New Triterpenoid Saponins from Fruit Specimens of *Panax japonicus* Collected in Toyama Prefecture and Hokkaido (2)

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Four new dammarane-type triterpenoid saponins, chikusetsusaponin FT_1 (1), chikusetsusaponin FT_2 (2), chikusetsusaponin FT_3 (3), chikusetsusaponin FT_4 (4), and six known triterpenoid saponins, chikusetsusaponin FK_4 (8), chikusetsusaponin FK_5 (9), chikusetsusaponin FK_2 (10), chikusetsusaponin FK_3 (11), chikusetsusaponin LN_4 (12), and chikusetsusaponin IVa (14), were isolated from the fruits of *Panax japonicus* C. A. Meyer, collected in Toyama prefecture, Japan, and five new dammarane-type triterpenoid saponins, chikusetsusaponin FT_1 (1), chikusetsusaponin FT_3 (3), chikusetsusaponin FT_4 (4), chikusetsusaponin FH_1 (5), chikusetsusaponin FH_2 (6), and eight known triterpenoid saponins, ginsenoside Re (7), chikusetsusaponin FK_5 (9), chikusetsusaponin FK_2 (10), chikusetsusaponin FK_3 (11), chikusetsusaponin LN_4 (12), 28-desglucosylchikusetsusaponin IVa (13), chikusetsusaponin IVa (14), and chikusetsusaponin V (15), were isolated from the fruits of *P. japonicus* C. A. Meyer, collected in Hokkaido, Japan. The structures of new chikusetsusaponins were elucidated on the basis of chemical and physicochemical evidences.

Key words *Panax japonicus*; fruit; chikusetsusaponin; triterpenoid saponin; dammarane type saponin

We have previously reported main dammarane-type triterpenoid saponins from the fruits of *Panax japonicus* C. A. Meyer (=*P. pseudo-ginseng* subsp. *japonicus* Hara) collected at Kyusyu area in Japan.[1)] We also had opportunities to collect the fruits of *P. japonicus* C. A. Meyer grown in Toyama prefecture and Hokkaido area therefore we continued analysis of saponins constituents in these materials. In this paper, we report the isolation and structure elucidation of four new dammarane-type triterpenoid saponin, chikusetsusaponin FT_1 (**1**), chikusetsusaponin FT_2 (**2**), chikusetsusaponin FT_3 (**3**), and chikusetsusaponin FT_4 (**4**), from the fruits of *P. japonicus* C. A. Meyer, collected in Toyama prefecture, Japan, together with six known triterpenoid saponins, chikusetsusaponin FK_4[1)] (**8**), chikusetsusaponin FK_5[1)] (**9**), chikusetsusaponin FK_2[1)] (**10**), chikusetsusaponin FK_3[1)] (**11**), chikusetsusaponin LN_4[2)] (**12**), and chikusetsusaponin IVa[3)] (**14**). In addition, we also report five new dammarane-type triterpenoid saponins, chikusetsusaponin FT_1 (**1**), chikusetsusaponin FT_3 (**3**), chikusetsusaponin FT_4 (**4**), chikusetsusaponin FH_1 (**5**), chikusetsusaponin FH_2 (**6**), from the fruits of *P. japonicus* C. A. Meyer, collected in Hokkaido, Japan, together with eight known triterpenoid saponins, ginsenoside Re[4,5)] (**7**), chikusetsusaponin FK_5 (**9**), chikusetsusaponin FK_2 (**10**), chikusetsusaponin FK_3 (**11**), chikusetsusaponin LN_4 (**12**), 28-desglucosylchikusetsusaponin IVa[6)] (**13**), chikusetsusaponin IVa (**14**), and chikusetsusaponin V[7)] (**15**).

Results and Discussion

The aqueous MeOH extracts from the fruits of *P. japonicus* C. A. Meyer, collected in Toyama prefecture and Hokkaido, were each subjected to reverse-phase polystyrene gel and ordinary-phase and reverse-phase silica gel column chromatography to afford compounds **1**–**15**.

Chikusetsusaponin FT_1 (**1**) was a white amorphous powder with positive optical rotation ($[\alpha]_D^{16}$ +12.7° in MeOH), and its molecular formula $C_{41}H_{68}O_{13}$ was determined from the quasimolecular ion peak at *m/z* 767 $(M-H)^-$ observed in the negative-ion fast atom bombardment (FAB)-MS and by high-resolution (HR)-FAB-MS measurement. On acid hydrolysis, it yielded glucose and arabinose which were identified by TLC comparison with authentic samples. The ^{1}H- and ^{13}C-NMR (Table 1) spectra of **1** showed signals assignable to be a dammarane-type triterpenoid part [δ 0.92, 1.02, 1.43, 1.46, 1.56, 1.67, 1.68, 1.97 (3H each, all s, H_3-30, 19, 29, 18, 21, 27, 26, 28), 1.24 (1H, d, J=10.4 Hz, H-5), 2.90 (1H, m, H-17), 3.50 (1H, dd, J=4.9, 11.1 Hz, H-3), 3.61 (1H, d, J=9.5 Hz, H-13), 5.37 (1H, m, H-24)], an α-arabinopyranosyl [δ 4.96 (1H, d, J=6.4 Hz, Ara-H-1″)], a β-glucopyranosyl [δ 5.03 (1H, d, J=7.6 Hz, 20Glc-H-1′)] moieties. The proton and carbon signals of **1** in the ^{1}H- and ^{13}C-NMR spectra resembled to those of ginsenoside Rh_8,[8)] except for the additional α-arabinopyranosyl moiety [δ_C 66.0, 68.8, 72.0, 74.2, 104.8] of **1**. This evidence indicated that **1** should be a 20-*O*-monodesmoside of dammar-24-ene-3β,6α,20(*S*)-triol-12-one. The structure of **1** was characterized using ^{1}H–^{1}H correlation spectroscopy (^{1}H–^{1}H COSY), ^{1}H–^{13}C heteronuclear multiple-quantum coherence (HMQC), and ^{1}H–^{13}C heteronuclear multiple bond correlation (HMBC) experiments. The HMBC experiment showed long-range correlations and some important ^{1}H–^{13}C correlations are shown by arrows (Fig. 1). In comparison with **1**, the carbon signals of 12-oxo-20(*S*)-protopanaxatriol[9)] in the ^{13}C-NMR spectra due to C-20 (δ 73.2) was displaced by +8.2 ppm (at δ 81.4), and the signals assignable to C-17 (δ 44.0), C-21 (δ 26.5), and C-22 (δ 41.9) of 12-oxo-20(*S*)-protopanaxatriol were each shielded by −1.4 ppm (at δ 42.6), −4.1 ppm (at δ 22.4), and −1.2 ppm (at δ 40.7), by the β-D-glucosylation shift effects.[10)] The difference of molecular optical rotations between **1** ($[M]_D$ +97.5° in MeOH) and 12-oxo-20(*S*)-protopanaxatriol ($[M]_D$ +217.6° in

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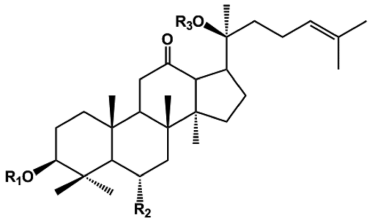
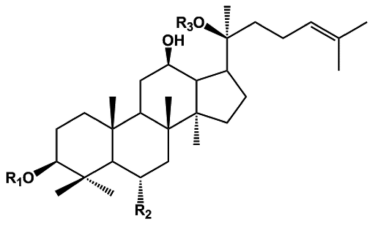
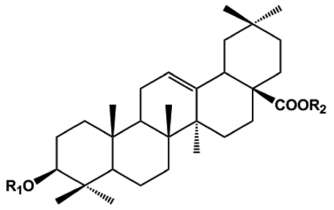


	R_1	R_2	R_3
12-oxo-20(*S*)-protopanaxatriol :	-H	-OH	-H
ginsenoisde Rh_8 :	-H	-OH	-Glc
chikusetsusaponin FT_1 (**1**):	-H	-OH	-Glc^6-Ara(p)
chikusetsusaponin FH_1 (**5**):	-H	-OH	-Glc^6-Ara(f)
chikusetsusaponin LT_8 :	-Glc	-H	-Glc
chikusetsusaponin FT_4 (**4**):	-Glc^6-Xyl	-H	-Glc
chikusetsusaponin LN_4 (**12**):	-Glc^6-Xyl	-H	-Glc^6-Ara(p)
chikusetsusaponin FK_2 (**10**):	-Glc^2-Glc	-H	-Glc
chikusetsusaponin FK_3 (**11**):	-Glc^2-Glc (6: Xyl)	-H	-Glc
chikusetsusaponin FT_2 (**2**):	-Glc^2-Glc (6: Xyl)	-H	-Glc^6-Glc
chikusetsusaponin FT_3 (**3**):	-Glc^2-Glc (6: Xyl)	-H	-Glc^6-Ara(p)
chikusetsusaponin FH_2 (**6**):	-Glc^2-Glc (6: Xyl)	-H	-Glc^6-Ara(f)



	R_1	R_2	R_3
ginsenoside Re (**7**):	-H	-O-Glc^2-Rha	-H
ginsenoisde Rh_2 :	-Glc	-H	-H
chikusetsusaponin FK_4 (**8**):	-Glc^2-Glc (6: Xyl)	-H	-Glc^6-Ara(f)
chikusetsusaponin FK_5 (**9**):	-Glc^2-Glc (6: Xyl)	-H	-Glc^6-Xyl



	R_1	R_2
28-desglucosyl-chikusetsusaponin IVa (**13**):	-GlcUA	-H
chikusetsusaponin IVa (**14**):	-GlcUA	-Glc
chikusetsusaponin V (**15**):	-GlcUA^2-Glc	-Glc

Glc: β-D-glucopyranosyl, Ara(p): α-L-arabinopyranosyl,
Ara(f): α-L-arabinofuranosyl, Xyl: β-D-xylopyranosyl,
Rha: α-L-rhamnopyranosyl, GlcUA: β-D-glucopyranosiduronic acid

Chart 1. Structures of Saponins from the Fruits of *P. japonicus* C. A. MEYER

MeOH) is −120.1°, which reveals the *α*-L-arabinopyranoside ($[M]_D$ of methyl-*α*-L-arabinopyranoside is +17.3°)[11] and *β*-D-glucopyranoside ($[M]_D$ of methyl-*β*-D-glucopyranoside is −66°)[11] in **1**. Consequently, the structure of chikusetsusaponin FT_1 (**1**) was confirmed as dammar-24-ene-3*β*,6*α*,20(*S*)-triol-12-one-20-*O*-*α*-L-arabinopyranosyl-(1→6)-*β*-D-glucopyranoside.

Chikusetsusaponin FT_2 (**2**) was a white amorphous powder with negative optical rotation ($[\alpha]_D^{14}$ −12.9° in MeOH), and its molecular formula $C_{59}H_{98}O_{27}$ was determined from the quasimolecular ion peak at *m/z* 1237 $(M-H)^-$ observed in the negative-ion FAB-MS and by HR-FAB-MS measurement. On acid hydrolysis, it yielded glucose and xylose which were identified by TLC comparison with authentic samples. The ^{1}H- and ^{13}C-NMR (Table 2) spectra of **2** showed signals assignable to be a dammarane-type triterpenoid part [*δ* 0.62 (1H, m, H-5), 0.81, 0.87, 1.09, 1.24, 1.27, 1.57 (3H each, all s, H_3-19, 30, 29, 28, 18, 21), 1.68 (6H, s, H_3-27, 26), 2.93 (1H, m, H-17), 3.21 (1H, dd, *J*=4.3, 11.9 Hz, H-3), 3.55 (1H, d, *J*=9.8 Hz, H-13), 5.37 (1H, m, H-24)], four *β*-glucopyranosyl [*δ* 4.86 (1H, d, *J*=7.3 Hz, 3Glc-H-1′), 5.05 (1H, d, *J*=7.3 Hz, 20Glc-H-1‴), 5.08 (1H, d, *J*=7.9 Hz, Glc-H-1⁗), 5.32 (1H, d, *J*=7.3 Hz, Glc-H-1″)], a *β*-xylopyranosyl [*δ* 4.96 (1H, d, *J*=7.9 Hz, Xyl-H-1‴)] moieties. The proton and carbon signals of **2** in the ^{1}H- and ^{13}C-NMR spectra resembled to those of chikusetsusaponin VI,[12] except for the signals due to the C-12 position, which were similar to that of **1**. This evidence indicated that **2** should be a 3, 20-*O*-bisdesmoside of dammar-24-ene-3*β*,20(*S*)-diol-12-one. The structure of **2** was characterized using ^{1}H–^{1}H COSY, HMQC, HMBC, and ^{1}H–^{1}H totally correlated spectroscopy (^{1}H–^{1}H TOCSY) experiments. The HMBC experiment showed long-range correlations, and some important ^{1}H–^{13}C correlations are shown by arrows (Fig. 1). In comparison with **2**, the carbon signals of dammar-24-ene-3*β*,20(*S*)-diol-12-one[2] in the ^{13}C-NMR spectra due to C-3 (*δ* 77.9), C-4 (*δ* 38.0), C-20 (*δ* 73.3), and C-22 (*δ* 39.9) were each displaced by +11.0 ppm (at *δ* 88.9), +2.0 ppm (at *δ* 40.0), +8.2 ppm (at *δ* 81.5), and +0.7 ppm (at *δ* 40.6), and the signals assignable to C-2 (*δ* 27.9), C-17 (*δ* 44.4), and C-21 (*δ* 26.6) of dammar-24-ene-3*β*,20(*S*)-diol-12-one were each shielded by −1.3 ppm (at *δ* 26.6), −1.8 ppm (at *δ* 42.6), and −4.3 ppm (at *δ* 22.3), by the *β*-D-glucosylation shift effects. The carbon signal of ginsenoside Rh_2[13] in the ^{13}C-NMR spectra due to C-2′ (*δ* 75.8) was displaced by +7.3 ppm (at *δ* 83.1), and the signal assignable to C-1′ (*δ* 106.7) of ginsenoside Rh_2 was shielded by −1.7 ppm (at *δ* 105.0) by the *β*-D-glucosylation shift effects. The difference of molecular optical rotations between **2** ($[M]_D$ −159.2° in MeOH) and chikusetsusaponin FK_2 ($[M]_D$ +94.4° in MeOH) is −253.6°, which reveals the *β*-D-glucopyranoside and *β*-D-xylopyranoside ($[M]_D$ of methyl-*β*-D-xylopyranoside is −108°)[11] in **2**. Consequently, the structure of chikusetsusaponin FT_2 (**2**) was confirmed as dammar-24-ene-3*β*,20(*S*)-diol-12-one-3-*O*-*β*-D-glucopyranosyl-(1→2)-[*β*-D-xylopyranosyl-(1→6)]-*β*-D-glucopyranoside-20-*O*-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranoside.

Chikusetsusaponin FT_3 (**3**) was a white amorphous powder with negative optical rotation ($[\alpha]_D^{14}$ −15.6° in MeOH), and its molecular formula $C_{58}H_{96}O_{26}$ was determined from the quasimolecular ion peak at *m/z* 1207 $(M-H)^-$ observed in the negative-ion FAB-MS and by HR-FAB-MS measurement. On acid hydrolysis, it yielded glucose, arabinose, and xylose which were identified by TLC comparison with authentic samples. The ^{1}H- and ^{13}C-NMR (Table 2) spectra of **3** showed

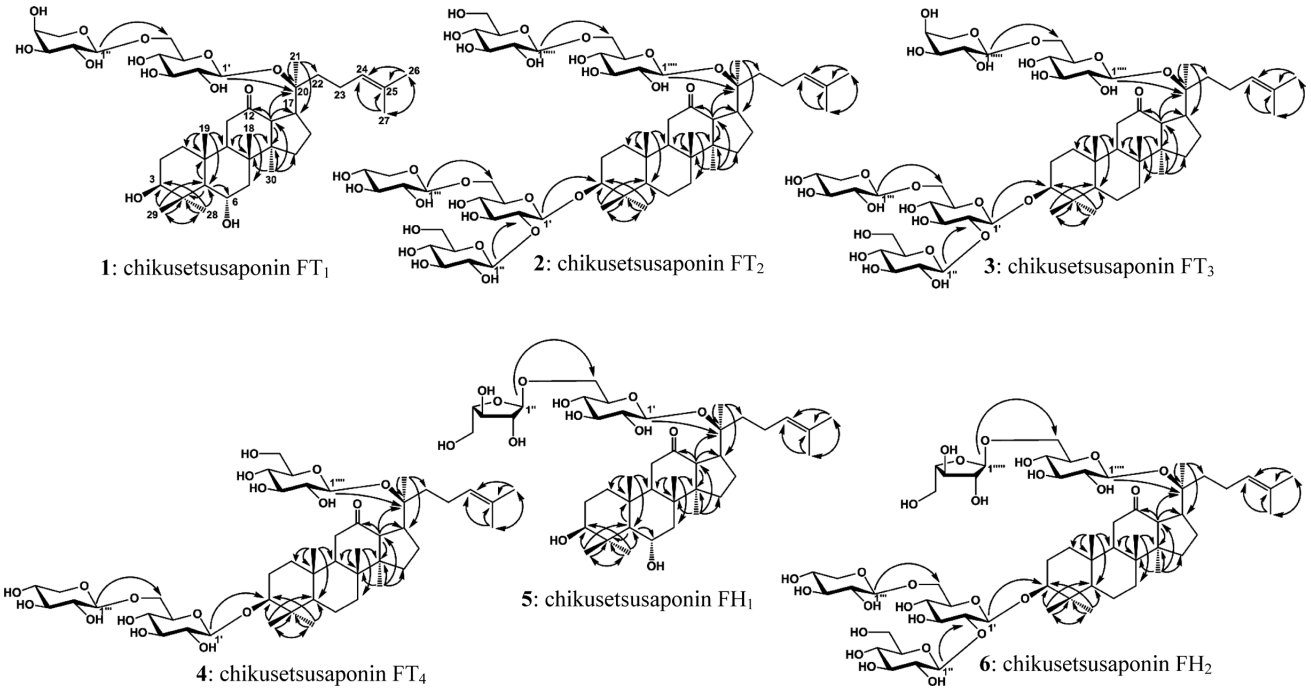


Fig. 1. Significant HMBC Correlations for **1**–**6**

Table 1. ^{13}C-NMR Data of **1** and **5** (in C_5D_5N)

	1	**5**		**1**	**5**
C-1	39.0	39.0	20Glc-C-1′	98.4	98.4
C-2	27.9	28.0	20Glc-C-2′	75.5	75.6
C-3	78.2	78.2	20Glc-C-3′	79.3	79.1
C-4	40.3	40.4	20Glc-C-4′	72.2[a)]	72.3
C-5	61.5	61.5	20Glc-C-5′	76.5	76.3
C-6	67.7	67.7	20Glc-C-6′	69.6	68.5
C-7	47.0	47.0	Ara-C-1″	104.8	110.0
C-8	41.9	41.9	Ara-C-2″	72.0[a)]	83.2
C-9	54.4	54.4	Ara-C-3″	74.2	78.9
C-10	39.5	39.5	Ara-C-4″	68.8	86.1
C-11	40.3	40.3	Ara-C-5″	66.0	62.6
C-12	211.3	211.3			
C-13	56.1	56.2			
C-14	56.0	56.0			
C-15	32.3	32.3			
C-16	24.1	24.0			
C-17	42.6	42.6			
C-18	17.6	17.6			
C-19	17.4	17.5			
C-20	81.4	81.5			
C-21	22.4	22.4			
C-22	40.7	40.5			
C-23	24.5	24.6			
C-24	125.9	125.9			
C-25	130.9	130.9			
C-26	25.8	25.8			
C-27	17.8	17.8			
C-28	31.8	31.8			
C-29	16.4	16.4			
C-30	17.1	17.1			

a) Interchangeable values.

Table 2. ^{13}C-NMR Data of **2**, **3**, **4**, and **6** (in C_5D_5N)

	2	**3**	**4**	**6**		**2**	**3**	**4**	**6**
C-1	38.8	38.7	38.8	38.7	3Glc-C-1′	105.0	105.0	106.9	104.9
C-2	26.6	26.6	26.6	26.6	3Glc-C-2′	83.1	83.0	75.5	83.0
C-3	88.9	88.8	88.7	88.8	3Glc-C-3′	78.2[a)]	78.1[a)]	78.5	78.1[a)]
C-4	40.0	39.6	39.6	39.6	3Glc-C-4′	71.3	71.2	71.6[a)]	71.2
C-5	56.2	56.4	56.2	56.1	3Glc-C-5′	76.5	76.4	76.8	76.4
C-6	18.5	18.5	18.5	18.5	3Glc-C-6′	70.4	69.9	70.1	69.9
C-7	34.8	34.7	34.7	34.7	Glc-C-1″	105.9	105.9		105.8
C-8	40.9	40.8	40.8	40.8	Glc-C-2″	77.0	76.9		76.9
C-9	54.9	54.8	54.8	54.8	Glc-C-3″	78.3[a)]	78.2[a)]		78.2[a)]
C-10	37.5	37.4	37.4	37.4	Glc-C-4″	71.8[b)]	71.8[b)]		71.6[b)]
C-11	40.1	40.0	40.0	40.0	Glc-C-5″	78.0[a)]	77.9[a)]		77.9[a)]
C-12	211.5	211.4	211.3	211.4	Glc-C-6″	62.8	62.7		62.7
C-13	56.5	56.4	56.4	56.5	Xyl-C-1‴	106.0	105.9	105.9	105.9
C-14	56.3	56.2	56.2	56.2	Xyl-C-2‴	74.8	74.7	74.7	74.7
C-15	32.3	32.2	32.3	32.2	Xyl-C-3‴	78.2[a)]	78.1[a)]	77.9	78.1[a)]
C-16	24.1	24.0	23.9	23.9	Xyl-C-4‴	71.1	71.1	71.1	71.0
C-17	42.6	42.5	42.6	42.6	Xyl-C-5‴	67.1	67.1	67.1	67.0
C-18	16.0	15.9	15.9	15.8	20Glc-C-1⁗	98.5	98.4	98.5	98.3
C-19	16.3	16.2	16.3	16.2	20Glc-C-2⁗	75.6[c)]	75.5	75.7	75.5
C-20	81.5	81.4	81.3	81.5	20Glc-C-3⁗	78.4[a)]	78.9	79.2	79.0
C-21	22.3	22.3	22.4	22.2	20Glc-C-4⁗	71.8[b)]	72.1[b)]	71.9[a)]	72.3[b)]
C-22	40.6	40.6	40.5	40.3	20Glc-C-5⁗	76.8	76.4	78.1	76.2
C-23	24.6	24.5	24.5	24.6	20Glc-C-6⁗	69.9	69.6	63.0	68.5
C-24	126.0	125.9	125.7	125.9	Glc-C-1⁗	105.4			
C-25	130.9	130.8	130.8	130.8	Glc-C-2⁗	75.2[c)]			
C-26	25.9	25.8	25.7	25.8	Glc-C-3⁗	78.4[a)]			
C-27	17.9	17.8	17.7	17.8	Glc-C-4⁗	71.8[b)]			
C-28	28.0	28.0	28.0	27.9	Glc-C-5⁗	78.4[a)]			
C-29	16.5	16.4	16.6	16.4	Glc-C-6⁗	62.9			
C-30	17.1	17.0	17.0	17.0	Ara-C-1⁗		104.8		109.9
					Ara-C-2⁗		72.0[b)]		83.1
					Ara-C-3⁗		74.1		78.8
					Ara-C-4⁗		68.7		86.0
					Ara-C-5⁗		65.9		62.5

a–c) Interchangeable values in each vertical column.

signals assignable to be a dammarane-type triterpenoid part [δ 0.62 (1H, m, H-5), 0.81, 0.86, 1.09, 1.24, 1.27, 1.55 (3H each, all s, H_3-19, 30, 29, 28, 18, 21), 1.68 (6H, s, H_3-27, 26), 2.92 (1H, m, H-17), 3.20 (1H, dd, J=4.6, 11.6 Hz, H-3), 3.55 (1H, d, J=9.8 Hz, H-13), 5.36 (1H, m, H-24)], an α-arabinopyranosyl [δ 4.96 (1H, d, J=6.1 Hz, Ara-H-1⁗)], three β-glucopyranosyl [δ 4.86 (1H, d, J=7.3 Hz, 3Glc-H-1′), 5.03 (1H, d, J=7.9 Hz, 20Glc-H-1‴), 5.30 (1H, d, J=7.9 Hz, Glc-H-1″)], a β-xylopyranosyl [δ 4.96 (1H, d, J=7.9 Hz, Xyl-H-1‴)] moieties. The proton and carbon signals of **3** in the ^{1}H- and ^{13}C-NMR spectra resembled to those of chikusetsusaponin LN_4 (**12**), except for the additional β-glucopyranosyl moiety [δ_C 62.7, 71.8, 76.9, 77.9, 78.2, 105.9] of **3**. This evidence indicated that **3** should be a 3,20-*O*-bisdesmoside of dammar-24-ene-3β,20(*S*)-diol-12-one. The structure of **3** was characterized using ^{1}H–^{1}H COSY, HMQC, HMBC, and ^{1}H–^{1}H TOCSY experiments. The HMBC experiment showed long-range correlations, and some important ^{1}H–^{13}C correlations are shown by arrows (Fig. 1). In comparison with **3**, the carbon signals of dammar-24-ene-3β,20(*S*)-diol-12-one in the ^{13}C-NMR spectra due to C-3 (δ 77.9), C-4 (δ 38.0), C-20 (δ 73.3), and C-22 (δ 39.9) were each displaced by +10.9 ppm (at δ 88.8), +1.6 ppm (at δ 39.6), +8.1 ppm (at δ 81.4), and +0.7 ppm (at δ 40.6), and the signals assignable to C-2 (δ 27.9), C-17 (δ 44.4), and C-21 (δ 26.6) of dammar-24-ene-3β,20(*S*)-diol-12-one were each shielded by −1.3 ppm (at δ 26.6), −1.9 ppm (at δ 42.5), and −4.3 ppm (at δ 22.3), by the β-D-glucosylation shift effects. The carbon signal of ginsenoside Rh_2 in the ^{13}C-NMR spectra due to C-2′ (δ 75.8) was displaced by +7.2 ppm (at δ 83.0), and the signal assignable to C-1′ (δ 106.7) of ginsenoside Rh_2 was shielded by −1.7 ppm (at δ 105.0) by the β-D-glucosylation shift effects. The difference of molecular optical rotations between **3** ($[M]_D$ −188.4° in MeOH) and chikusetsusaponin FK_2 ($[M]_D$ +94.4° in MeOH) is −282.8°, which reveals the α-L-arabinopyranoside and β-D-xylopyranoside in **3**. Consequently, the structure of chikusetsu-saponin FT_3 (**3**) was confirmed as dammar-24-ene-3β,20(*S*)-diol-12-one-3-*O*-β-D-glucopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→6)]-β-D-glucopyranoside-20-*O*-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranoside.

Chikusetsusaponin FT_4 (**4**) was a white amorphous powder with negative optical rotation ($[\alpha]_D^{15}$ −8.1° in MeOH), and its molecular formula $C_{47}H_{78}O_{17}$ was determined from the quasi-molecular ion peak at m/z 913 $(M-H)^-$ observed in the negative-ion FAB-MS and by HR-FAB-MS measurement. On acid hydrolysis, it yielded glucose and xylose which were identified by TLC comparison with authentic samples. The ^{1}H- and

^{13}C-NMR (Table 2) spectra of **4** showed signals assignable to be a dammarane-type triterpenoid part [δ 0.69 (1H, m, H-5), 0.81, 0.89, 0.98, 1.56, 1.63, 1.64 (3H each, all s, H_3-19, 30, 29, 21, 26, 27), 1.28 (6H, s, H_3-28, 18), 2.93 (1H, m, H-17), 3.31 (1H, dd, J=4.3, 11.6 Hz, H-3), 3.59 (1H, d, J= 9.2 Hz, H-13), 5.22 (1H, m, H-24)], two β-glucopyranosyl [δ 4.95 (1H, d, J=7.6 Hz, 3Glc-H-1′), 5.09 (1H, d, J=7.6 Hz, 20Glc-H-1‴)], a β-xylopyranosyl [δ 5.00 (1H, d, J=7.6 Hz, Xyl-H-1‴)] moieties. The proton and carbon signals of **4** in the ^{1}H- and ^{13}C-NMR spectra resembled to those of chikusetsusaponin FK_3 (**11**), except for the additional β-glucopyranosyl moiety [δ_C 62.8, 71.8, 77.0, 78.0, 78.3, 105.9] of **11**. This evidence indicated that **4** should be a 3,20-*O*-bisdesmoside of dammar-24-ene-3β,20(*S*)-diol-12-one. The structure of **4** was characterized using ^{1}H–^{1}H COSY, HMQC, HMBC, and ^{1}H–^{1}H TOCSY experiments. The HMBC experiment showed long-range correlations, and some important ^{1}H–^{13}C correlations are shown by arrows (Fig. 1). In comparison with **4**, the carbon signals of dammar-24-ene-3β,20(*S*)-diol-12-one in the ^{13}C-NMR spectra due to C-3 (δ 77.9), C-4 (δ 38.0), C-20 (δ 73.3), and C-22 (δ 39.9) were each displaced by +10.8 ppm (at δ 88.7), +1.6 ppm (at δ 39.6), +8.0 ppm (at δ 81.3), and +0.6 ppm (at δ 40.5), and the signals assignable to C-2 (δ 27.9), C-17 (δ 44.4), and C-21 (δ 26.6) of dammar-24-ene-3β,20(*S*)-diol-12-one were each shielded by −1.3 ppm (at δ 26.6), −1.8 ppm (at δ 42.6), and −4.2 ppm (at δ 22.4), by the β-D-glucosylation shift effects. The difference of molecular optical rotations between **4** ($[M]_D$ −74.0° in MeOH) and chikusetsusaponin LT_8[2] ($[M]_D$ +132.2° in MeOH) is −206.2°, which reveals the β-D-xylopyranoside in **4**. Consequently, the structure of chikusetsusaponin FT_4 (**4**) was confirmed as dammar-24-ene-3β,20(*S*)-diol-12-one-3-*O*-β-D-xylopyranosyl-(1→6)-β-D-glucopyranoside-20-*O*-β-D-glucopyranoside.

Chikusetsusaponin FH_1 (**5**) was a white amorphous powder with positive optical rotation ($[\alpha]_D^{16}$ +0.3° in MeOH), and its molecular formula $C_{41}H_{68}O_{13}$ was determined from the quasimolecular ion peak at m/z 767 $(M-H)^-$ observed in the negative-ion FAB-MS and by HR-FAB-MS measurement. On acid hydrolysis, it yielded glucose and arabinose which were identified by TLC comparison with authentic samples. The ^{1}H- and ^{13}C-NMR (Table 1) spectra of **5** showed signals assignable to be a dammarane-type triterpenoid part [δ 0.93, 1.02, 1.44, 1.44, 1.56, 1.67, 1.70, 1.98 (3H each, all s, H_3-30, 19, 29, 18, 21, 27, 26, 28), 1.23 (1H, d, J=10.4 Hz, H-5), 2.92 (1H, m, H-17), 3.50 (1H, dd, J=4.9, 11.6 Hz, H-3), 3.59 (1H, d, J=9.5 Hz, H-13), 5.39 (1H, m, H-24)], an α-arabinofuranosyl [δ 5.66 (1H, brs, Ara-H-1″)], a β-glucopyranosyl [δ 5.00 (1H, d, J=7.6 Hz, 20Glc-H-1′)] moieties. The proton and carbon signals of **5** in the ^{1}H- and ^{13}C-NMR spectra resembled to those of ginsenoside Rh_8, except for the additional α-arabinofuranosyl moiety [δ_C 62.6, 78.9, 83.2, 86.1, 110.0] of **5**. This evidence indicated that **5** should be a 20-*O*-monodesmoside of dammar-24-ene-3β,6α,20(*S*)-triol-12-one. The structure of **5** was characterized using ^{1}H–^{1}H COSY, HMQC, and HMBC experiments. The HMBC experiment showed long-range correlations, and some important ^{1}H–^{13}C correlations are shown by arrows (Fig. 1). In comparison with **5**, the carbon signals of 12-oxo-20(*S*)-protopanaxatriol in the ^{13}C-NMR spectra due to C-20 (δ 73.2) was displaced by +8.3 ppm (at δ 81.5), and the signals assignable to C-17 (δ 44.0), C-21 (δ 26.5), and C-22 (δ 41.9) of 12-oxo-20(*S*)-protopanaxatriol were each shielded by −1.4 ppm (at δ 42.6), −4.1 ppm (at δ 22.4), and −1.4 ppm (at δ 40.5), by the β-D-glucosylation shift effects. The difference of molecular optical rotations between **5** ($[M]_D$ +2.3° in MeOH) and 12-oxo-20(*S*)-protopanaxatriol ($[M]_D$ +217.6° in MeOH) is −215.3°, which reveals the α-L-arabinofuranoside ($[M]_D$ of methyl-α-L-arabinofuranoside is −226°)[14] and β-D-glucopyranoside in **5**. Consequently, the structure of chikusetsusaponin FH_1 (**5**) was confirmed as dammar-24-ene-3β,6α,20(*S*)-triol-12-one-20-*O*-α-L-arabinofuranosyl-(1→6)-β-D-glucopyranoside.

Chikusetsusaponin FH_2 (**6**) was a white amorphous powder with negative optical rotation ($[\alpha]_D^{15}$ −21.4° in MeOH), and its molecular formula $C_{58}H_{96}O_{26}$ was determined from the quasimolecular ion peak at m/z 1207 $(M-H)^-$ observed in the negative-ion FAB-MS and by HR-FAB-MS measurement. On acid hydrolysis, it yielded glucose, arabinose, and xylose which were identified by TLC comparison with authentic samples. The ^{1}H- and ^{13}C-NMR (Table 2) spectra of **6** showed signals assignable to be a dammarane-type triterpenoid part [δ 0.62 (1H, m, H-5), 0.80, 0.88, 1.09, 1.23, 1.26, 1.54, 1.68, 1.70 (3H each, all s, H_3-19, 30, 29, 28, 18, 21, 27, 26), 2.93 (1H, m, H-17), 3.19 (1H, dd, J=4.6, 11.6 Hz, H-3), 3.51 (1H, d, J= 9.5 Hz, H-13), 5.39 (1H, m, H-24)], an α-arabinofuranosyl [δ 5.64 (1H, brs, Ara-H-1⁗)], three β-glucopyranosyl [δ 4.86 (1H, d, J=7.3 Hz, 3Glc-H-1′), 5.04 (1H, d, J=7.6 Hz, 20Glc-H-1⁗), 5.30 (1H, d, J=7.6 Hz, Glc-H-1″)], a β-xylopyranosyl [δ 4.96 (1H, d, J=7.3 Hz, Xyl-H-1‴)] moieties. The proton and carbon signals of **6** in the ^{1}H- and ^{13}C-NMR spectra resembled to those of chikusetsusaponin FK_3 (**11**), except for the additional α-arabinofuranosyl moiety [δ_C 62.5, 78.8, 83.1, 86.0, 109.9] of **6**. This evidence indicated that **6** should be a 3, 20-*O*-bisdesmoside of dammar-24-ene-3β,20(*S*)-diol-12-one. The structure of **6** was characterized using ^{1}H–^{1}H COSY, HMQC, HMBC, and ^{1}H–^{1}H TOCSY experiments. The HMBC experiment showed long-range correlations, and some important ^{1}H–^{13}C correlations are shown by arrows (Fig. 1). In comparison with **6**, the carbon signals of dammar-24-ene-3β,20(*S*)-diol-12-one in the ^{13}C-NMR spectra due to C-3 (δ 77.9), C-4 (δ 38.0), C-20 (δ 73.3), and C-22 (δ 39.9) were each displaced by +10.9 ppm (at δ 88.8), +1.6 ppm (at δ 39.6), +8.2 ppm (at δ 81.5), and +0.4 ppm (at δ 40.3), and the signals assignable to C-2 (δ 27.9), C-17 (δ 44.4), and C-21 (δ 26.6) of dammar-24-ene-3β,20(*S*)-diol-12-one were each shielded by −1.3 ppm (at δ 26.6), −1.8 ppm (at δ 42.6), and −4.4 ppm (at δ 22.2), by the β-D-glucosylation shift effects. The carbon signal of ginsenoside Rh_2 in the ^{13}C-NMR spectra due to C-2′ (δ 75.8) was displaced by +7.2 ppm (at δ 83.0), and the signal assignable to C-1′ (δ 106.7) of ginsenoside Rh_2 was shielded by −1.8 ppm (at δ 104.9) by the β-D-glucosylation shift effects. The difference of molecular optical rotations between **6** ($[M]_D$ −258.8° in MeOH) and chikusetsusaponin FK_2 ($[M]_D$ +94.4° in MeOH) is −353.2°, which reveals the α-L-arabinofuranoside and β-D-xylopyranoside in **6**. Consequently, the structure of chikusetsusaponin FH_2 (**6**) was confirmed as dammar-24-ene-3β,20(*S*)-diol-12-one-3-*O*-β-D-glucopyranosyl-(1→2)-[β-D-xylopyranosyl-(1→6)]-β-D-glucopyranoside-20-*O*-α-L-arabinofuranosyl-(1→6)-β-D-glucopyranoside.

Previously, it was reported that saponin compositions between rhizome or leaves of *P. japonicus* C. A. MEYER cultivated at Hokkaido and upper area of Honshu didn't have significant difference.[2,15] In this study, we also observed the

Table 3. Comparison of Saponins from Rhizomes of *Panax japonicus* C. A. Meyer Collected in Hokkaido and Toyama Prefecture

Aglycone		Yield (mg)	
		Toyama	Hokkaido
Dammar-24-ene-3β,6α,20(*S*)-triol-12-one	Chikusetsusaponin FT_1 (**1**)	3	21
	Chikusetsusaponin FH_1 (**5**)	—	4
Dammar-24-ene-3β,20(*S*)-diol-12-one	Chikusetsusaponin FT_4 (**4**)	5	38
	Chikusetsusaponin LN_4 (**12**)	37	382
	Chikusetsusaponin FK_2 (**10**)	17	11
	Chikusetsusaponin FK_3 (**11**)	114	143
	Chikusetsusaponin FT_2 (**2**)	17	—
	Chikusetsusaponin FT_3 (**3**)	69	331
	Chikusetsusaponin FH_2 (**6**)	—	42
20(*S*)-Protopanaxatriol	Ginsenoside Re (**7**)	—	4
20(*S*)-Protopanaxadiol	Chikusetsusaponin FK_4 (**8**)	4	—
	Chikusetsusaponin FK_5 (**9**)	13	6
Oleanolic acid	28-Desglucosyl-chikusetsusaponin IVa (**13**)	—	17
	Chikusetsusaponin IVa (**14**)	7	26
	Chikusetsusaponin V (**15**)	—	42

similarity on the main saponin compositions in the fruits of *P. japonicus* C. A. Meyer collected in Hokkaido and Toyama prefecture. Both fruit samples of *P. japonicus* C. A. Meyer collected in Toyama prefecture and Hokkaido contained richly dammar-24-ene-3β,20(*S*)-diol-12-one type saponins such as chikusetsusaponin FT_3, FK_3, and LN_4 (Table 3). In contrast, we observed differences in main saponin compositions in fruits collected from Kumamoto or Miyazaki prefecture.[1)] The main saponins were chikusetsusaponins FK_4 and FK_5 in the fruit samples collected in Kumamoto prefecture where as ginsenoside Rb_3 and Rc in the fruit samples collected from Miyazaki prefecture.[1)] We don't have any logical explanation about saponin constituents similarities and variations yet in the plant species grown in different geographical region. From a geographical point of view, further studies on the saponin constituents on the fruits of *P. japonicus* C. A. Meyer grown other area in Japan are in progress.

Experimental

The following instruments were used to obtain physical data: specific rotations, JASCO DIP-1000KUY digital polarimeter (l=5 cm); FAB-MS and high-resolution MS, JEOL JMS-700 MStation spectrometer; ^{1}H-NMR spectra, JEOL α-500 (500 MHz, 27°C) spectrometer; ^{13}C-NMR spectra, JEOL α-500 (125 MHz, 27°C) spectrometer; and ^{1}H–^{1}H COSY, TOCSY, HMQC and HMBC spectra, JEOL α-500 spectrometer, with tetramethylsilane (TMS) as an internal standard.

The following experimental conditions were used for chromatography; reverse-phase polystyrene gel column chromatography, MCI GEL CHP20P (Mitsubishi Kasei Co., Japan, 75–150 μm); ordinary-phase silica gel column chromatography, Silica gel 60 (Merck Ltd., Japan, 0.040–0.063 mm); reverse-phase silica gel column chromatography, Chromatrex ODS (Fuji Silysia Chemical Ltd., Japan, 30–50 μm); pre-coated TLC plates with Silica gel 60 F_{254} (Merck, 0.2 mm) (ordinary phase); and detection was achieved by spraying with 10% aqueous H_2SO_4 followed by heating.

Plant Materials Dried fruits of *P. japonicus* were collected in July 26, 2006 at near Katakai River, Uozu-shi, Toyama prefecture, Japan. These voucher specimens have been deposited at Experimental Station for Medicinal Plant Research, University of Toyama. And fresh fruits of *P. japonicus* were collected in August 29, 2007 at Medicinal Botanic Garden, Health Sciences University of Hokkaido, Hokkaido, Japan. This voucher specimen has been deposited at Medicinal Botanic Garden, Health Sciences University of Hokkaido.

Isolation of Saponins from the Dried Fruits of *P. japonicus* Collected in Toyama Prefecture The dried fruits of *P. japonicus* C. A. Meyer (21 g) were extracted with hot 50% aqueous MeOH and then followed with hot MeOH. Evaporation of the solvent under reduced pressure provided the methanolic extract (4.3 g). The methanolic extract (4.3 g) was subjected to reverse-phase polystyrene gel column chromatography [H_2O→MeOH–H_2O (30 : 70→40 : 60→50 : 50→60 : 40→70 : 30, v/v)→ MeOH] to give fractions 1–12. Fraction 6 (361 mg) was separated by reverse-phase silica gel column chromatography [MeOH–H_2O (50 : 50→55 : 45→60 : 40→65 : 35→70 : 30, v/v)→MeOH] to give 17 fractions, include chikusetsusaponin FK_3 (fr. 6-12, **11**, 107 mg) and chikusetsusaponin LN_4 (fr. 6-14, **12**, 24 mg). Fraction 6-4 (15 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (8 : 2.5 : 0.2, v/v)] to give chikusetsusaponin IVa (**14**, 7 mg). Fraction 6-7 (22 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.3, v/v)] to give chikusetsusaponin FT_1 (**1**, 3 mg) and chikusetsusaponin FT_2 (**2**, 17 mg). Fraction 6-9 (71 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (8 : 2.5 : 0.2→7 : 3.5 : 0.3, v/v)] to give chikusetsusaponin FT_3 (**3**, 69 mg). Fraction 7 (90 mg) was separated by reverse-phase silica gel column chromatography [MeOH–H_2O (50 : 50→55 : 45→60 : 40→65 : 35→70 : 30→75 : 25, v/v)→MeOH] to give 9 fractions. Fraction 7-2 (31 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (8 : 2.5 : 0.2, v/v)] to give chikusetsusaponin FK_3 (**11**, 7 mg). Fraction 7-4 (13 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (9 : 2 : 0.1, v/v)] to give chikusetsusaponin FK_2 (**10**, 10 mg). Fraction 7-6 (13 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (8 : 2.5 : 0.2, v/v)] to give chikusetsusaponin LN_4 (**12**, 13 mg). Fraction 7-8

(6 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.3, v/v)] to give chikusetsusaponin FK_4 (**8**, 4 mg). Fraction 9 (85 mg) was separated by reverse-phase silica gel column chromatography [MeOH–H_2O (60 : 40→65 : 35→70 : 30→75 : 25, v/v)→MeOH] to give 10 fractions, include chikusetsusaponin FT_4 (fr. 9-7, **4**, 5 mg) and chikusetsusaponin FK_5 (fr. 9-9, **9**, 13 mg). Fraction 9-3 (9 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (9 : 2 : 0.1, v/v)] to give chikusetsusaponin FK_2 (**10**, 7 mg).

Isolation of Saponins from the Fresh Fruits of *P. japonicus* Collected in Hokkaido The fresh fruits of *P. japonicus* C. A. MEYER (310 g) were extracted with hot 60% aqueous MeOH and then followed with MeOH. Evaporation of the solvent under reduced pressure provided the methanolic extract (10.0 g). The methanolic extract (10.0 g) was subjected to reverse-phase polystyrene gel column chromatography [H_2O→MeOH–H_2O (30 : 70→40 : 60→50 : 50→60 : 40→70 : 30→80 : 20, v/v)→MeOH] to give fractions 1–8, include 28-desglucosylchikusetsusaponin IVa (fr. 7, **13**, 17 mg). Fraction 4 (1767 mg) was separated by reverse-phase silica gel column chromatography [MeOH–H_2O (35 : 65→40 : 60→45 : 55→50 : 50→55 : 45→60 : 40→65 : 35, v/v)→MeOH] to give 23 fractions, include chikusetsusaponin FT_4 (fr. 4-21, **4**, 31 mg). Fraction 4-6 (67 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.4, v/v)] to give chikusetsusaponin FT_1 (**1**, 7 mg). Fraction 4-8 (45 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.3, v/v)] to give ginsenoside Re (**7**, 4 mg). Fraction 4-10 (87 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.3, v/v)] to give 7 fractions. Fraction 4-10-7 (43 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (6 : 4 : 1, v/v)] to give 3 fractions. Fraction 4-10-7-1 (19 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.5, v/v)] to give chikusetsusaponin FK_3 (**11**, 14 mg). Fraction 4-11 (27 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (8 : 2.5 : 0.2, v/v)] to give chikusetsusaponin FH_1 (**5**, 4 mg). Fraction 4-12 (48 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.3, v/v)] to give chikusetsusaponin FT_1 (**1**, 14 mg). Fraction 4-14 (59 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.3, v/v)] to give chikusetsusaponin FH_2 (**6**, 42 mg). Fraction 4-15 (397 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.3, v/v)] to give chikusetsusaponin FT_3 (**3**, 331 mg) and chikusetsusaponin V (**15**, 20 mg). Fraction 4-17 (162 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (8 : 2.5 : 0.2→7 : 3 : 0.4, v/v)] to give 7 fractions, include chikusetsusaponin FK_3 (fr.4-17-3, **11**, 124 mg). Fraction 4-17-6 (21 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.3→6 : 4 : 1, v/v)] to give chikusetsusaponin V (**15**, 16 mg). Fraction 4-18 (124 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (8 : 2.5 : 0.2→7 : 3 : 0.4, v/v)] to give chikusetsusaponin FK_2 (**10**, 11 mg) and chikusetsusaponin V (**15**, 6 mg). Fraction 4-19 (461 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (8 : 2.5 : 0.2, v/v)] to give chikusetsusaponin LN_4 (**12**, 362 mg). Fraction 4-22 (46 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.4, v/v)] to give 6 fractions. Fraction 4-22-3 (9 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (9 : 1.5 : 0.1, v/v)] to give chikusetsusaponin FT_4 (**4**, 7 mg). Fraction 5 (205 mg) was separated by reverse-phase silica gel column chromatography [MeOH–H_2O (60 : 40→65 : 35→70 : 30→75 : 25, v/v)→MeOH] to give 9 fractions. Fraction 5-5 (21 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.4, v/v)] to give chikusetsusaponin FK_3 (**11**, 5 mg) and chikusetsusaponin IVa (**14**, 6 mg). Fraction 5-6 (78 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.4, v/v)] to give chikusetsusaponin LN_4 (**12**, 20 mg) and chikusetsusaponin IVa (**14**, 13 mg). Fraction 5-8 (11 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (7 : 3 : 0.4, v/v)] to give chikusetsusaponin FK_5 (**9**, 6 mg). Fraction 6 (94 mg) was separated by reverse-phase silica gel column chromatography [MeOH–H_2O (50 : 50→60 : 40→65 : 35→70 : 30→75 : 25→80 : 20, v/v)→MeOH] to give 5 fractions. Fraction 6-2 (38 mg) was separated by ordinary-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (8 : 2.5 : 0.2→7 : 3 : 0.4, v/v)] to give chikusetsusaponin IVa (**14**, 7 mg).

Chikusetsusaponin FT_1 (**1**): A white amorphous powder; $[\alpha]_D^{16}$ +12.7° (c=0.66, MeOH); ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.92, 1.02, 1.43, 1.46, 1.56, 1.67, 1.68, 1.97 (3H each, all s, H_3-30, 19, 29, 18, 21, 27, 26, 28), 1.24 (1H, d, J=10.4 Hz, H-5), 2.90 (1H, m, H-17), 3.50 (1H, dd, J=4.9, 11.1 Hz, H-3), 3.61 (1H, d, J=9.5 Hz, H-13), 4.96 (1H, d, J=6.4 Hz, Ara-H-1″), 5.03 (1H, d, J=7.6 Hz, 20Glc-H-1′), 5.37 (1H, m, H-24); ^{13}C-NMR data, see Table 1; negative-ion FAB-MS m/z 767 $(M-H)^-$; negative-ion HR-FAB-MS: m/z 767.4545 (Calcd for $C_{41}H_{67}O_{13}$ $[M-H]^-$, 767.4582).

Chikusetsusaponin FT_2 (**2**): A white amorphous powder; $[\alpha]_D^{14}$ −12.9° (c=0.91, MeOH); ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.62 (1H, m, H-5), 0.81, 0.87, 1.09, 1.24, 1.27, 1.57 (3H each, all s, H_3-19, 30, 29, 28, 18, 21), 1.68 (6H, s, H_3-27, 26), 2.93 (1H, m, H-17), 3.21 (1H, dd, J=4.3, 11.9 Hz, H-3), 3.55 (1H, d, J=9.8 Hz, H-13), 4.86 (1H, d, J=7.3 Hz, 3Glc-H-1′), 4.96 (1H, d, J=7.9 Hz, Xyl-H-1‴), 5.05 (1H, d, J=7.3 Hz, 20Glc-H-1⁗), 5.08 (1H, d, J=7.9 Hz, Glc-H-1⁗), 5.32 (1H, d, J=7.3 Hz, Glc-H-1″), 5.37 (1H, m, H-24); ^{13}C-NMR data, see Table 2; negative-ion FAB-MS m/z 1237 $(M-H)^-$, 1105 $(M-C_5H_9O_4)^-$, 1075 $(M-C_6H_{11}O_5)^-$, 943 $(M-C_{11}H_{19}O_9)^-$, 913 $(M-C_{12}H_{21}O_{10})^-$; negative-ion HR-FAB-MS: m/z 1237.6191 (Calcd for $C_{59}H_{97}O_{27}$ $[M-H]^-$, 1237.6217).

Chikusetsusaponin FT_3 (**3**): A white amorphous powder; $[\alpha]_D^{14}$ −15.6° (c=0.34, MeOH); ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.62 (1H, m, H-5), 0.81, 0.86, 1.09, 1.24, 1.27, 1.55 (3H each, all s, H_3-19, 30, 29, 28, 18, 21), 1.68 (6H, s, H_3-27, 26), 2.92 (1H, m, H-17), 3.20 (1H, dd, J=4.6, 11.6 Hz, H-3), 3.55 (1H, d, J=9.8 Hz, H-13), 4.86 (1H, d, J=7.3 Hz, 3Glc-H-1′), 4.96 (1H, d, J=6.1 Hz, Ara-H-1⁗), 4.96 (1H, d, J=7.9 Hz, Xyl-H-1‴), 5.03 (1H, d, J=7.9 Hz, 20Glc-H-1‴), 5.30 (1H, d, J=7.9 Hz, Glc-H-1″), 5.36 (1H, m, H-24) ; ^{13}C-NMR data, see Table 2; negative-ion FAB-MS m/z 1207 $(M-H)^-$, 1075 $(M-C_5H_9O_4)^-$, 1045 $(M-C_6H_{11}O_5)^-$, 913 $(M-C_{11}H_{19}O_9)^-$; negative-ion HR-FAB-MS: m/z 1207.6101 (Calcd for $C_{58}H_{95}O_{26}$ $[M-H]^-$, 1207.6112).

Chikusetsusaponin FT_4 (**4**): A white amorphous powder;

$[\alpha]_D^{15}$ −8.1° (*c*=0.65, MeOH); ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.69 (1H, m, H-5), 0.81, 0.89, 0.98, 1.56, 1.63, 1.64 (3H each, all s, H_3-19, 30, 29, 21, 26, 27), 1.28 (6H, s, H_3-28, 18), 2.93 (1H, m, H-17), 3.31 (1H, dd, *J*=4.3, 11.6 Hz, H-3), 3.59 (1H, d, *J*=9.2 Hz, H-13), 4.95 (1H, d, *J*=7.6 Hz, 3Glc-H-1′), 5.00 (1H, d, *J*=7.6 Hz, Xyl-H-1‴), 5.09 (1H, d, *J*=7.6 Hz, 20Glc-H-1⁗), 5.22 (1H, m, H-24); ^{13}C-NMR data, see Table 2; negative-ion FAB-MS *m/z* 913 $(M-H)^-$, 781 $(M-C_5H_9O_4)^-$, 751 $(M-C_6H_{11}O_5)^-$, 619 $(M-C_{11}H_{19}O_9)^-$; negative-ion HR-FAB-MS: *m/z* 913.5204 (Calcd for $C_{47}H_{77}O_{17}$ $[M-H]^-$, 913.5161).

Chikusetsusaponin FH_1 (**5**): A white amorphous powder; $[\alpha]_D^{16}$ +0.3° (*c*=0.39, MeOH); ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.93, 1.02, 1.44, 1.44, 1.56, 1.67, 1.70, 1.98 (3H each, all s, H_3-30, 19, 29, 18, 21, 27, 26, 28), 1.23 (1H, d, *J*=10.4 Hz, H-5), 2.92 (1H, m, H-17), 3.50 (1H, dd, *J*=4.9, 11.6 Hz, H-3), 3.59 (1H, d, *J*=9.5 Hz, H-13), 5.00 (1H, d, *J*=7.6 Hz, 20Glc-H-1′), 5.39 (1H, m, H-24), 5.66 (1H, brs, Ara-H-1″); ^{13}C-NMR data, see Table 1; negative-ion FAB-MS *m/z* 767 $(M-H)^-$, 635 $(M-C_5H_9O_4)^-$, 473 $(M-C_{11}H_{19}O_9)^-$; negative-ion HR-FAB-MS: *m/z* 767.4545 (Calcd for $C_{41}H_{67}O_{13}$ $[M-H]^-$, 767.4582).

Chikusetsusaponin FH_2 (**6**): A white amorphous powder; $[\alpha]_D^{15}$ −21.4° (*c*=0.81, MeOH); ^{1}H-NMR (pyridine-d_5, 500 MHz) δ: 0.62 (1H, m, H-5), 0.80, 0.88, 1.09, 1.23, 1.26, 1.54, 1.68, 1.70 (3H each, all s, H_3-19, 30, 29, 28, 18, 21, 27, 26), 2.93 (1H, m, H-17), 3.19 (1H, dd, *J*=4.6, 11.6 Hz, H-3), 3.51 (1H, d, *J*=9.5 Hz, H-13), 4.86 (1H, d, *J*=7.3 Hz, 3Glc-H-1′), 4.96 (1H, d, *J*=7.3 Hz, Xyl-H-1‴), 5.04 (1H, d, *J*=7.6 Hz, 20Glc-H-1⁗) 5.30 (1H, d, *J*=7.6 Hz, Glc-H-1″), 5.64 (1H, brs, Ara-H-1⁗), 5.39 (1H, m, H-24); ^{13}C-NMR data, see Table 2; negative-ion FAB-MS *m/z* 1207 $(M-H)^-$, 1075 $(M-C_5H_9O_4)^-$, 1045 $(M-C_6H_{11}O_5)^-$; negative-ion HR-FAB-MS: *m/z* 1207.6066 (Calcd for $C_{58}H_{95}O_{26}$ $[M-H]^-$, 1207.6112).

Acid Hydrolysis of 1–6 A solution of **1**–**6** (1 mg, each) in 2 N HCl (0.2 mL) was heated at 70°C for 3 h separately. Each reaction mixture was subjected to silica gel TLC, together with the standard samples, using $CHCl_3$–MeOH–H_2O (6 : 4 : 1, v/v/v) and *n*-BuOH–AcOEt–H_2O (5 : 1 : 4, v/v/v, upper phase) as the developing solvents and using 10% aqueous H_2SO_4 as the detection reagent. Glucose and arabinose were detected from **1** and **5**. Glucose and xylose were detected from **2** and **4**. Glucose, arabinose, and xylose were detected from **3** and **6**.

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