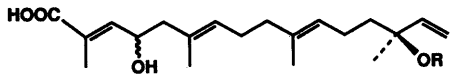
capsianoside A(1): R=H, R'=OH
capsianoside C(3): R= Glc, R'=OH
capsianoside E(5): R= Glc, R'=H



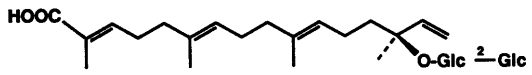
capsianoside B(2): R= H, R'=OH
capsianoside D(4): R= Glc, R'=OH
capsianoside F(6): R= Glc, R'=H



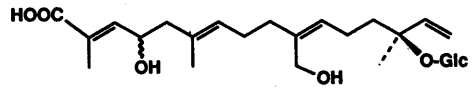
capsianoside I (7): R=H
capsianoside I' (3a): R=Na



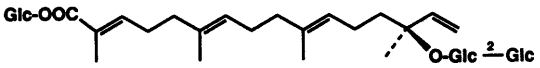
1a : R= Glc
1c : R= H



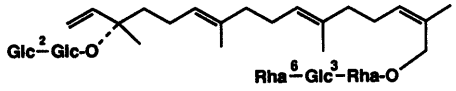
5a



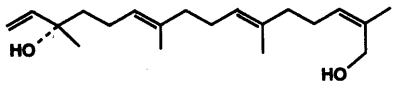
capsianoside V (8)



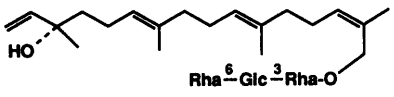
capsianoside IV (9)



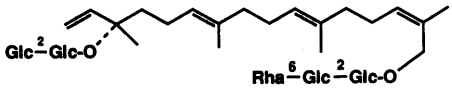
capsianoside II (1b)



1d



1e



capsianoside III (10)

comparing with those of **1a**: H-2, +0.23 ppm; H-13 and H-14, −0.03 and −0.29 ppm. The ^{13}C-NMR spectrum (Table II) of **3a** showed signals due to C-14—C-17 at δ 139.2, 135.1, 177.2 and 14.4, which shifted by −5.2, +5.6, +5.2 and +1.3 ppm, respectively, compared with those of **1a**. Moreover, signals due to the C-3 of the aglycone and the C-1, C-2 and C-3 of the glucosyl moiety shifted to δ 82.1 (+0.6), 98.4 (−0.9), 83.3 (+8.1) and 77.6 (−0.6), indicating that sugar moiety, a β-sophorosyl residue combined to C-3–OH. Next, NOE experiments disclosed that the double bonds at C-6, C-10 and C-14 were all of *E*-configuration. From the above accumulated evidence, it was suspected that **3a** might be a carboxyl salt. Treatment with acid on **3a** gave a product identical with capsianoside I (**7**) described later in this paper. Configuration at C-3 was deduced to be *S* by the ^{13}C-NMR spectrum, of which signals at C-1—C-10 and the sugar moiety in **3a** appeared at the same chemical shifts compared with those of **1b**. Therefore, **3** was concluded as shown in the formula. The location of the ester bond between **1b** and **3a** was determined by comparing the ^{1}H-NMR spectra of **3** with those of **1b**, **1** and **2**. Namely, signals due to H-1, H-2 and H-3 appeared at δ 4.90 (1H, s), 4.97 (1H, d, J=3 Hz) and 3.89 (1H, dd, J=3, 10 Hz) showing acylation shifts and their chemical shifts were coincident with those of **1**. Moreover, the signal pattern due to the aglycone was the same as that of **1**. This means that **3** was deduced to have an ester linkage between the hydroxyl group at C-2 of the terminal rhamnosyl residue of **1b** and 16-oic acid group of **3a**. The ^{13}C-NMR and ^{1}H–^{13}C COSY data were also consistent with the above result. Consequently, capsianoside C (**3**) could be represented as shown in the formulae.

Capsianoside D (**4**), a white powder, $[\alpha]_D$ −19.9°, showed absorptions at 3440 cm^{-1} (OH), 1716, 1646 cm^{-1} (α,β-unsaturated carbonyl) in its IR spectrum and peaks at *m/z* 1725, 1563, 1083, 937, 775, 659 and 497 in the negative

FAB-MS, whose pattern was superimposable with that of **3**, indicating **4** to be an isomer of **3** such as the relation between **1** and **2**. Saponification of **4** with alkali gave **1b** and **3a** as in the case of **3**. Their identifications were made by measurements of $[\alpha]_D$ and ^{1}H-NMR spectrum. In comparing the ^{1}H-NMR spectrum of **4** with those of **1b**, **1** and **3**, the H-3 of the terminal rhamnosyl moiety in **4** showed acylation shifts into δ 4.99 (dd, $J=3$, 10 Hz) together with the shifts of H-1 (δ 4.81, s) and H-2 (δ 4.02, d, $J=3$ Hz). This observation was quite similar to the case of **2**. Signals due to the aglycone were the same as those of **2**. From the above evidence, **4** was regarded to be a compound possessing an ester linkage between the C-3–OH group of the terminal rhamnosyl residue of **1b** and 16-oic acid group of **3a**. The ^{13}C-NMR and ^{1}H–^{13}C COSY data also supported this structure. Therefore, capsianoside D (**4**) could be represented as shown in the formula.

Capsianoside E (**5**), a white powder, $[\alpha]_D$ $-21.9°$, showed a peak due to $[M-H]^-$ at m/z 1709 together with fragment peaks at m/z 1547 [m/z 1709 − hexose]$^-$, 1385 [m/z 1547 − hexose]$^-$, 1083 [corresponding to **1b**], 937 [m/z 1083 − deoxyhexose]$^-$, 775 [m/z 937 − hexose]$^-$, 643 corresponding to **5a**, a saponified product later described and 481 [m/z 643 − hexose]$^-$ in the negative FAB-MS. Since **5** indicated the presence of an ester carbonyl group at δ 169.2 in its ^{13}C-NMR spectrum, **5** was regarded as an analogous compounds such as **1**—**4**. Thus, treatment with alkali on **5** furnished two products, **1b** and **5a**, the latter of which was obtained as a white powder, $[\alpha]_D$ $-14.0°$. Compound **5a** showed cluster ions due to molecular ion at m/z 667 $[M+Na]^+$ and 645 $[M+H]^+$ in the positive FAB-MS. The ^{1}H-NMR spectrum of **5a** displayed signals due to four methyl groups [δ 1.38 (s), 1.60 (s), 1.63 (s) and 1.80 (s)], six olefinic protons [δ 5.12 (2H, m), 5.22 (1H, dd, $J=1$, 11 Hz), 5.23 (1H, dd, $J=1$, 18 Hz), 6.13 (1H, dd, $J=11$, 18 Hz) and 6.74 (1H, t, $J=7$ Hz)] together with signals of the sophorosyl residue [δ 4.45, 4.54 (each 1H, d, $J=8$ Hz)]. These data resembled those of **3a**, however, a signal [δ 4.47 (1H, ddd, $J=7$, 7, 9 Hz)] assignable to H-13, which appeared in **3a**, vanished, and a signal [δ 6.33 (1H, dd, $J=$ 1, 9 Hz)] due to H-14 occurred at δ 6.74 (1H, t, $J=7$ Hz) in **5a**, thus suggesting the occurrence of the methylene group at C-13 in **5a**. This was also supported from the evidence of the ^{13}C-NMR spectrum that the methine carbon due to C-13 at δ 68.5 in **3a** appeared at δ 28.5 as methylene carbon in **5a**. Consequently, **5a** was demonstrated as shown in the formula. The location of the ester linkage between **1b** and **5a** was determined by comparison of the ^{1}H-NMR spectra of **5** with those of **1b** and **5a**, namely signals due to the H-1, H-2 and H-3 of the rhamnosyl moiety showed acylation shifts to appear at δ 4.89 (1H, s), 4.99 (1H, d, $J=3$ Hz) and 3.88 (1H, dd, $J=3$, 10 Hz), which were coincident with those of **1** and **3** having an ester ring at the C-3–OH of the terminal rhamnosyl residue. Furtheremore, patterns of the ^{1}H- and ^{13}C-NMR spectra were superimposable on those of **3**, thus the location of the ester group to exist at the C-2–OH of the terminal rhamnosyl moiety. Therefore, capsianoside E (**5**) was demonstrated as shown in the formula.

Capsianoside F (**6**), a white powder, $[\alpha]_D$ $-22.7°$, showed a similar pattern at m/z 1709, 1547, 1385, 1083, 937, 775, 643, 481 with that of **5** in the negative FAB-MS, suggesting **6** to be an isomer of **5**. Therefore, alkaline treatment of **6** gave products identical with **1b** and **5a**. The ^{1}H-NMR spectrum of **6** was very similar with that of **5**, signals due to the H-1, H-2 and H-3 of the terminal rhamnosyl residue appeared at δ 4.71 (1H, s), 4.02 (1H, d, $J=3$ Hz) and 4.98 (1H, dd, $J=3$, 10 Hz) as in the case of **2** and **4**. This fact revealed that **6** possesed an ester linkage between the C-3-OH group of the terminal rhamnosyl group and 16-oic acid in **5a**. The evidence from the ^{13}C-NMR spectrum of **6** was also consistent with that of the ^{1}H-NMR spectrum. From the above results, capsianoside F could be represented as the formula **6**.

The Monomers Capsianosides I′ and II were identical with **3a** and **1b** with respect to TLC, $[\alpha]_D$, ^{1}H- and ^{13}C-NMR spectra.

Capsianoside I (**7**), a white powder, $[\alpha]_D$ $-7.6°$, showed absorptions due to hydroxyl (3452 cm^{-1}) and α,β-unsaturated carbonyl groups (1708, 1653 cm^{-1}) in the IR spectrum and a peak originated from mlecular ion $[M-H]^-$ at m/z 659 in the negative FAB-MS, which also displayed fragment ion peaks at m/z 497 [m/z 659 − hexose], 335 [m/z 497 − hexose]. Enzymatic hydrolysis of **7** gave an aglycone (**1c**) and a partial hydrolysate (**1a**). In comparing the ^{13}C-NMR spectrum of **7** with those of **1a**, signals due to C-1, C-2 and C-3 of the glucosyl moiety were shifted by -1.2, $+8.1$ and -0.7 ppm, indicating the terminal glucosyl moiety linked at C-2–OH group in the inner glucosyl moiety. Absolute configuration at C-3 was estimated as *S* by showing a good coincidence with chemical shifts at C-1—C-11 and C-18—C-20 on the ^{13}C-NMR spectra in both **7** and **1b**. Consequently, capsianoside I (**7**) was represented as 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-6*E*,10*E*,14*E*-13-hydroxy-(3*S*)-geranyllinalool-16-oic acid. Namely, **7** corresponds to the carboxyl free compound of **3a**.

Capsianoside V (**8**), a white powder, $[\alpha]_D$ $+0.0°$, exhibited peaks due to $[M-H]^-$ and [m/z 513 − hexose]$^-$ at m/z 513 and 351 in the negative FAB-MS. The ^{1}H-NMR spectrum showed one anomeric proton signal at 4.35 (1H, d, $J=8$ Hz) whose pattern was analogous with that of **1a**. However, **8** showed signals due to a hydroxymethyl group at δ 4.09 (2H, s) and one methyl group less than those of **1a**, thus suggesting that a methyl group at either C-17, C-18, C-19 or C-20 in **1a** was oxydized in **8**. The NOEs were observed between H_3-17 and H-13; H_2-19 and H_2-5, H-8; H-13 and H_3-18, a methyl group at C-19 in **1a** changed to a hydroxymethyl group in **8**. Moreover, its ^{13}C-NMR spectrum was also coincident with the above result from the ^{1}H-NMR spectrum. Namely, signals due to C-6, C-7 and C-8 in **8** appeared at δ 129.4, 139.3 and 35.8, each indicating hydroxylation shifts[9] by $+3.5$, $+3.5$ and -4.7 ppm. From the above evidence capsianoside VI was determined as shown in the formula **8**.

Capsianoside IV (**9**), a white powder, $[\alpha]_D$ $-8.4°$, a molecular peak $[M-H]^-$ at m/z 805 along with fragment peaks at m/z 643 [m/z 805 − hexose]$^-$, 481 [m/z 643 − hexose]$^-$ and 319 [m/z 481 − hexose]$^-$. The ^{1}H-NMR spectrum of **9** showed three anomeric proton signals [δ 4.46 (1H, d, $J=8$ Hz), 4.55 (1H, d, $J=8$ Hz) and 5.53 (1H, d, $J=8$ Hz)], among which a signal at δ 5.53 appeared at a lower field than the other two anomeric proton signals, suggesting that it too participates in the ester bond. While signals due to the aglycone part were similar with those of **7**,

9 exhibited a triplet signal at δ 6.90 distinct from that of **7**. This means that **9** is a methylene at C-13 as well as **5a**. The ^{13}C-NMR spectrum of **9** exhibited the anomeric carbon signal of a β-glucopyranosyl moiety at δ 95.9 (J=159 Hz). Other signals were superimposable on those of **5a**. Therefore, **9** was assumed to possess a β-D-glucopyranosyl moiety attached to the carboxylic acid at C-16 in **5a**. In comparing the ^{13}C-NMR spectrum of **9** with that of **5a**, a signal ascribable to C-16 in **9**, to which the β-glucosyl residue linked, was shifted to 168.2 (−3.9 ppm). Signals due to C-14 and C-15 were shifted by −0.1 and −2.8 ppm, respectively. Consequently, capsianoside IV was represented as shown in formula **9**.

Capsianoside III (**10**), $[\alpha]_D$ −26.4°, a white powder, showed peaks due to $[M-H]^-$ at m/z 1099, [m/z 1099 − hexose]$^-$ at 937, [m/z 937 − hexose]$^-$ at 775 and [m/z 775 − deoxyhexose]$^-$ at 613. Compound **10** has one more oxygen than **1b** and on acid hydrolysis liberated glucose and rhamnose. The ^{1}H-NMR spectrum of **10** was similar to that of **1b**. However, **10** was shown to be composed of four moles of β-glucosyl and one mole of rhamnosyl moieties from the evidence of signals due to anomeric protons [δ 4.35 (1H, d, J=8 Hz), 4.47 (1H, d, J=8 Hz), 4.56 (1H, d, J=8 Hz), 4.63 (1H, d, J=8 Hz) and 4.75 (1H, s)]. Moreover, the ^{13}C-NMR spectra exhibited five anomeric carbon signals due to four β-glucosyl moieties and one α-rhamnosyl moiety at δ 105.8 (J=159 Hz), 104.7 (J=159 Hz), 102.0 (J=168 Hz), 100.9 (J=159 Hz) and 98.3 (J=156 Hz). Regarding the sugar structure, a signal due to the C-2 at the inner glucose appeared at δ 82.1 (+6.9 ppm shift) in the ^{13}C-NMR spectrum, while C-1 and C-3 shifted −4.2 and −0.2 ppm, respectively, and so C-6 and C-5 in the middle glucose shifted by +4.7 and −1.9 ppm, thus suggesting that a sugar part is constituted with β-D-glucopyranosyl-(1→2)-β-D-glucopyranosyl-(1→6)-α-L-rhamnopyranosyl and β-sophorosyl residues. Chemical shifts due to the aglycone were coincident with those of **1b**. Therefore, capsianoside III was shown in the formula **10**.

These acyclic diterpenes occur rarely in nature. Capsianosides C and D were shown to have inhibitory activity for the angiotensin converting enzyme. We plan to perform various pharmacological tests and to practice cyclization by the aid of catalytic acid or enzyme with regard to these novel compounds.

Experimental

The optical rotations were measured with a JASCO DIP 360 digital polarimeter. The IR spectra were recorded with a Hitachi 270—30 type spectrometer. The EI-MS were measured with a JEOL JMS-01SG and JMS-DX 303HF (ionizing voltage, 70—75 eV; ionizing current, 200—300 μA; ion source temperature, 130—180 °C) and the FAB-MS were obtained with a JEOL JMS-DX-300 and JMS-DX 303 HF (ion source, Xe atom beam; accelating voltage, 2—3 kV; matrix, MeOH/glycerin). The ^{1}H- and ^{13}C-NMR spectra were recorded with JEOL JNM-GX-400 (^{1}H, 400 MHz; ^{13}C, 100.4 MHz) spectrometer; chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. Column chromatography was carried out with MCI-gel CHP 20P (75—150 μ, Mitsubishi Chemical Industries, Ltd.), Bondapak C_{18} (Waters Associates, Inc.) and Kieselgel 60 (70—230, 230—400 mesh, Merck). TLC was performed on precoated Kieselgel 60 F_{254} plates (0.2 mm, Merck) using $CHCl_3$–MeOH–H_2O and benzene–AcOEt systems as the developing solvent for the free compounds and detection was achieved by spraying 10% H_2SO_4 reagent followed by heating.

Isolation *Capsicum annuum* L. var. *grossum* BAILEY (shishitougarashi): The fresh fruit (4 kg) was extracted with MeOH and its extract was evaporated under reduced pressure to afford a residue (180 g) which was shaken with benzene and water. After removal of the solvent of the aqueous phase, 170 g of the residue was obtained. This was subjected to column chromatographies of MCI gel CHP 20P (eluted with H_2O–20%–40%–60%–80%–100% MeOH, gradiently), silica gel (eluted with $CHCl_3$: MeOH : H_2O = 7 : 3 : 0.5) and Bondapak C_{18} (eluted with 40%–60%–70% MeOH, gradiently) furnished capsianosides A (**1**, 133 mg), B (**2**, 10 mg), C (**3**, 244 mg), D (**4**, 139 mg), I (**7**, 29 mg), II (**1b**, 285 mg), I′ (**3a**, 35 mg), III (**10**, 418 mg) and V (**8**, 8 mg). In a similar way as the above plant, the fresh fruit of *C. annuum* L. var. *fasciculatum* BAILEY (yatsubusa, 4 kg) was extracted and separated to afford capsianoside A (**1**, 150 mg), B (**2**, 70 mg), C (**3**, 150 mg), D (**4**, 150 mg), I (**7**, 72 mg), II (**1b**, 480 mg) and III (**10**, 60 mg). *C. annuum* L. var. *conoides* BAILEY (takanotsume): The fresh fruit (1.5 kg) was extracted with MeOH and separated similarily as in the case of *C. annuum* var. *grossum* to afford capsianoside II (**1b**, 65 mg), III (**10**, 84 mg), C (**3**, 155 mg) and D (**4**, 42 mg). Analogous to the above Capsicum plants, from the fresh plants (1.9 kg) of commercial pimiento (the fruit of *C. annuum* L. var. *grossum* BAILEY), capsianoside II (**1b**, 263 mg), I′ (**3a**, 7 mg), III (**10**, 68 mg), IV (**9**, 17 mg), C (**3**, 67 mg), D (**4**, 41 mg), E (**5**, 29 mg) and F (**6**, 10 mg) were isolated. In a similar way, from *C. annuum* sp. in Thailand, capsianosides II (**1b**, 1.9 g), III (**10**, 146 mg), E (**5**, 14 mg) and F (**6**, 7 mg) were obtained.

Capsianoside A (1) A white powder, $[\alpha]_D^{20}$ −23.0° (c=0.59, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3432 (OH), 1714, 1650 (α,β-unsaturated carbonyl ester). Negative FAB-MS m/z: 1563 $[M-H]^-$, 1083, 937, 775, 629, 497, 479. ^{1}H-NMR (CD_3OD) δ: 1.26, 1.27 (each 3H, d, J=6 Hz, H_3-6), 1.38, 1.39, 1.59, 1.61×2, 1.66, 1.77 (each 3H, s, H_3-20, H_3-20′, H_3-19, H_3-19′, H_3-18, H_3-18′, H_3-16′), 1.60 (4H; m, H_2-4, H_2-4′), 1.88 (3H, d, J=1.5 Hz, H_3-17), 1.90—2.20 (17H, m, H_2-5, H_2-8, H_2-9, H_2-5′, H_2-8′, H_2-9′, H_2-12′, H_2-13′, H-12), 2.28 (1H, dd, J=7, 14 Hz, H-12), 3.10—3.80 (m, sugar), 3.89 (1H, dd, J=3, 10 Hz, rha H-3), 3.93 (1H, dd, J=2, 10 Hz), 4.12, 4.34 (each 1H, d, J=11 Hz, H-17′), 4.20, 4.35, 4.56 (each 1H, d, J=8 Hz, 3×glc H-1), 4.57 (1H, m, H-13), 4.81, 4.90 (each 1H, s, 3×rha H-1), 4.97 (1H, d, J=3 Hz, rha H-2), 5.12—5.20 (8H, m, H_2-1, H_2-1′, H-6, H-6′, H-10, H-10′), 5.40 (1H, d, J=7 Hz, H-14′), 5.93, 6.13 (each 1H, dd, J=11, 18 Hz, H-2, H-2′), 6.71 (1H, dd, J=1, 9 Hz, H-14).

Peracetate of 1 Compound **1** (55 mg) was acetylated with pyridine (0.5 ml) and acetic anhydride (0.3 ml) in the usual manner and the product was purified over silica gel column chromatography (solv., $CHCl_3$: MeOH = 30 : 1) to afford the corresponding peracetate (45 mg). A white powder, EI-MS m/z: 273, 331, 561, 619, 749. ^{1}H-NMR ($CDCl_3$) δ: 1.15, 1.21 (each 3H, d, J=6 Hz, rha H_3-6), 1.32×2, 1.56, 1.58, 1.60, 1.68, 1.90 (each s, total H_3×8), 1.95—2.11 (total 19×Ac), 2.20 (1H, dd, J=4, 14 Hz, H-12), 2.36 (1H, dd, J=9, 14 Hz, H-12), 3.48—4.30 (m), 4.45, 4.51, 4.58, 4.72 (each 1H, d, J=8 Hz, glc H-1), 4.85, 4.88 (each 1H, s, rha H-1), 4.85—5.28 (m), 5.40 (1H, t, J=7 Hz, H-14′), 5.67 (1H, ddd, J=7, 7, 8 Hz, H-13), 5.73, 5.87 (each 1H, dd, J=11, 18 Hz, H-2, H-2′), 6.57 (1H, d, J=9 Hz, H-14).

Acid Hydrolysis of 1 A solution of **1** (45 mg) in 1 N HCl–MeOH (5 ml) was refluxed for 1.5 h on the hot bath and neutralized with 3% KOH–MeOH. The reaction mixture was passed through Sephadex LH-20 to give the methyl glycosides, which were separated by silica gel column chromatography (solv., $CHCl_3$: MeOH : water = 8 : 2 : 0.2) to afford each methyl glycoside of glucose and rhamnose. They were treated with mineral acid to give respective free sugar. Glucose: $[\alpha]_D$ +48.0° (c=0.32, water); rhamnose: +10.1° (c=0.21, water).

Alkaline Hydrolysis of 1 **1** (27 mg) was dissolved in 1 N sodium carbonate solution (10 ml) and heated at 65 °C for 45 min. After cooling, the reaction mixture was passed through MCI-gel CHP 20P, wshed with water until it was neutral and eluted with MeOH. The methanolic eluent was evaporated under reduced pressure to give a residue, which was chromatographed over silica gel with $CHCl_3$: MeOH : H_2O = 7 : 3 : 0.5 as solvent to yield **1a** (3 mg) and **1b** (7 mg). **1a**, a white powder, $[\alpha]_D^{20}$ −8.2° (c=1.03, MeOH), negative FAB-MS m/z: 497 $[M-H]^-$, 335. ^{1}H-NMR (CD_3OD) δ: 1.37, 1.58, 1.65, 1.81 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-17), 1.60 (2H, m, H_2-4), 1.95—2.15 (6H, m, H_2-5, H_2-8, H_2-9), 2.09, 2.28 (each 1H, dd, J=7, 13 Hz, H-12), 3.13—3.35 (4H, m, sugar), 3.62 (1H, dd, J=6, 12 Hz), 3.90 (1H, dd, J=3, 12 Hz), 4.35 (1H, d, J=8 Hz, glc H-1), 4.50 (1H, ddd, J=7, 7, 8 Hz), 5.11 (1H, t, J=6 Hz, H-6), 5.18 (1H, d, J=11 Hz, H-1), 5.21 (1H, d, J=18 Hz, H-1), 5.22 (1H, t, J=7 Hz, H-10), 5.90 (1H, dd, J=11, 18 Hz, H-2), 6.62 (1H, d, J=8 Hz, H-14). **1b**, a white powder, $[\alpha]_D^{20}$ −35.5° (c=1.07, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3436 (OH), 1638 (double bond). Negative FAB-MS m/z: 1083 $[M-H]^-$, 921, 775, 613. ^{1}H-NMR (CD_3OD) δ: 1.26, 1.27 (each 3H, J=6 Hz, rha H_3-6), 1.38, 1.60×2,

1.77 (each 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), 3.10—4.00 (m, sugar), 4.13, 4.33 (each 1H, d, J=12 Hz, H_2-17), 4.20, 4.47, 4.56 (each 1H, d, J=8 Hz, 3 × glc-anomeric proton), 4.71, 4.81 (each 1H, s, 2 × rha-anomeric proton), 5.12 (2H, m, H-6, H-10), 5.22 (1H, d, J=18 Hz, H-1), 5.23 (1H, d, J=11 Hz, H-1), 5.40 (1H, t, J=7 Hz, H-14), 6.12 (1H, dd, J=11, 18 Hz, H-2).

Enzymatic Hydrolysis of 1a A mixture of **1a** (20 mg), crude naringinase and acetate buffer (pH 4.2, 50 ml) was incubated at 37 °C for seven days. The reaction mixture was passed through MCI-gel CHP 20P and washed with water and eluted with MeOH. The methanolic eluate was purified over silica gel ($CHCl_3$: MeOH = 30 : 1) to provide **1c** (9 mg), a colorless oil, $[\alpha]_D^{29}$ +24.0° (c=1.40, $CHCl_3$). Negative FAB-MS m/z: 335 $[M-H]^-$. ^{1}H-NMR (CD_3OD) δ: 1.24, 1.59, 1.65 (each 3H, s, H_3-20, H_3-19, H_3-18), 1.50 (2H, m, H_2-4), 1.81 (3H, d, J=1.5 Hz, H_3-17), 1.99 (4H, m, H_2-8, H_2-9), 2.07 (2H, m, H_2-5), 2.12, 2.29 (each 1H, dd, J=7, 13 Hz, H-12), 4.53 (1H, ddd, J=7, 7, 9 Hz, H-13), 5.01 (1H, dd, J=1.5, 11 Hz, H-1), 5.11, 5.18 (each 1H, t, J=7 Hz, H-6, H-10), 5.19 (1H, dd, J=1.5, 18 Hz, H-1), 5.90 (1H, dd, J=11, 18 Hz, H-2), 6.62 (1H, dd, J=1.5, 8 Hz, H-14).

Enzymatic Hydrolysis of 1b A mixture of **1b** (100 mg), crude naringinase and acetate buffer (pH 4.5, 50 ml) was incubated at 37 °C for 7 d. The reaction mixture was passed through MCI-gel CHP 20P, washed with water and eluted with MeOH to give a methanolic eluate, which was purified by silica gel column chromatography (benzene : AcOEt = 3 : 1 and $CHCl_3$: MeOH : water = 8 : 2 : 0.2) to give **1d** (8 mg) and **1e** (34 mg). **1d**, a colorless oil, $[\alpha]_D^{29}$ +6.3° (c=0.89, $CHCl_3$). Negative FAB-MS m/z: 305 $[M-H]^-$. ^{1}H-NMR (CD_3OD) δ: 1.24, 1.59 × 2, 1.75 (each s, H_3-20, H_3-19, H_3-18, H_3-16), 1.51 (2H, t-like, J=7 Hz, H_2-4), 1.96—2.17 (10H, m, H_2-5, H_2-8, H_2-9, H_2-12, H_2-13), 4.05 (2H, s, H_2-17), 5.02 (1H, dd, J=1.5, 11 Hz, H-1), 5.11 (2H, t, J=7 Hz, H-6, H-10), 5.18 (1H, dd, J=1.5, 18 Hz, H-1), 5.25 (1H, t, J=7 Hz, H-14), 5.91 (1H, dd, J=11, 18 Hz, H-2). **1e**, a white powder, $[\alpha]_D^{16}$ −37.5° (c=1.04, MeOH). ^{1}H-NMR (CD_3OD) δ: 1.27, 1.28 (each 3H, d, J=6 Hz, rha H_3-6), 1.25, 1.60 × 2, 1.77 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-16), 1.98—2.18 (10H, m, H_2-5, H_2-8, H_2-9, H_2-12, H_2-13), 3.21—4.00 (m, sugar), 4.22 (1H, d, J=8 Hz, glc H-1), 4.15, 4.30 (each 1H, d, J=12 Hz, H_2-17), 4.72, 4.83 (each 1H, s, 2 × rha H-1), 5.02 (1H, dd, J=1.5, 11 Hz, H-1), 5.12 (2H, m, H-6, 10), 5.19 (1H, dd, J=1.5, 18 Hz, H-1), 5.38 (1H, t, J=7 Hz, H-14), 5.91 (1H, dd, J=11, 18 Hz, H-2).

Peracetate of 1e After a mixture of **1e** (10 mg), Ac_2O (0.2 ml) and pyridine (0.4 ml) was kept at room temperature for 16 h, the reaction mixture was blown with N_2 gas to remove the solvent. The resulting residue was purified by silica gel column chromatography (benzene : AcOEt = 2 : 1) to afford peracetate of **2e** (5 mg). EI-MS m/z: 273 (terminal rha·3Ac), 561 (terminal rha-glc·6Ac), 791 (terminal rha-glc-rha·8Ac). ^{1}H-NMR ($CDCl_3$) δ: 1.16, 1.20 (each 3H, d, J=6 Hz rha H_3-6), 1.28, 1.58, 1.60, 1.68 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-16), 1.96, 1.97, 2.03, 2.04, 2.07, 2.08, 2.10, 2.12 (each 3H, s, Ac × 8), 3.43 (1H, t, J=10 Hz, glc H-6), 4.02 (1H, dq, J=6, 10 Hz, rha H-5), 4.11, 4.26 (each 1H, d, J=11 Hz, H_2-17), 4.44 (1H, d, J=8 Hz, glc H-1), 4.81, 4.85 (each 1H, d, J=2 Hz, 2 × rha H-1), 4.91 (1H, dd, J=8, 9 Hz, glc H-2), 5.20—5.24 (11H, m), 5.07 (1H, m, terminal rha H-2), 5.17 (1H, inner rha H-2), 5.40 (1H, d, J=7 Hz, H-14), 5.92 (1H, dd, J=11, 17 Hz, H-2).

Ozonolysis of 1b To a solution of **1b** (100 mg) in MeOH (50 ml), ozone gas was introduced at 0 °C for 30 min. The reaction mixture was concentrated under reduced pressure to half its volume and stirred at room temperature for 1 h after the addition of $NaBH_4$ (200 mg). The mixture was then concentrated under reduced pressure to give a residue, which was added with water and passed through MCI-gel CHP 20P eluted with water and subsequently with MeOH. The methanolic eluate was evaporated under reduced pressure to give a residue, which was purified by silica gel column chromatography to yield 2ψ-hydroxy propanol glycoside (**1f**, 10 mg). ^{1}H-NMR (pyridine-d_5) δ: 1.26, 1.30 (total 3H, each d, J=6.5 Hz, γ-Me), 1.63, 1.69 (each 3H, d, J=6 Hz, 2 × rha Me-6), 4.82, 4.83 (total 1H, each d, J=8 Hz, glc H-1), 5.36, 5.61 (each 1H, s, 2 × rha H-1). ^{13}C-NMR (pyridine-d_5) δ: 18.5, 18.6 (2 × rha Me-6), 20.0, 20.2 (C-γ), 66.4, 66.7 (C-α), 67.2, 67.4 (glc C-6), 69.8 (terminal rha C-5), 70.6 (inner rha C-5), 72.2 (terminal rha C-2), 72.5 (inner rha C-2), 2 × 72.7 (glc C-4, terminal rha C-3), 73.9 (inner rha C-4), 74.0 (terminal rha C-4), 75.0, 75.2 (glc C-2), 75.5, 75.6 (glc C-5), 76.6 (C-β), 76.7 (glc C-3), 79.3, 79.6 (rha C-3), 102.1, 102.2 (inner rha C-1), 102.9 (terminal rha C-1), 104.8, 105.0 (glc C-1).

Capsianoside B (2) A white powder, $[\alpha]_D^{20}$ −18.0° (c=0.68, MeOH), IR ν_{max}^{KBr} cm^{-1}: 3432 (OH), 1710, 1648 (α,β-unsaturated ester carbonyl). Negative FAB-MS m/z: 1563 $[M-H]^-$, 1083, 937, 775, 629, 497, 479. ^{1}H-NMR (CD_3OD) δ: 1.27, 1.28 (each 3H, d, J=6 Hz, rha H_3-6), 1.38, 1.39, 1.59, 1.61 × 2, 1.66, 1.78, 1.88 (each s, H_3-20, H_3-20′, H_3-19, H_3-19′, H_3-18, H_3-18′, H_3-16′, H_3-17), 1.60 (4H, m, H-4, H-4′), 1.90—2.20 (17H, m, H_2-5, H_2-8, H_2-9, H_2-5′, H_2-8′, H_2-9′, H_2-12′, H_2-13′, H-12), 2.27 (1H, dd, J=7, 14 Hz, H-12), 3.14—3.83 (m, sugar), 3.94 (1H, d, J=10 Hz), 4.02 (1H, d, J=3 Hz, rha H-2), 4.14, 4.34 (each 1H, d, J=11 Hz, H-17), 4.23, 4.35, 4.47, 4.55 (each 1H, d, J=8 Hz, glc H-1), 4.55 (1H, m, H-13), 4.71, 4.84 (each 1H, s, rha H-1), 4.99 (1H, dd, J=3, 10 Hz, rha H-3), 5.12—5.25 (8H, m, H_2-1, H_2-1′, H-6, H-6′, H-10, H-10′), 5.40 (1H, t, J=7 Hz, H-14′), 5.93, 6.13 (each 1H, dd, J=11, 18 Hz, H-2, H-2′), 6.73 (1H, dd, J=1, 9 Hz, H-14).

Alkaline Hydrolysis of 2 **2** (10 mg) was dissolved in 0.5 N sodium hydroxide solution (3 ml) and the mixture was heated at 65 °C for 45 min. After cooling, the reaction mixture was passed through MCI-gel CHP 20P column and washed with water until it was neutral, and was then subsequently eluted with MeOH. The methanolic fraction was evaporated under reduced pressure to afford a residue, which was purified by silica gel column chromatography ($CHCl_3$: MeOH : water = 7 : 3 : 0.5) to give two products identical with **1a** and **1b**.

Capsianoside C (3) A white powder, $[\alpha]_D^{20}$ −21.0° (c=0.50, MeOH), IR ν_{max}^{KBr} cm^{-1}: 3448 (OH), 1712, 1652 (α,β-unsaturated ester carbonyl). Negative FAB-MS m/z: 1725 $[M-H]^-$, 1563, 937, 775, 659, 497. ^{1}H-NMR (CD_3OD) δ: 1.26, 1.27 (each 3H, d, J=6 Hz, rha H_3-6), 1.38 × 2, 1.60, 1.61 × 2, 1.65, 1.77, 1.88 (each s, H_3-20, H_3-20′, H_3-19, H_3-19′, H_3-18, H_3-18′, H_3-16′, H_3-17), 1.90—2.20 (17H, m, H_2-5, H_2-8, H_2-9, H_2-5′, H_2-8′, H_2-9′, H_2-12′, H_2-13′ and H-12), 2.28 (1H, dd, J=7, 14 Hz, H-12), 3.10—3.80 (m, sugar), 3.89 (1H, dd, J=3, 10 Hz, rha H-3), 3.93 (1H, dd, J=2, 10 Hz), 4.12, 4.34 (each 1H, d, J=11 Hz, H-17), 4.20, 4.46 × 2, 4.56 × 2 (each d, J=8 Hz, glc H-1), 4.56 (1H, m, H-13), 4.81, 4.90 (1H, s, rha H-1), 4.97 (1H, d, J=3 Hz, rha H-2), 5.13—5.21 (8H, H_2-1, H_2-1′, H-6, H-6′, H-10, H-10′), 5.40 (1H, t, J=7 Hz, H-14′), 6.13 (2H, dd, J=11, 18 Hz, H-2, H-2′), 6.71 (1H, dd, J=1, 9 Hz, H-14).

Alkaline Hydrolysis of 3 A solution (10 ml) of **3** (30 mg) in 1 N sodium carbonate was heated at 65 °C for 30 min and passed through MCI-gel CHP 20P eluted with water and successively MeOH. The solvent of the methanolic eluate was removed by reduced pressure to give a residue, which was subjected to Bondapak C_{18} column chromatography. From the 50% methanolic eluate **1b** (8 mg) was obtained and from the 60% methanolic eluate **3a** (6 mg) was obtained. **3a**, a white powder, $[\alpha]_D^{24}$ −1.7° (c=0.70, MeOH), negative FAB-MS m/z: 659 $[M-H]^-$, 497, 335. ^{1}H-NMR (CD_3OD) δ: 1.38, 1.59, 1.65, 1.81 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-17), 1.60 (2H, m, H-4), 1.95—2.15 (7H, m, H_2-5, H_2-8, H_2-9, H-12), 2.26 (1H, dd, J=7, 13 Hz, H′-12), 3.10—3.83 (m, sugar), 4.46, 4.55 (each 1H, d, J=8 Hz, glc H-1), 4.47 (1H, ddd, J=7, 7, 9 Hz, H-13), 5.12, 5.19 (each 1H, t, J=7 Hz, H-6, H-10), 5.22 (1H, d, J=11 Hz, H-1), 5.22 (1H, d, J=18 Hz, H-1), 6.13 (1H, dd, J=11, 18 Hz, H-2), 6.33 (1H, dd, J=1, 9 Hz, H-14).

Capsianoside D (4) A white powder, $[\alpha]_D^{20}$ −19.9° (c=0.71, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 1716, 1646 (α,β-unsaturated ester carbonyl). Negative FAB-MS m/z: 1725 $[M-H]^-$, 1563, 1083, 937, 775, 659, 497. ^{1}H-NMR (CD_3OD) δ: 1.26, 1.29 (each 3H, s, J=6 Hz, rha H_3-6), 1.38 × 2, 1.60 × 2, 1.61, 1.67, 1.77, 1.88 (each s, H_3-20, H_3-20′, H_3-19, H_3-19′, H_3-18, H_3-18′, H_3-16′, H_3-17), 1.90—2.20 (17H, m, H_2-5, H_2-8, H_2-9, H_2-5′, H_2-8′, H_2-9′, H_2-12′, H_2-13′, H-12), 2.28 (1H, dd, J=7, 14 Hz, H-12), 3.10 3.80 (m, sugar), 3.93 (1H, d, J=2, 10 Hz), 4.02 (1H, d, J=3 Hz, rha H-2), 4.14, 4.33 (each 1H, d, J=12 Hz, H-17), 4.23, 4.47 × 2 (each d, J=8 Hz, glc H-1), 4.56 (1H, m, H-13), 4.71, 4.81 (each 1H, s, rha-1), 4.99 (1H, dd, J=3, 10 Hz, rha H-3), 5.12—5.25 (8H, m, H_2-1, H_2-1′, H-6, H-6′, H-10, H-10′), 5.38 (1H, t, J=7 Hz, H-14′), 6.12 (2H, dd, J=11, 18 Hz, H-2, H-2′), 6.74 (1H, dd, J=1, 9 Hz, H-14).

Alkaline Hydrolysis of 4 A solution of **4** (32 mg) in 1 N sodium carbonate solution (10 ml) was heated at 65 °C for 30 min and was then passed through MCI-gel CHP 20P eluting with water and subsequently with MeOH. The solvent of the methanolic eluate was removed by evaporation under reduced pressure to give a residue, which was subjected to Bondapak C_{18} column chromatography eluting with 50% MeOH (giving **3a**, 20 mg) and 60% MeOH (giving **1b**, 8 mg), which were identified with the authentic specimens in respect to $[\alpha]_D$ and ^{1}H-NMR spectra.

Capsianoside E (5) A white powder, $[\alpha]_D^{19}$ −21.9° (c=1.07, MeOH), Negative FAB-MS m/z: 1709 $[M-H]^-$, 1547, 1385, 1083, 937, 775, 643, 481. ^{1}H-NMR (CD_3OD) δ: 1.26 × 2 (each 3H, d, J=6 Hz, rha H_3-6), 1.38 × 2, 1.60 × 4, 1.76, 1.85 (each 3H, s, H_3-20, H_3-20′, H_3-18, H_3-18′, H_3-19, H_3-19′, H_3-16′, H_3-17), 1.63 (4H, m, H_2-4, H_2-4′), 1.99—2.13 (20H, m, H_2-5, H_2-5′, H_2-8, H_2-8′, H_2-9, H_2-9′, H_2-12, H_2-12′, H_2-13, H_2-13′), 3.14—3.83 (m, sugar), 3.88 (1H, dd, J=3, 10 Hz, rha H-3), 4.12, 4.34 (each 1H, d, J=12 Hz, H-17′), 4.20, 4.46 × 2, 4.55 × 2 (each 1H, d, J=8 Hz, glc H-1), 4.80, 4.89 (each 1H, s, rha H-1), 4.99 (1H, d, J=3 Hz, rha H-2), 5.12 (4H, br t, H-6, H-6′, H-10, H-10′), 5.20—5.24 (4H, m, H-1, H-1′), 5.40 (1H, t, J=7 Hz, H-14′), 6.13 (2H, dd, J=11, 18 Hz, H-2, H-2′), 6.85 (1H,

br t, H-14).

Alkaline Hydrolysis of 5 A solution (2 ml) of **5** (10 mg) in 0.5 N sodium hydroxide was heated at 70 °C for 1 h and was then passed through MCI gel CHP 20P column eluting with water and successively with MeOH. The methanolic eluate was concentrated under reduced pressure to give a syrup, which was subjected to silica gel column chromatography (solv. $CHCl_3$: MeOH : water = 7 : 3 : 0.5) to afford two compounds **1b** and **5a**, the former of which was identical with the specimen previously obtained with respect to the ^{1}H-NMR spectra. **5a**, a white powder, $[\alpha]_D^{23}$ −14.0° (c = 1.03, MeOH), positive FAB-MS m/z: 667 $[M+Na]^+$, 645 $[M+H]^+$. ^{1}H-NMR (CD_3OD) δ: 1.38, 1.60, 1.63, 1.80 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-17), 1.60 (2H, m, H_2-4), 1.96—2.13 (8H, m, H_2-5, H_2-8, H_2-9, H_2-12), 2.29 (2H, m, H_2-13), 3.14—3.83 (m, sugar), 4.45 (1H, d, J = 8 Hz, glc H-1), 4.54 (1H, d, J = 8 Hz, glc H-1), 5.12 (2H, m, H-6, H-10), 5.22 (1H, dd, J = 1, 11 Hz, H-1), 5.23 (1H, dd, J = 1, 18 Hz, H-1), 6.13 (1H, dd, J = 11, 18 Hz, H-2), 6.74 (1H, t, J = 7 Hz, H-14).

Capsianoside F (6) A white powder, $[\alpha]_D^{19}$ −22.7° (c = 0.57, MeOH), negative FAB-MS m/z: 1709 $[M-H]^-$, 1547, 1385, 1083, 937, 775, 643, 481. ^{1}H-NMR (CD_3OD) δ: 1.26, 1.29 (each 3H, d, J = 6 Hz, rha H_3-6), 1.38 × 2, 1.60 × 3, 1.63, 1.77, 1.86 (each 3H, s, H_3-20, H_3-20′, H_3-18, H_3-18′, H_3-19, H_3-19′, H_3-16′, H_3-17), 1.60 (4H, m, H_2-4, H_2-4′), 1.90—2.31 (20H, m, H_2-5, H_2-5′, H_2-8, H_2-8′, H_2-9, H_2-9′, H_2-12, H_2-12′, H_2-13, H_2-13′), 3.93 (1H, dd, J = 2, 10 Hz), 4.02 (1H, d, J = 3 Hz, rha H-2), 4.14, 4.33 (each 1H, d, J = 12 Hz, H-17′), 4.23, 4.46 × 2, 4.55 × 2 (each d, J = 8 Hz, glc H-1), 4.71, 4.87 (each 1H, s, rha H-1), 4.98 (1H, dd, J = 3, 10 Hz, rha H-3), 5.12 (4H, t, J = 8 Hz, H-6, H-6′, H-10, H-10′), 5.20—5.24 (4H, m, H_2-1, H_2-1′), 5.40 (1H, t, J = 7 Hz, H-14′), 6.12 (2H, dd, J = 11, 18 Hz, H-2, H-2′), 6.89 (1H, t, J = 9 Hz, H-14).

Alkaline Hydrolysis of 6 A solution (2 ml) of **6** (5 mg) in 0.5 N sodium hydroxide was passed through MCI gel CHP 20P column eluting with water and successively with MeOH. The methanolic eluate was concentrated under reduced pressure to give a syrup, which was subjected to silica gel column chromatography (solv. $CHCl_3$: MeOH : water = 7 : 3 : 0.5) to yield two compounds identical with **1b** and **5a**.

Capsianoside I (7) A white powder, $[\alpha]_D^{23}$ −7.6° (c = 0.50, MeOH), IR ν_{max}^{KBr} cm^{-1}: 3452 (OH), 1708, 1653 (α,β-unsaturated carbonyl ester), negative FAB-MS m/z: 659 $[M-H]^-$, 497, 335. ^{1}H-NMR (CD_3OD) δ: 1.38, 1.59, 1.66, 1.81 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-17), 1.60 (2H, m, H_2-4), 1.45—2.15 (7H, m, H_2-5, H_2-8, H_2-9, H-12), 2.29 (1H, dd, J = 8, 13 Hz, H-12), 3.10—3.85 (m, sugar), 4.47, 4.56 (each 1H, d, J = 8 Hz, glc H-1), 4.53 (1H, ddd, J = 7, 7, 8 Hz, H-13), 5.12, 5.18 (each 1H, t, J = 7 Hz, H-6, H-10), 5.22 (1H, d, J = 11 Hz, H-1), 5.22 (1H, d, J = 18 Hz, H-1), 6.12 (1H, dd, J = 11, 18 Hz, H-2), 6.56 (1H, d, J = 8, H-14).

Enzymatic Hydrolysis of 7 A solution of **7** (20 mg) and crude naringinase (20 mg) in acetate buffer (pH 4.2, 50 ml) was incubated at 37 °C for 7 d and passed through MCI gel CHP 20P eluting with water and successively with MeOH. The methanolic eluate was concentrated under reduced pressure to give a syrup, which was subjected to silica gel column chromatography (solv. $CHCl_3$: MeOH : water = 7 : 3 : 0.5) to give two products identical with **1a** (1 mg) and **1c** (5 mg).

Capsianoside V (8) A white powder, $[\alpha]_D^{24}$ +0.0° (c = 0.88, MeOH), negative FAB-MS m/z: 513 $[M-H]^-$, 351. ^{1}H-NMR (CD_3OD) δ: 1.37, 1.65 (each 3H, s, H_3-20, H_3-18), 1.81 (3H, s, H_3-17), 1.62 (2H, m, H_2-4), 2.11 (7H, m, H_2-8, H_2-9, H_2-13, H-12), 2.28 (1H, dd, J = 7, 14 Hz, H-12), 3.15—3.82 (m, sugar), 4.09 (2H, s, H_2-19), 4.35 (1H, d, J = 8 Hz, glc H-1), 4.52 (1H, ddd, J = 7, 7, 9 Hz, H-13), 5.19 (1H, t, J = 7 Hz, H-6), 5.20 (1H, d, J = 11 Hz, H-1), 5.24 (1H, d, J = 18 Hz, H-1), 5.28 (1H, t, J = 7 Hz, H-10), 5.94 (1H, dd, J = 11, 18 Hz, H-2), 6.50 (1H, d, J = 9 Hz, H-14).

Capsianoside IV (9) A white powder, $[\alpha]_D^{30}$ −8.4° (c = 0.61, MeOH), negative FAB-MS m/z: 805 $[M-H]^-$, 643, 481, 319. ^{1}H-NMR (CD_3OD) δ: 1.38, 1.60, 1.63, 1.85 (each 3H, s, H_3-20, H_3-19, H_3-18, H_3-17), 1.60 (2H, m, H_2-4), 1.91—2.12 (8H, m, H_2-5, H_2-8, H_2-9, H_2-12), 2.32 (2H, m, H-13), 3.10—3.90 (m, sugar), 4.46, 4.55, 5.53 (each 1H, d, J = 8 Hz, glc H-1), 5.13, 5.16 (each 1H, t, J = 7 Hz, H-6, H-10), 5.21 (1H, dd, J = 11, 18 Hz, H-2), 6.90 (1H, t, J = 8 Hz, H-14).

Capsianoside III (10) A white powder, $[\alpha]_D^{20}$ −26.4° (c = 0.97, MeOH), IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1650 (double bond), negative FAB-MS m/z: 1099 $[M-H]^-$, 937, 775, 613. ^{1}H-NMR (CD_3OD) δ: 1.28 (3H, d, J = 6 Hz, rha H_3-6), 1.38, 1.60 × 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), 3.10—4.00 (m, sugar), 4.21, 4.30 (each 1H, d, J = 12 Hz, H_2-17), 4.35, 4.47, 4.56, 4.63 (each 1H, d, J = 8 Hz, glc H-1), 4.75 (1H, s, rha H-1), 5.12 (2H, t, J = 7 Hz, H-6, H-10), 5.22 (1H, d, J = 18 Hz, H-1), 5.23 (1H, d, J = 11 Hz, H-1), 5.39 (1H, t, J = 7 Hz, H-14), 6.12 (1H, dd, J = 11, 18 Hz, H-2).

Peracetate of 10 A mixture of **2** (30 mg), acetic anhydride (3 ml) and pyridine (3 ml) was heated at 60 °C for 3 h at room temperature and evaporated under reduced pressure to give a residue, which was purified by silica gel column chromatography with n-hexane : AcOEt = 3 : 1 as eluent to yield the peracetate (34 mg). A white powder, EI-MS m/z: 273 (terminal rha·3Ac), 561 (terminal rha-glc·6Ac), 849 (terminal rha-glc-glc·9Ac), 331 (terminal glc·4Ac), 619 (terminal glc-glc·7Ac).

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