Studies on the Constituents of *Clematis* Species. VII.[1] Triterpenoid Saponins from the Roots of *Clematis terniflora* DC. var. *robusta* TAMURA[2]

Yukio KAWATA, Haruhisa KIZU, and Tsuyoshi TOMIMORI*

Faculty of Pharmaceutical Sciences, Hokuriku University, Ho-3, Kanagawa-machi, Kanazawa 920–1181, Japan.
Received August 6, 1998; accepted October 1, 1998

From the roots of *Clematis terniflora*, nine new oleanolic acid 3,28-*O*-bisdesmosides called clematernosides A, B, E, F, G, H, I, J and K, and two new hederagenin 3,28-*O*-bisdesmosides called clematernosides C and D, have been isolated together with two known saponins, huzhangoside B and clematichinenoside C. The structures of the new saponins have been elucidated based on chemical and spectral evidence. Among the new saponins, clematernosides I and J have a nonasaccharide moiety and a total of twelve monosaccharide moieties in the molecule. This is the first report of the isolation and structure elucidation of such "big" glycosides.

Key words *Clematis terniflora*; clematernoside; saponin; oleanolic acid bisdesmoside; hederagenin bisdesmoside; Ranunculaceae

Clematis terniflora DC. var. *robusta* TAMURA (Japanese name: sen-nin-soh) is a viny plant of the family Ranunculaceae, which is widely distributed in Japan, Korea, Taiwan and continental China. On the Japanese market, the roots of *C. terniflora* are regarded as a substitute of a traditional chinese drug "Wei Ling Xian (the roots of *C. chinensis* OSBECK, 威霊仙)," and are used in the same way as "Wei Ling Xian."[3]

As a continuation of our study on the constituents from *Clematis* species,[1] the dried roots of *C. terniflora*, whose constituents are almost unknown except for sapogenin,[4] have been investigated.

The water-soluble portion of a hot MeOH ext. was successively extracted with ether, EtOAc and BuOH. The BuOH-soluble part and the mother liquor of BuOH extraction were subjected to repeated chromatography to give ten compounds (**1**—**10**) and three compounds (**11**—**13**), respectively, as described in the experimental section.

Compound **3** was identified as huzhangoside B[1,5] by direct comparison with an authentic sample, and **4** as clematichinenoside C[6] based on the chemical data, ^{13}C-NMR spectra and specific rotation data.

New compounds were named clematernosides A (**1**), B (**2**), C (**5**), D (**6**), E (**7**), F (**8**), G (**9**), H (**10**), I (**11**), J (**12**) and K (**13**). On acid-hydrolysis, all of the new compounds afforded arabinose, rhamnose, ribose and glucose as sugar components, and C (**5**) and D (**6**) gave hederagenin and the others gave oleanolic acid as an aglycone. The molecular formula of these compounds were determined from their HR-FAB-MS and ^{13}C-NMR spectral data as summarized in Table 1.

All of these compounds were deduced to be 3,28-*O*-bisdesmosides of oleanolic acid or hederagenin from the chemical shifts of carbon signals due to an A-ring and C-28 in an aglycone moiety (Table 2).[1]

Clematernoside A (**1**), $C_{86}H_{132}O_{42}$, was obtained as an amorphous powder and its ^{13}C-NMR spectrum showed eight anomeric carbon signals together with signals assignable to a 3-hydroxy-4-methoxycinnamoyl (isoferuloyl) group (Tables 3, 4). The ^{1}H-NMR and UV spectra of **1** also supported the presence of an isoferuloyl group (Table 5). Alkaline-hydrolysis of **1** afforded a prosapogenin (**1a**) which was identified as CP_9 [oleanolic acid 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-β-D-ribopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside (abbreviation: $G^4G^3RiR^2AOle$)] by direct comparison.[7] Consequently, **1** was deduced to be a monoisoferulate of CP_9-28-triglycosyl ester. Compound **1** was hydrolyzed with mild alkali, 0.1 N KOH aq., at room temperature to give a deacylated compound (**1b**). Comparison of the ^{13}C-NMR spectrum of **1b** with those of **1a** and **3** revealed that the 28-*O*-glycosyl moiety was α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl group (abbreviation: $G^1G^2R^1$). The assignments of proton and carbon signals due to sugar moiety of **1**, **1a** and **1b** were confirmed based on the ^{1}H–^{1}H correlation spectroscopy (COSY) and ^{1}H–^{13}C COSY spectral data. In comparison of the ^{1}H- and ^{13}C-NMR data for **1** with those for **1b**, the H-2 and C-2 signals of the terminal glucose moiety (Glc^4) in **1** were observed at a lower field by 1.68 and 0.5 ppm, respectively, and the C-1 and C-3 signals of Glc^4 at higher field by 2.2 and 1.8 ppm, respectively, than the corresponding signals in **1b** (Tables 3, 6). These results show that an isoferuloyl group in **1** is connected to the C-2 position of the terminal glucose moiety.

From these facts, the structure of clematernoside A (**1**) was concluded to be 3-*O*-(2-*O*-isofeluroyl)-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-β-D-ribopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl oleanolic acid 28-*O*-α-L-rhamnopyranosyl-(1→4)-β-D-glu-

Table 1. HR-FAB-MS Data for Clematernosides A—K

	Formula	Found[a]	Calcd[b]
A (**1**)	$C_{86}H_{132}O_{42}$	1835.8148	1835.8117
B (**2**)	$C_{86}H_{132}O_{42}$	1835.8064	1835.8117
C (**5**)	$C_{86}H_{132}O_{43}$	1851.8014	1851.8066
D (**6**)	$C_{98}H_{152}O_{52}$	2159.9138	2159.9171
E (**7**)	$C_{98}H_{152}O_{51}$	2143.9253	2143.9225
F (**8**)	$C_{87}H_{134}O_{42}$	1849.8300	1849.8274
G (**9**)	$C_{104}H_{162}O_{56}$	2305.9805	2305.9753
H (**10**)	$C_{104}H_{162}O_{55}$	2289.9751	2289.9804
I (**11**)	$C_{110}H_{172}O_{61}$	2468.0254	2468.0282
J (**12**)	$C_{110}H_{172}O_{61}$	2468.0352	2468.0282
K (**13**)	$C_{104}H_{162}O_{56}$	2305.9707	2305.9753

a) $(M-H)^-$ ion. *b*) Calculated by $(M-H)^-$ ion.

* To whom correspondence should be addressed.

3: Rib (1→3) Rha^2 (1→2) Ara (1→3) Ole (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

4: Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Ole (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

1: IF (1→2) Glc^4 (1→4) Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Ole(28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

2: IF (1→3) Glc^4 (1→4) Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Ole (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

8: DMC (1→2) Glc^4 (1→4) Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Ole (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

5: IF (1→2) Glc^4 (1→4) Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Hed (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

6: Rha^3 (1→6) Glc^5 (1→3), IF (1→2) > Glc^4 (1→4) Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Hed (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

7: Rha^3 (1→6) Glc^5 (1→3), IF (1→2) > Glc^4 (1→4) Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Ole (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

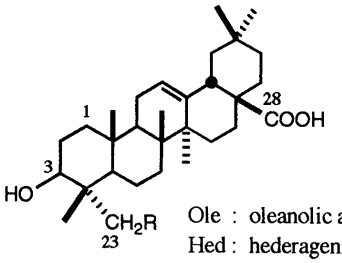
9: Rha^3 (1→6), Glc^6 (1→4) > Glc^5 (1→3), IF (1→2) > Glc^4 (1→4) Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Ole (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

10: Rha^3 (1→6), Glc^6 (1→4) > Glc^5 (1→3), MC (1→2) > Glc^4 (1→4) Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Ole (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

13: Glc^7 (1→2) Rha^3 (1→6) Glc^5 (1→3), IF (1→2) > Glc^4 (1→4) Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Ole (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

11: Glc^7 (1→2) Rha^3 (1→6), Glc^6 (1→4) > Glc^5 (1→3), IF (1→2) > Glc^4 (1→4) Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Ole (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1

12: Rha^3 (1→6), Glc^8 (1→2) Glc^6 (1→4) > Glc^5 (1→3), IF (1→2) > Glc^4 (1→4) Glc^3 (1→4) Rib (1→3) Rha^2 (1→2) Ara (1→3) Ole (28←1) Glc^1(6←1) Glc^2 (4←1)Rha^1



Ole : oleanolic acid (R=H)
Hed : hederagenin (R=OH)

Ara : α-L-arabinopyranosyl
Rha : α-L-rhamnopyranosyl
Rib : β-D-ribopyranosyl
Glc : β-D-glucopyranosyl

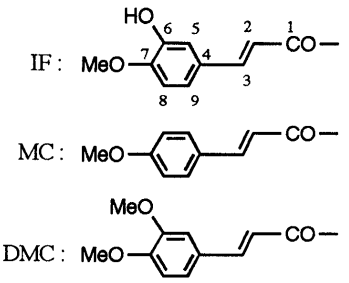


Chart 1

copyranosyl-(1→6)-β-D-glucopyranoside [abbreviation: (2-*O*-IF-G^4)G^3RiR^2AOle$G^1G^2R^1$].

Clematernoside B (**2**), $C_{86}H_{132}O_{42}$, showed eight anomeric carbon signals together with siganls due to an isoferuloyl group in its ^{13}C-NMR spectrum. On mild alkaline-hydrolysis, **2** gave isoferulic acid and a deacyl compound which was identified as **1b**. Detailed comparison of the ^{1}H- and ^{13}C-NMR spectra of **2** with those of **1b** revealed that the linkage site of the isoferuloyl group in **2** was the C-3 position of the terminal glucose moiety of **1b**: acylation shifts were observed at the H-3 (+1.80 ppm), C-2 (−2.3 ppm), C-3 (+0.7 ppm) and C-4 (−2.4 ppm) positions of the terminal glucose moiety (Table 3).

Based on these facts, the structure of clematernoside B (**2**) was concluded to be (3-*O*-IF-G^4)G^3RiR^2AOle $G^1G^2R^1$ (Chart 1).

Clematernoside F (**8**), $C_{87}H_{134}O_{42}$, showed the presence of a 3,4-dimethoxycinnamoly group in the NMR spectra (Tables 4, 5) and gave 3,4-dimethoxycinnamic acid and a deacyl compound on mild alkaline-hydrolysis. The deacyl compound was identified as **1b**. Thus, compound **8** was a 3,4-dimethoxycinnamate of **1b**. The acyl group was deduced to be linking to the C_2-oxygen of the terminal glucose[4] moiety of **1b** because the proton and carbon signals due to sugar moieties in **8** were observed at almost the same positions as those in **1**. Therefore, the structure of clematernoside F (**8**) is represented as shown in Chart 1.

Clematernoside C (**5**), $C_{86}H_{132}O_{43}$, on alkaline-hydrolysis, gave isoferulic acid and a prosapogenin (**5a**) which was identified as CP_{10} [hederagenin 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→4)-β-D-ribopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside (abbreviation: G^4G^3RiR^2AHed)] by direct comparison.[7] In the NMR spectra of **5**, signals due to sugar moieties were found at al-

Table 2. ^{13}C-NMR Spectral Data for the Aglycone Moiety of **1**—**13** in Pyridine-d_5

C No.	3	4	1	2	8	5	6	7	9	10	13	11	12
1	38.8	38.9	38.9	38.8	38.9	39.0	39.1	38.9	38.9	38.9	38.9	38.9	38.9
2	26.5	26.6	26.6	26.5	26.6	26.3	26.4	26.6	26.7	26.6	26.6	26.6	26.6
3	88.6	88.6	88.6	88.6	88.6	80.9	81.0	88.7	88.7	88.7	88.7	88.7	88.7
4	39.5	39.5	39.5	39.4	39.5	43.5	43.6	39.5	39.6	39.6	39.6	39.6	39.5
5	55.9	55.9	56.0	55.9	55.9	47.6	47.6	56.0	56.0	56.0	56.0	56.0	56.0
6	18.4	18.4	18.4	18.4	18.4	18.1	18.1	18.5	18.5	18.5	18.4	18.5	18.4
7	33.0	33.0	33.1	33.0	33.0	32.7	32.7	33.1	33.1	33.1	33.0	33.0	33.0
8	39.8	39.8	39.8	39.7	39.8	39.8	39.9	39.8	39.9	39.9	39.9	39.8	39.8
9	47.9	48.0	48.0	47.9	48.0	48.1	48.2	48.0	48.0	48.1	48.0	48.0	48.0
10	36.9	37.0	37.0	36.9	36.9	36.8	36.9	37.0	37.0	37.0	37.0	37.0	37.0
11	23.7	23.7	23.7	23.6	23.7	23.8	23.8	23.8	23.8	23.8	23.8	23.7	23.7
12	122.7	122.8	122.8	122.7	122.8	122.9	123.0	122.8	122.8	122.8	122.8	122.8	122.8
13	144.0	144.0	144.1	144.0	144.0	144.0	144.1	144.2	144.1	144.1	144.1	144.1	144.1
14	42.0	42.0	42.0	42.0	42.0	42.0	42.1	42.1	42.1	42.1	42.1	42.1	42.1
15	28.1	28.2	28.2	28.1	28.2	28.2	28.3	28.2	28.3	28.3	28.2	28.2	28.2
16	23.2	23.3	23.3	23.2	23.3	23.3	23.3	23.3	23.3	23.4	23.3	23.3	23.3
17	46.9	47.0	47.0	46.9	46.9	46.9	47.0	47.0	47.0	47.0	47.0	47.0	47.0
18	41.5	41.6	41.6	41.5	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6
19	46.1	46.1	46.1	46.1	46.1	46.1	46.2	46.2	46.2	46.2	46.2	46.2	46.2
20	30.6	30.7	30.7	30.6	30.6	30.7	30.7	30.7	30.7	30.7	30.7	30.7	30.7
21	33.9	33.9	33.9	33.8	33.9	33.9	34.0	34.0	34.0	34.0	34.0	33.9	33.9
22	32.4	32.4	32.5	32.4	32.4	32.5	32.5	32.5	32.5	32.5	32.5	32.5	32.5
23	28.1	28.1	28.1	28.0	28.1	63.8	63.8	28.1	28.1	28.1	28.1	28.1	28.1
24	17.0	17.0	17.1	17.0	17.0	14.0	14.1	17.1	17.1	17.1	17.1	17.0	17.1
25	15.5	15.6	15.6	15.5	15.8	16.1	16.2	15.6	15.6	15.6	15.6	15.6	15.6
26	17.4	17.4	17.4	17.3	17.4	17.5	17.5	17.4	17.5	17.5	17.5	17.4	17.4
27	26.0	26.0	26.0	25.9	26.0	26.0	26.0	26.0	26.0	26.1	26.0	26.0	26.0
28	176.4	176.4	176.5	176.4	176.4	176.5	176.5	176.5	176.5	176.5	176.5	176.5	176.5
29	33.0	33.1	33.1	33.0	33.0	33.0	33.1	33.1	33.1	33.1	33.1	33.1	33.1
30	23.5	23.6	23.6	23.5	23.6	23.6	23.7	23.8	23.7	23.7	23.7	23.6	23.6

most the same positions as those in **1**, except for signals due to an arabinose moiety connected to an aglycone. From these data, the structure of clematernoside C (**5**) is represented as shown in Chart 1.

Clematernoside E (**7**), $C_{98}H_{152}O_{51}$, exhibited signals due to ten anomeric carbons together with those assignable to an isoferuloyl group in the ^{13}C-NMR spectrum (Tables 3, 4). The ^{1}H-NMR spectrum of **7** also indicated the presence of an isoferuloyl group. On alkaline-hydrolysis, **7** gave a prosapogenin (**7a**) which showed seven anomeric signals in the ^{1}H- and ^{13}C-NMR spectra. By comparison of the ^{1}H- and ^{13}C-NMR spectra of **7** with those of **7a** and **3**, 28-*O*-sugar moiety in **7** was deduced to be $G^1G^2R^1$ (Table 3).

In the negative FAB-MS of **7a**, an $(M-H)^-$ ion appeared at *m/z* 1497.7 and clear fragment ion peaks were observed as shown in Fig. 1. These ion peaks indicated that **7a** had a sequence of aglycone–pentose–deoxyhexose–pentose–hexose–hexose–hexose–deoxyhexose.

Among the ninety-eight carbon signals observed in the ^{13}C-NMR spectrum of **7**, the seventy signals appeared at almost the same positions as corresponding signals in **4**, suggesting that **7** had a $G^3RiR^2AOle\ G^1G^2R^1$ moiety.

The proton and carbon signals due to sugar moiety of **7** were assigned based on the ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY and heteronuclear multiple bond connectivity (HMBC) spectral data with the aid of the informations as mentioned above.

The significant ^{1}H–^{13}C long-range correlations observed in the HMBC spectrum of **7** are shown by arrows in Fig. 2 and these correlations established the sequence and the linking position of the sugar moieties and an isoferuloyl group. The nuclear Overhauser effect (NOE) observed in the difference NOE spectra also supported the linking position of the rhamnose[3] and glucose[5] moieties (Fig. 2).

The configurations of C-1 positions of the glucose[4] and glucose[5] moieties were regarded as β from the $J_{H\text{-}1,H\text{-}2}$ value (both 8 Hz) and that of the rhamnose[3] moiety as α from its carbon signal pattern.[8]

From these facts, the structure of clematernoside E (**7**) was concluded to be 3-*O*-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyl-(1→3)-(2-*O*-isoferuloyl)-β-D-glucopyanosyl-(1→4)-β-D-glucopyranosyl-(1→4)-β-D-ribopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl oleanolic acid 28-*O*-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside [abbreviation: $R^3G^5(2\text{-}O\text{-}IF\text{-}G^4)G^3RiR^2AOle\ G^1G^2R^1$] (Chart 1).

Clematernoside D (**6**), $C_{98}H_{152}O_{52}$, was concluded to be hederagenin bisdesmoside possessing the same sugar moieties as **7** from comparisons of its ^{1}H- and ^{13}C-NMR spectra with those of **7** and **5**.

Clematernoside G (**9**), $C_{104}H_{162}O_{56}$, showed signals due to eleven anomeric carbons together with those assignable to an isoferuloyl group in its ^{13}C-NMR spectrum and it gave **7** on enzymatic hydrolysis with cellulase. From these data and the molecular formula, **9** was deduced to be a monoglucoside of **7**.

The FAB-MS of the alkaline hydrolysate (**9a**) of **9** indicated the fragment ion peaks at *m/z* 1497.7 [(M−glucosyl moiety)$^-$] and 1513.6 [(M−rhamnosyl moiety)$^-$], suggesting that 3-*O*-glycosyl chain branched at the sixth sugar (glucose[5]) moiety (Fig. 1). Detailed analyses of the ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY and HMBC spectra of **9** with the aid of the NMR data for **7** revealed the assignments of most of

Table 3. ^{13}C-NMR Spectral Data for the Sugar Moiety of **1**—**13**, **1a**, **1b**, **5a**, **7a** and **9a** in Pyridine-d_5

	3	**4**	**1**	**1a**	**1b**	**2**	**8**	**5**	**5a**	**6**	**7**	**7a**	**9**	**9a**	**10**	**13**	**11**	**12**
28-*O*-Glycosyl moiety																		
Glc^1-1	95.5	95.6	95.6		95.6	95.5	95.6	95.6		95.6	95.6		95.6		95.6	95.6	95.6	95.6
2	73.7	73.8	73.8		73.8	73.7	73.8	73.8		73.9	73.8		73.9		73.9	73.8	73.8	73.8
3	78.6	78.6	78.6		78.7	78.5	78.6	78.6		78.7	78.6		78.7		78.7	78.7	78.6	78.6
4	70.7	70.8	70.8		70.8	70.7	70.7	70.8		70.8	70.8		70.9		70.9	70.8	70.8	70.8
5	77.9	78.0	78.0		78.0	77.9	78.0	78.0		78.0	78.0		78.1		78.0	78.0	78.0	78.0
6	69.0	69.1	69.1		69.2	69.0	69.1	69.1		69.2	69.2		69.2		69.2	69.2	69.1	69.1
Glc^2-1	104.7	104.8	104.8		104.8	104.7	104.8	104.8		104.8	104.8		104.8		104.8	104.8	104.7	104.7
2	75.2	75.3	75.3		75.3	75.2	75.3	75.3		75.3	75.3		75.4		75.4	75.3	75.3	75.3
3	76.4	76.4	76.4		76.4	76.3	76.3	76.3		76.3	76.3		76.5		76.5	76.5	76.4	76.4
4	78.1	78.1	78.2		78.1	78.1	78.1	78.1		78.2	78.2		78.2		78.2	78.2	78.3	78.2
5	77.0	77.1	77.0		77.1	77.0	77.1	77.1		77.1	77.1		77.2		77.1	77.1	77.1	77.1
6	61.1	61.2	61.2		61.2	61.1	61.2	61.2		61.3	61.2		61.3		61.3	61.3	61.2	61.2
Rha^1-1	102.6	102.7	102.7		102.7	102.6	102.7	102.7		102.7	102.7		102.7		102.7	102.7	102.7	102.7
2	72.4	72.5	72.5		72.5	72.4	72.5	72.5		72.5	72.5		72.6		72.6	72.5	72.5	72.5
3	72.7	72.7	72.7		72.7	72.7	72.7	72.7		72.8	72.7		72.8		72.8	72.7	72.7	72.7
4	73.9	73.9	73.9		73.9	73.8	73.9	73.9		74.0	73.9		74.0		74.0	74.0	73.9	73.9
5	70.1	70.2	70.2		70.2	70.1	70.2	70.2		70.3	70.3		70.3		70.3	70.3	70.2	70.2
6	18.4	18.4	18.4		18.5	18.4	18.4	18.5		18.5	18.5		18.5		18.5	18.5	18.5	18.5
3-*O*-Glycosyl moiety																		
Ara-1	105.2	105.2	105.2	105.2	105.2	105.1	105.2	104.7	104.7	104.7	105.2	105.2	105.2	105.2	105.2	105.2	105.1	105.2
2	75.1	75.3	75.4	75.4	75.3	75.2	75.3	75.3	75.5	75.3	75.3	75.6	75.4	75.6	75.5	75.4	75.4	75.4
3	74.8	74.6	74.6	74.6	74.7	74.6	74.7	75.2	75.1	75.2	74.7	74.6	74.7	74.7	74.6	74.7	74.6	74.6
4	69.4	69.3	69.3	69.3	69.4	69.1	69.3	69.6	69.7	69.7	69.4	69.3	69.4	69.3	69.3	69.3	69.3	69.3
5	65.7	65.6	65.6	65.6	65.7	65.5	65.7	66.3	66.2	66.4	65.7	65.6	65.7	65.6	65.7	65.7	65.6	65.6
Rha^2-1	101.3	101.3	101.4	101.5	101.3	101.2	101.4	101.3	101.5	101.4	101.4	101.5	101.5	101.5	101.5	101.4	101.4	101.4
2	71.9	71.9	71.9	71.9	71.9	71.8	71.9	71.9	71.9	71.9	71.9	72.0	71.9	72.0	71.9	71.9	71.9	71.9
3	81.1	82.0	82.0	82.1	82.1	82.0	82.0	82.0	82.1	82.1	82.1	82.1	82.1	82.2	82.1	82.0	82.0	82.0
4	72.7	72.7	72.7	72.7	72.7	72.6	72.7	72.8	72.8	72.8	72.7	72.8	72.8	72.8	72.8	72.7	72.7	72.7
5	69.7	69.7	69.7	69.7	69.7	69.6	69.7	69.8	69.7	69.8	69.7	69.8	69.8	69.8	69.8	69.8	69.7	69.8
6	18.3	18.4	18.4	18.4	18.4	18.3	18.4	18.4	18.4	18.4	18.4	18.5	18.4	18.5	18.4	18.4	18.4	18.4
Rib-1	104.6	104.6	104.6	104.7	104.7	104.5	104.6	104.7	104.6	104.7	104.7	104.7	104.7	104.8	104.7	104.7	104.6	104.6
2	72.6	72.5	72.5	72.5	72.5	72.4	72.5	72.5	72.5	72.5	72.5	72.5	72.5	72.6	72.6	72.5	72.5	72.5
3	68.9	69.5	69.6	69.6	69.6	69.6	69.4	69.5	69.6	69.5	69.6	69.6	69.6	69.6	69.6	69.6	69.6	69.6
4	70.2	76.3	76.3	76.3	76.3	76.3	76.2	76.3	76.3	76.3	76.3	76.4	76.5	76.4	76.5	76.3	76.2	76.4
5	65.2	61.7	61.5	61.6	61.6	61.6	61.4	61.5	61.6	61.6	61.5	61.6	61.6	61.6	61.6	61.6	61.6	61.5
Glc^3-1		103.4	102.8	103.0	103.1	103.0	102.8	102.8	103.1	102.9	102.9	103.1	102.9	103.1	102.9	102.8	102.8	102.9
2		74.5	74.2	74.2	74.2	74.1	74.1	74.1	74.2	74.2	74.2	74.2	74.2	74.2	74.2	74.2	74.2	74.1
3		78.3	76.4	76.5	76.5	76.5	76.4	76.4	76.6	76.6	76.6	76.7	76.5	76.7	76.5	76.4	76.4	76.4
4		71.4	81.2	80.9	80.9	79.7	81.3	81.2	81.0	81.1	81.1	80.8	81.2	81.0	81.2	81.1	81.0	81.1
5		78.6	76.3	76.6	76.6	76.2	76.3	76.4	76.6	76.3	76.2	76.4	76.3	76.4	76.3	76.1	76.2	76.3
6		62.5	60.7	61.8	61.8	61.3	60.9	60.7	61.9	60.7	60.7	62.0	60.7	62.0	60.8	60.7	60.7	60.7
Glc^4-1			102.5	104.9	104.9	104.3	102.5	102.5	104.9	102.2	102.2	104.4	102.3	104.4	102.2	102.2	102.2	102.2
2			75.2	74.7	74.7	72.5	75.3	75.2	74.8	72.9	72.9	73.5	72.8	73.5	72.9	72.8	72.7	72.9
3			76.3	78.2	78.1	78.9	76.4	76.3	78.2	86.7	86.7	88.1	86.5	87.9	86.5	87.4	87.1	86.0
4			71.9	71.4	71.4	69.1	71.9	71.9	71.5	70.2	70.2	69.5	70.1	69.3	70.1	70.1	70.0	70.0
5			78.6	78.4	78.4	78.1	78.5	78.6	78.5	77.9	77.8	77.8	77.8	77.8	77.8	77.8	77.7	77.7
6			62.4	62.4	62.4	61.7	62.4	62.4	62.4	62.1	62.1	61.5	62.1	61.5	62.1	62.0	62.0	62.0
Glc^5-1										105.7	105.7	105.6	105.3	105.4	105.2	105.8	105.3	105.2
2										74.4	74.4	75.2	73.8	75.2	73.9	74.4	73.8	73.9
3										78.2	78.2	78.3	76.4	76.4	76.4	78.2	76.2	76.4
4										71.9	71.8	72.0	82.0	82.4	82.0	71.9	81.8	81.7
5										76.5	76.4	76.9	74.8	74.8	74.8	76.3	74.2	74.7
6										68.9	68.9	68.8	68.1	68.0	68.1	68.9	68.1	67.9
Rha^3-1										102.8	102.8	102.9	102.7	102.8	102.7	101.4	101.2	102.7
2										71.9	71.9	72.0	72.0	72.1	71.9	82.0	82.1	71.9
3										72.6	72.6	72.6	72.7	72.7	72.7	72.6	72.7	72.5
4										74.0	74.0	74.1	74.0	74.1	73.9	74.5	74.4	74.1
5										69.9	69.9	69.8	69.9	69.8	69.9	69.7	69.6	69.8
6										18.6	18.6	18.6	18.6	18.6	18.6	18.5	18.5	18.7
Glc^6-1													105.3	105.1	105.3		105.1	102.4
2													74.7	74.7	74.7		74.7	84.4
3													78.3	78.4	78.3		78.3	78.0
4													71.5	71.7	71.6		71.5	71.1
5													78.5	78.5	78.5		78.4	78.8
6													62.6	62.7	62.6		62.5	62.2
																		(Glc^8)
Glc^7-1																107.3	107.3	106.7
(Glc^8) 2																76.0	75.9	76.0
3																78.4	78.3	78.2
4																71.2	71.4	71.6
5																78.6	78.4	78.2
6																62.4	62.6	63.0

Table 4. ^{13}C-NMR Data for Acyl Group Moiety of **1**, **2** and **5**—**13** in Pyridine-d_5

C No.	1	2	8	5	6	7	9	10	13	11	12
1	166.7	167.2	166.6	166.7	166.7	166.7	166.6	166.6	166.7	166.6	166.6
2	116.2	116.5	116.4	116.2	116.4	116.4	116.4	116.6	116.4	116.4	116.4
3	145.8	145.2	145.5	145.8	145.7	145.7	145.6	145.0	145.7	145.6	145.7
4	128.4	128.2	127.8	128.4	128.6	128.6	128.6	127.8	128.6	128.5	128.5
5	115.3	115.1	111.9	115.3	115.4	115.4	115.5	130.3	115.4	115.4	115.4
6	148.4	148.2	149.9	148.4	148.5	148.4	148.5	114.7	148.4	148.4	148.4
7	150.9	150.7	151.9	150.9	150.9	150.9	150.9	161.8	150.9	150.9	150.9
8	112.0	111.9	111.0	112.0	112.1	112.1	112.1	114.7	112.1	112.1	112.1
9	121.4	121.2	122.7	121.4	121.5	121.5	121.5	130.3	121.5	121.4	121.5
OMe	55.8	55.6 55.7	55.7	55.7	55.9	55.8	55.8	55.3	55.9	55.8	55.8

Table 5. ^{1}H-NMR Data for Acyl Group Moiety of **1**, **2** and **5**—**13** in Pyridine-d_5[a)]

H No.	1	2	8	5	6	7
2	6.75 d (16)	6.55 d (16)	6.80 d (16)	6.75 d (16)	6.91 d (16)	6.90 d (16)
3	8.07 d (16)	7.85 d (16)	8.07 d (16)	8.07 d (16)	8.11 d (16)	8.10 d (16)
5	7.53 d (2)	7.42 d (2)	7.22 d (2)	7.53 d (2)	7.54 d (2)	7.54 d (2)
6	—	—	—	—	—	—
8	6.90 d (8.5)	6.89 d (8.5)	6.89 d (8.5)	6.90 d (8.5)	6.88 d (8.5)	6.87 d (8.5)
9	7.09 dd (8.5, 2)	6.99 dd (8.5, 2)	7.18 dd (8.5, 2)	7.09 dd (8.5, 2)	7.09 dd (8.5, 2)	7.08 dd (8.5, 2)
OMe	3.73 s	3.71 s	3.74, 6H, s	3.73 s	3.75 s	3.74 s

H No.	9	10	13	11	12
2	6.91 d (16)	6.90 d (16)	6.90 d (16)	6.89 d (16)	6.90 d (16)
3	8.12 d (16)	8.09 d (16)	8.09 d (16)	8.09 d (16)	8.11 d (16)
5	7.54 d (2)	7.52 m	7.53 d (2)	7.54 d (2)	7.54 d (2)
6	—	6.99 m	—	—	—
8	6.88 d (8.5)	6.99 m	6.88 d (8.5)	6.87 d (8.5)	6.88 d (8.5)
9	7.09 dd (8.5, 2)	7.52 m	7.09 dd (8.5, 2)	7.09 dd (8.5, 2)	7.11 dd (8.5, 2)
OMe	3.73 s	3.75 s	3.74 s	3.73 s	3.73 s

a) Coupling constants (J) in Hz are given in parentheses.

the NMR signals, and the linking position of the additional glucose moiety in **9** was determined to be C_4-oxygen of the glucose[5] moiety in **7** based on the facts that ^{1}H–^{13}C long-range correlation was observed between H-1 of the glucose[6] moiety and C-4 of the glucose[5] moiety, and that the NOE correlation between H-1 of the glucose[6] moiety and H-4 of the glucose[5] moiety was observed in the NOE correlation spectroscopy (NOESY) spectrum (Fig. 2). The configuration of the glucosyl[6] anomeric position was deduced to be β based on the $J_{\text{H-1,H-2}}$ value (8 Hz) of the anomeric proton signal.

On the basis of these findings, the structure of clematernoside G (**9**) is as shown in Chart 1.

The ^{1}H- and ^{13}C-NMR spectra of clematernoside H (**10**) were almost the same as those of **9** except that **10** showed the presence of a 4-methoxycinnamoyl group in place of the isoferuloyl group in **9** (Tables 3—6). Consequently, the structure of clematernoside H (**10**) is represented as shown in Chart 1.

Clematernoside K (**13**), $C_{104}H_{162}O_{56}$, showed the signals due to eleven anomeic carbons together with those assignable to an isoferuloyl group in the ^{13}C-NMR spectrum (Tables 3, 4). The FAB-MS of the alkaline-hydrolysis product (**13a**) of **13** exhibited the $(M-H)^-$ ion peak and the fragment ion peaks as shown in Fig. 1, suggesting that 3-*O*-glycosyl chain was linear.

From these data and the molecular formula, **13** was suggested to be a monoglucoside of **7**. The additional glucose moiety in **13** was presumed to be connected to the C-2 position of the rhamnosyl[3] moiety in **7** because the signal due to C-1 of the rhamnosyl[3] moiety in **13** was observed at the upper field by 1.5 ppm compared with that in **7**.

Detailed analyses of the ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY and HMBC spectra of **13** and comparison of the ^{1}H- and ^{13}C-NMR spectral data of **13** with those of **7** revealed the assignments of most of the NMR signals due to the sugar moieties, and the linking position of the additional glucose moiety in **13** was confirmed to be C_2-oxygen of the rhamnose[3] moiety in **7**. The configuration of the glucosyl[7] anomeric position was deduced to be β based on the $J_{\text{H-1,H-2}}$ value (8 Hz) of the anomeric proton signal.

On the basis of these findings, the structure of clematernoside K (**13**) is as shown in Chart 1.

Clematernoside I (**11**), $C_{110}H_{172}O_{61}$, showed the signals due to twelve anomeic carbons together with those assignable to an isoferuloyl group in the ^{13}C-NMR spectrum (Tables 3, 4). Enzymatic hydrolysis of **11** with cellulase afforded **13**, suggesting that **11** was a monoglucoside of **13**.

Most of the NMR signals due to the sugar moieties, especially the terminal ones in **11** were assigned based on the ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY and HMBC spectral data with the aid of the data for **7**, **9** and **13**. The HMBC spectrum of

Table 6. ^{1}H-NMR Data for Sugar Moiety of **1**, **7**, **9** and **11**—**13** in Pyridine-d_5 [a]

	1	**7**	**9**	**13**	**11**	**12**
28-*O*-Glycosyl moiety						
Glc^1-1	6.21 d (8)	6.22 d (8)	6.23 d (8)	6.22 d (8)	6.20 d (8)	6.21 d (8)
2	4.08 dd (9, 8)	4.11[b]	4.10[b]	4.11[b]	4.10[b]	4.09[b]
3	4.20[b]	4.20 dd (9, 9)	4.20[b]	4.20 dd (9, 9)	4.19 dd (9, 9)	4.19[b]
4	4.29[b]	4.29[b]	4.30[b]	4.31[b]	4.30[b]	4.29[b]
5	4.10[b]	4.06[b]	4.11[b]	4.08[b]	4.08[b]	4.08[b]
6	4.32[b]	4.32[b]	4.33[b]	4.32[b]	4.31[b]	4.30[b]
	4.65[b]	4.65[b]	4.67[b]	4.66[b]	4.66[b]	4.64[b]
Glc^2-1	4.98 d (8)	4.98 d (8)	4.99 d (8)	4.98 d (8)	4.97 d (8)	4.98 d (8)
2	3.92 dd (9, 8)	3.93 dd (9, 8)	3.94 dd (9, 8)	3.93 dd (9, 8)	3.92 dd (9, 8)	3.94 dd (9, 8)
3	4.13 dd (9, 9)	4.14 dd (9, 9)	4.14[b]	4.14 dd (9, 9)	4.13 dd (9, 9)	4.13 dd (9, 9)
4	4.39 dd (9, 9)	4.41 dd (9, 9)	4.42 dd (9, 9)	4.40 dd (9, 9)	4.39 dd (9, 9)	4.40[b]
5	3.66 m	3.65 m	3.66 m	3.64 m	3.63 m	3.64 m
6	4.05[b]	4.07[b]	4.09[b]	4.06[b]	4.06[b]	4.06[b]
	4.19[b]	4.20[b]	4.20[b]	4.20[b]	4.19[b]	4.19[b]
Rha^1-1	5.83 br s	5.85 d (1.5)	5.86 br s	5.84 br s	5.82 br s	5.83 br s
2	4.65[b]	4.67[b]	4.67[b]	4.67[b]	4.65[b]	4.66[b]
3	4.53[b]	4.54 dd (9, 3.5)	4.55 dd (9, 3)	4.54 dd (9, 3)	4.53 dd (9, 3)	4.53 dd (9, 3)
4	4.33 dd (9, 9)	4.32 dd (9, 9)	4.33 dd (9, 9)	4.32 dd (9, 9)	4.31 dd (9, 9)	4.31 dd (9, 9)
5	4.94 m	4.97 dq (9, 6)	4.98 m	4.96 m	4.94 m	4.94 m
6	1.68 d (6.5)	1.69 d (6)	1.70 d (6)	1.69 d (6)	1.67 d (6)	1.67 d (6)
3-*O*-Glycosyl moiety						
Ara-1	4.81 d (6)	4.82 d (6)	4.83 d (6)	4.83 d (6)	4.81 d (6)	4.81 d (6)
2	4.54 dd (6.5, 6.5)	4.56[b]	4.56[b]	4.54[b]	4.54[b]	4.54[b]
3	4.21[b]	4.24[b]	4.25[b]	4.25[b]	4.23[b]	4.26[b]
4	4.18[b]	4.21[b]	4.21[b]	4.22[b]	4.21[b]	4.21[b]
5	3.81 br d (11)	3.81 br d (10.5)	3.81 br d (10)	3.80 br d (10)	3.79 br d (10)	3.80 br d (10)
	4.28[b]	4.31[b]	4.27[b]	4.28[b]	4.28[b]	4.28[b]
Rha^2-1	6.23 br s	6.25 br s	6.24 br s	6.23 br s	6.22 br s	6.22 br s
2	4.85 br s	4.86 br s	4.86 br s	4.86 br s	4.85[b]	4.85 br s
3	4.65[b]	4.68[b]	4.68 dd (9, 3)	4.68[b]	4.65[b]	4.65[b]
4	4.39 dd (9, 9)	4.40 dd (9, 9)	4.41 dd (9, 9)	4.40 dd (9, 9)	4.40 dd (9, 9)	4.39 dd (9, 9)
5	4.59[b]	4.65[b]	4.61[b]	4.63[b]	4.58[b]	4.58[b]
6	1.50 d (6)	1.50 d (6)	1.52 d (6)	1.51 d (6)	1.50 d (6)	1.50 d (6)
Rib-1	5.80 d (5.5)	5.81 d (6)	5.82 d (5.5)	5.81 d (6)	5.80 d (5)	5.80 d (5.5)
2	4.07[b]	4.09[b]	4.10[b]	4.09[b]	4.09[b]	4.08[b]
3	4.65[b]	4.64[b]	4.67[b]	4.64[b]	4.65[b]	4.63[b]
4	4.30[b]	4.30[b]	4.29[b]	4.30[b]	4.31[b]	4.30[b]
5	4.28[b]	4.29[b]	4.30[b]	4.32[b]	4.27[b]	4.27[b]
	4.28[b]	4.29[b]	4.30[b]	4.32[b]	4.27[b]	4.27[b]
Glc^3-1	4.90 d (7.5)	4.90 d (8)	4.90 d (8)	4.90 d (8)	4.88 d (8)	4.88 d (8)
2	3.89 dd (8, 7.5)	3.86 dd (8, 8)	3.87 dd (8, 8)	3.87 dd (8, 8)	3.86 dd (8, 8)	3.86 dd (8, 8)
3	4.17[b]	4.14[b]	4.15[b]	4.16[b]	4.13[b]	4.13[b]
4	4.27[b]	4.27[b]	4.26[b]	4.26[b]	4.27[b]	4.25[b]
5	3.64 m	3.65 m	3.65 m	3.64 m	3.63 m	3.63 m
6	4.14[b]	4.09[b]	4.08[b]	4.11[b]	4.05[b]	4.01[b]
	4.22[b]	4.39[b]	4.37[b]	4.22[b]	4.15[b]	4.24[b]
Glc^4-1	5.38 d (8)	5.31 d (8)	5.30 d (8.5)	5.31 d (8.5)	5.29 d (8)	5.27 d (8)
2	5.77 dd (9, 8)	5.76 dd (9, 8)	5.75 dd (9, 8.5)	5.74 dd (9, 8.5)	5.71 dd (9, 8)	5.72 dd (9, 8)
3	4.33[b]	4.20 dd (9, 9)	4.16[b]	4.14[b]	4.11[b]	4.15[b]
4	4.18[b]	4.02 dd (9, 9)	3.99 dd (9,9)	4.05 dd (9, 9)	3.97 dd (9,9)	3.96[b]
5	4.05[b]	3.94[b]	3.94[b]	3.93[b]	3.90[b]	3.93[b]
6	4.21[b]	4.13[b]	4.14[b]	4.22[b]	4.17[b]	4.06[b]
	4.54[b]	4.23[b]	4.23[b]	4.47 br d (10)	4.44 br d (11)	4.38[b]
Glc^5-1		4.91 d (8)	4.90 d (8)	4.86 d (8)	4.84 d (8)	4.91 d (8)
2		3.87 dd (9, 8)	3.90 dd (9, 8)	3.88 dd (9, 8)	3.89 dd (9, 8)	3.86 dd (9, 8)
3		4.04[b]	4.15[b]	4.08 dd (9, 9)	4.14[b]	4.13 dd (9, 9)
4		3.87 dd (9, 9)	3.92 dd (9, 9)	3.82 dd (9, 9)	3.91 dd (9, 9)	3.92 dd (9, 9)
5		4.14 dd (9, 9)	4.13[b]	4.06[b]	4.07[b]	4.30[b]
6		3.91[b]	4.05[b]	3.69 br d (10)	3.83[b]	4.32[b]
		4.67[b]	4.88[b]	4.59[b]	4.73 br d (10)	4.92[b]
Rha^3-1		5.41 d (1.5)	5.48 d (1.5)	5.46 d (1.5)	5.53 br s	5.63 br s
2		4.73 dd (3, 1.5)	4.73 m	4.79 br d (3.5)	4.78 br d (3.5)	4.71 m
3		4.57 dd (9, 3)	4.53 dd (9, 3)	4.58 dd (9, 3.5)	4.53 dd (9, 3.5)	4.53 dd (9, 3.5)
4		4.27[b]	4.24[b]	4.18 dd (9, 9)	4.16[b]	4.20 dd (9, 9)
5		4.30[b]	4.32[b]	4.25[b]	4.25[b]	4.46 m
6		1.60 d (6)	1.65 d (6)	1.56 d (6)	1.59 d (6)	1.64 d (6)
Glc^6-1			4.94 d (8)		4.90 d (8)	4.97 d (8)
2			3.98 dd (9, 8)		3.93[b]	3.99 dd (9, 8)
3			4.14[b]		4.17 dd (9, 9)	4.17 dd (9, 9)
4			4.10[b]		4.08[b]	4.04 dd (9, 9)
5			3.97[b]		3.99[b]	3.93[b]
6			4.23[b]		4.25[b]	4.13[b]
			4.52[b]		4.48[b]	4.44[b]
						(Glc8)
Glc^7-1				5.32 d (8)	5.31 d (8)	5.22 d (7.5)
(Glc^8) 2				4.07[b]	4.05 dd (9, 8)	4.12 dd (9, 7.5)
3				4.22[b]	4.19[b]	4.17 dd (9, 9)
4				4.25[b]	4.16[b]	4.22[b]
5				3.98[b]	3.99[b]	3.86[b]
6				4.35 dd (12, 5)	4.30[b]	4.38[b]
				4.49 dd (12, 2.5)	4.50[b]	4.55[b]

a) Coupling constants (*J*) in Hz are given in parentheses. *b*) Overlapped signals.

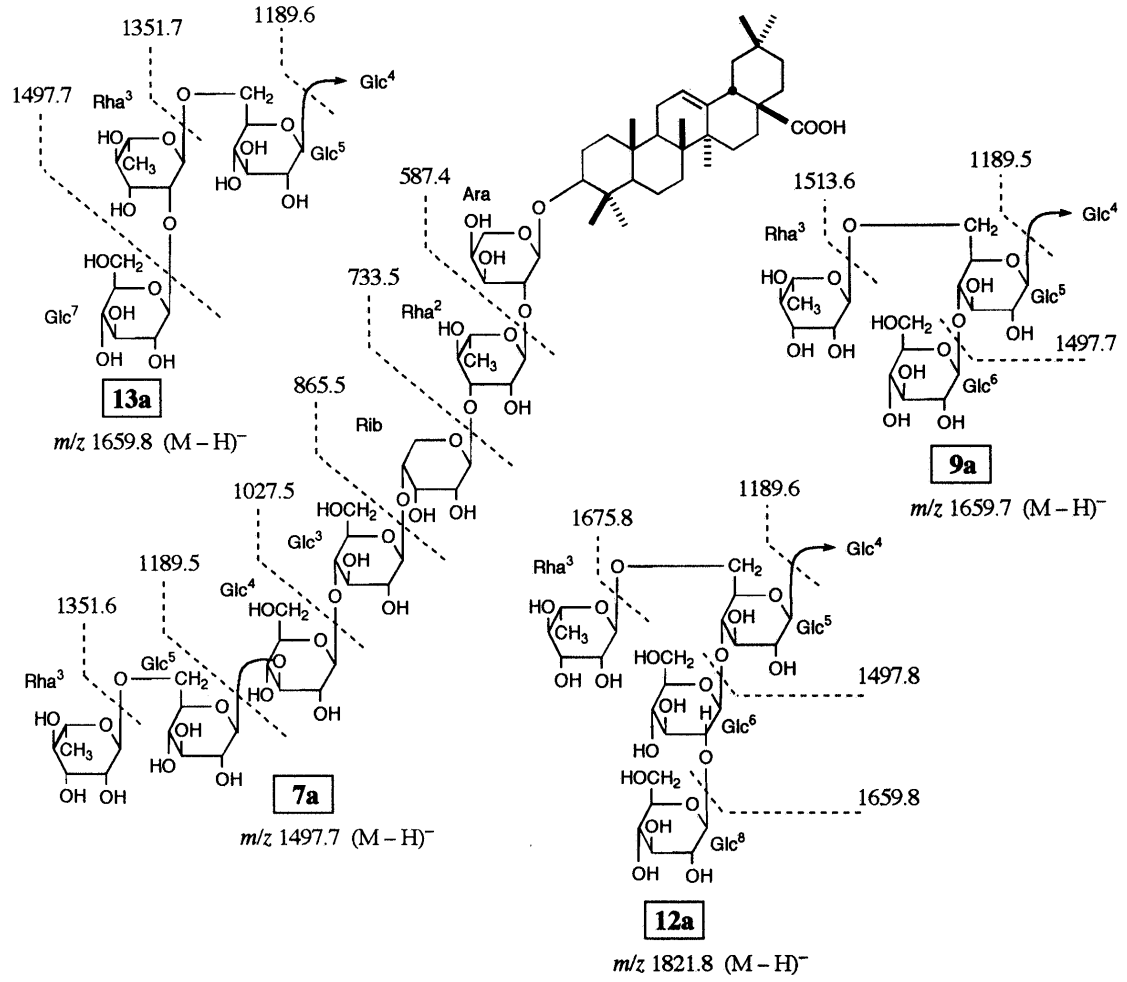


Fig. 1. FAB-MS (Negative Mode) Fragments of **7a**, **9a**, **12a** and **13a**

11 indicated the presence of the ^{1}H–^{13}C long-range correlations as shown by arrows in Fig. 2. Furthermore, the NOESY spectrum of **11** showed the presence of the ^{1}H–^{1}H correlations as shown by dotted arrows in Fig. 2. These data denoted that the connecting position of the additional glucose[6] moiety in **11** was the C_4-oxygen of the glucose[5] moiety in **13**. The configuration of the glucosyl[6] anomeric position was deduced to be β based on the $J_{H\text{-}1,H\text{-}2}$ value (8 Hz) and carbon signal pattern of the glucosyl[6] moiety.

From these findings, the structure of clematernoside I (**11**) is as shown in Chart 1.

Clematernoside J (**12**), $C_{110}H_{172}O_{61}$, showed the signals due to twelve anomeic carbons together with those assignable to an isoferuloyl group in the ^{13}C-NMR spectrum (Tables 3, 4). The FAB-MS of the alkaline-hydrolysis product (**12a**) of **12** exhibited the $(M-H)^-$ ion peak and the fragment ion peaks as shown in Fig. 1, suggesting that 3-*O*-glycosyl chain branched at the glucose[5] moiety.

In comparing the ^{13}C-NMR spectrum of **12** with that of **9**, ninety-eight carbons, which were assignable to a R^3G^5 (2-*O*-IF-G^4) $G^3RiR^2AOleG^1G^2R^1$ moiety in **9**, were observed at almost the same positions in **12**. Accordingly, **12** was suggested to be a monoglucoside of **9**. Most of the NMR signals due to the sugar moieties in **12** were assigned based on the ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY and HMBC spectral data with the aid of the data for **9**. The HMBC spectrum of **12** indicated the presence of the ^{1}H–^{13}C long-range correlations as shown by arrows in Fig. 2. In addition, the NOESY spectrum of **12** showed the presence of the ^{1}H–^{1}H correlations *via* space as shown by dotted arrows in Fig. 2. These data revealed that the connecting position of the additional glucosyl[8] moiety was the C_2-oxygen of the glucose[6] moiety. The configuration of the glucosyl[8] anomeric position was deduced to be β based on the $J_{H\text{-}1,H\text{-}2}$ value (7.5 Hz) and the carbon signal pattern of the glucosyl[8] moiety.

On the basis of these findings, the structure of clematernoside J (**12**) was concluded to be as shown in Chart 1.

Thus the saponin constituents of *Clematis terniflora* were examined, and eleven new saponins termed clematernosides A—K (**1**, **2**, **5**—**13**) were isolated and characterized.

The structural characteristics of the clematernosides are summarized as follows. An aglycone is oleanolic acid or hederagenin as is very often seen in other *Clematis* species. The clematernosides are all 3,28-*O*-bisdesmoside and their 28-*O*-glycosyl group is all α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl one, as is also commonly found in other *Clematis* species. All clematernosides have a substituted-cinnamoyl group in the molecule. The major substituted-cinnamoyl group is a 3-hydroxy-4-methoxycinnamoyl (isoferuloyl) one. Clematernoside K (**13**) has a linear octasaccharide moiety and clematernoside I (**11**) as well as J (**12**) has a nonasaccharide moiety. Furthermore, clematernoside I (**11**) and J (**12**) have a total of twelve monosaccharides in the molecule. This is the first report of the iso-

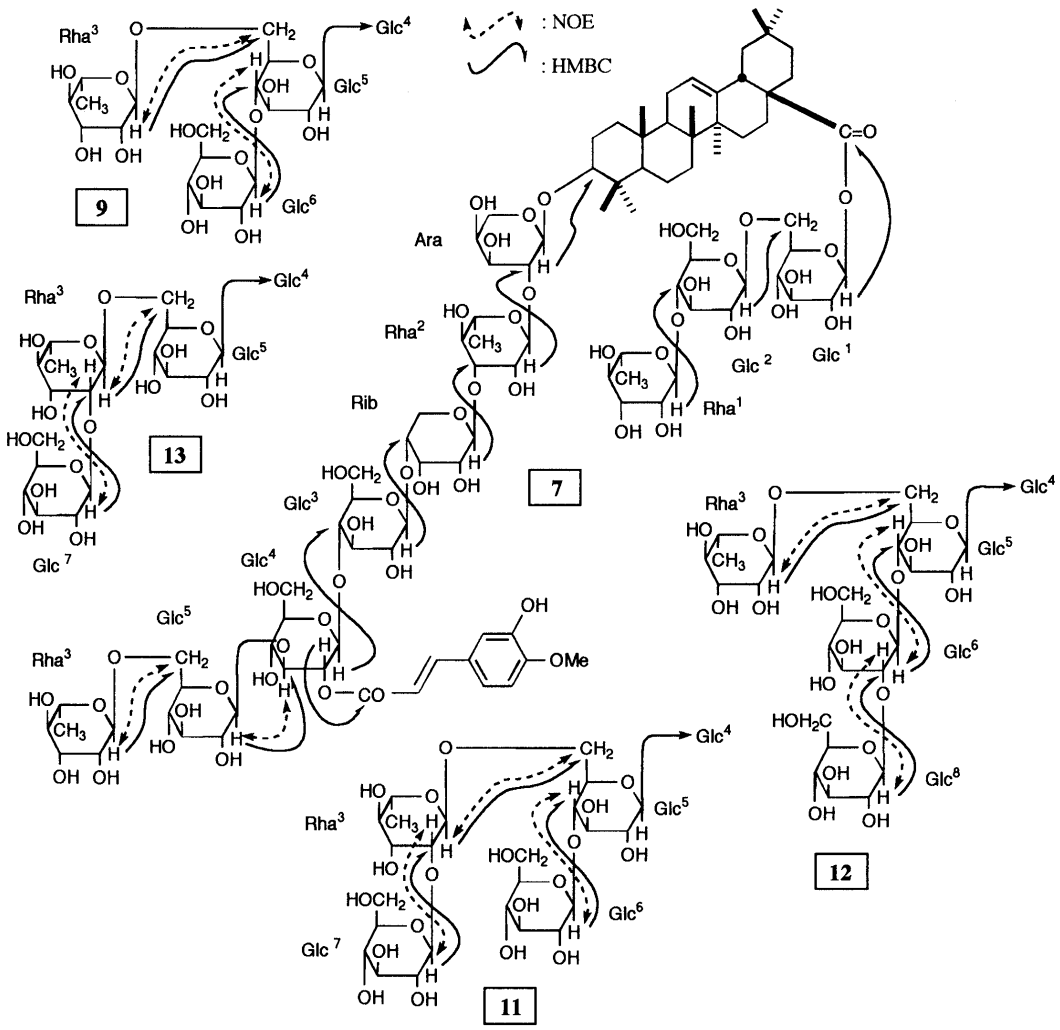


Fig. 2. NOE and HMBC Correlations on the Sugar Linkage Sites

lation and characterization of such "big" saponins to our knowledge.

Experimental

General Procedures All melting points were determined on a Yanagimoto micromelting point apparatus and were uncorrected. NMR spectra were taken in pyridine-d_5 on a JEOL GSX-400 spectrometer (^{1}H-NMR at 400 MHz and ^{13}C-NMR at 100 MHz), and the chemical shifts are given in δ (ppm). MS were taken on a JEOL JMS-SX-102A mass spectrometer, using triethanolamine as a matrix. UV spectra were taken in MeOH on a Shimadzu dual-wavelength/doublebeam recording spectrophotometer. IR spectra were taken in KBr disk on a Hitachi 270-30 IR spectrophotometer. Optical rotation was measured by a JASCO DIP-370 digital polarimeter. The HPLC system was composed of TOSO CCPE pump with recycling valve and a JASCO 875 UV detector. For TLC, pre-coated plates of Silica-gel $60F_{254}$, RP-18 and HP Silica-gel $60F_{254}$ (Merck) were used.

Medium pressure liquid chromatography (MPLC) was conducted on an octadecyl silica (ODS) column (stuffed Merck Licroprep RP-18 No.13900 in 500 mm×32 mm i.d.) eluted with MeOH–propanol–H_2O (5 : 1 : 6) (MPLC-1). Purification by preparative recycling HPLC was carried out under the following conditions: column A, COSMOSIL $5C_{18}$-AR (250 mm×20 mm i.d.); column B, Develosil ODS-10 (250 mm×20 mm i.d.); column C, YMC-Pack Polyamine-II (250 mm×20 mm i.d.); mobile phase, CH_3CN : propanol : H_2O=3 : 1 : 7 (solv. 1), 2.5 : 1 : 7.5 (solv. 2), 2.3 : 1 : 7.7 (solv. 3), 2.8 : 1 : 7.2 (solv. 4), 2.5 : 1.2 : 7.5 (solv. 5), 3 : 1.3 : 7 (solv. 6), 6 : 2 : 3.5 (solv. 7); detection, $UV_{210\,nm}$.

Materials The roots of *C. terniflora* DC. var. *robusta* TAMURA (collected in Gunma prefecture, Japan) were purchased from Tochimoto-tenkaido Co., Inc. (Osaka, Japan). Cellulase (from *Aspergillus niger*) was obtained from Sigma-Aldrich Japan K. K.

Extraction and Isolation The dried roots (173.3 kg) of the plant were extracted by boiling with MeOH. The MeOH extract was concentrated to dryness under reduced pressure. The residue (28.7 kg) was suspended in H_2O and successively extracted with Et_2O and BuOH. The BuOH layer was concentrated and the residue was dissolved in a small amount of MeOH. This solution was poured into EtOAc and the resulting precipitate (1323 g) was collected. The precipitate (500 g) was chromatographed on an Amberlite XAD-2 column eluted with a stepwise gradient of H_2O–MeOH (10 : 0→8 : 2→6 : 4→4 : 6→2 : 8→0 : 10) to give six fractions. Fraction 4 (eluted with H_2O : MeOH=4 : 6) and fraction 5 (eluted with H_2O : MeOH=2 : 8) contained saponis. Fractions 4 and 5 were combined and then subjected to silica gel column chromatography eluted with $CHCl_3$-MeOH (100 : 4→100 : 6→100 : 8) and $CHCl_3$–MeOH–H_2O (25 : 3 : 0.3→25 : 5 : 0.5→25 : 7 : 0.9→25 : 10 : 1.8→25 : 12 : 2.5→25 : 14 : 3) to give one hundred fractions. Fraction 40 (20 g) was chromatographed on a silica-gel column eluted with $CHCl_3$–MeOH–H_2O (25 : 3 : 0.3→25 : 5 : 0.5→25 : 7 : 0.9) to give three fractions (I, II and III). Fraction I (1 g) was separated by MPLC-1 to give crude **3**, which was purified by preparative recycling HPLC (column A, solv. 1) to give pure **3** (30 mg). Fraction III (1 g) was purified in the same way as for **3** to give **1** (250 mg).

Fraction 35 (3.5 g) was separated by MPLC-1 and then purified by preparative recycling HPLC (column A, solv.1) to give **2** (50 mg) and **8** (50 mg). Fraction 48 (6.5 g) was chromatographed by MPLC-1 to give hederagenin glycoside and oleanolic acid glycoside fractions. These fractions were purified by preparative recycling HPLC (column A, solv. 2) to give **5** (78 mg) and **4** (98 mg), respectively. In the same manner as for fraction 35, fraction 55 (1 g) was purified to give **7** (75 mg). Fraction 63 (3.1 g) was separated by MPLC-1 to give hederagenin glycoside and oleanolic acid glycoside fractions. The hederagenin glycoside fraction was purified by repeated preparative recycling HPLC (column A, solv. 3; column B, solv. 2) to give **6** (50 mg). The oleanolic acid glycoside fraction was purified by recycling HPLC (column A, solv. 4; column B, solv. 1) to give **10** (40 mg). Fraction 70

(2 g) was separated by MPLC-1 and then purified by recycling HPLC (column A, solv. 5; column B, solv. 6) to give **9** (45 mg).

The mother liquor of BuOH extraction was concentrated *in vacuo*. The residue (100 g) was dissolved in H_2O and chromatographed on an Amberlite XAD-2 column eluted with H_2O–MeOH (MeOH 0→20→40→60→80→100%). The saponin containing fraction (15.6 g) was separated by MPLC-1 to give hederagenin glycoside (7.0 g) and oleanolic acid glycoside (7.8 g) fractions. The oleanolic acid glycoside fraction was separated into three fractions (1′—3′) by preparative recycling HPLC (column B, solv. 5). Fraction 1′ was purified with the recycling separation system (column C, solv. 7) to give **11** (79 mg) and **12** (80 mg). Fraction 2′ was purified with the recycling separation system (column C, solv., CH_3CN : EtOAc : H_2O=6 : 2 : 3) to give **13** (34 mg).

Acid-Hydrolysis of Saponins A few milligrams of each sample (**1**—**13**) was dissolved in 2 N H_2SO_4–50% dioxane (2—4 ml) and heated at 90 °C for 2 h. After cooling, the reaction mixture was diluted with H_2O and concentrated to about half volume to yield precipitate, which was collected by filtration. The precipitate was examined by TLC (solv., benzene : EtOAc=1 : 1), which revealed the presence of hederagenin (in the cases of **5** and **6**) or oleanolic acid (in the cases of other saponins). The filtrate was neutralized with saturated Ba $(OH)_2$ aq. and centrifuged. The supernatant was evaporated and the residue was dissolved in H_2O (*ca.* 0.5 ml) and subjected to HPLC analysis [column, YMC-Pack Polyamine II (250 mm×4.6 mm i.d.); solv., CH_3CN : H_2O : H_3PO_4=86 : 14 : 0.05; detector, Shimadzu RID-2A refractive index detector and JASCO OR-990 optical rotation detector; temperature, 50 °C], which revealed the presence of L-rhamnose (t_R 6.3 min), D-ribose (t_R 7.2 min), L-arabinose (t_R 10.5 min) and D-glucose (t_R 16.9 min) in all cases of **1**—**13**.

Clematernoside A (1) Amorphous powder, $[\alpha]_D^{28}$ −54.5° (*c*=0.53, MeOH). IR (KBr) cm^{-1}: 3436, 2946, 1720, 1514, 1266, 1060. FAB-MS (negative mode) *m/z*: 1835.8 [(M−H)$^-$], 1659.8 [(M−isoferuloyl−H)$^-$], 1365.7 [(M−Rha−Glc−Glc−H)$^-$], 1189.6, 1027.6, 865.5, 733.5, 587.4. HR-FAB-MS: Table 1. UV λ_{max} nm (log ε): 216 (4.33), 244 (4.19), 297 (4.31), 326 (4.38). ^{13}C-NMR: Tables 2—4. ^{1}H-NMR: Tables 5, 6.

Alkaline-Hydrolysis of 1 Compound **1** (70 mg) was dissolved in 0.5 N KOH (5 ml) and heated at 90 °C for 1 h. After cooling, the reaction mixture was neutralized with dil. H_2SO_4 and extracted with BuOH (5 ml×4). The BuOH layer was concentrated and purified by preparative HPLC (column A, solv. 6) to give **1a** (30 mg). Compound **1a**, $[\alpha]_D^{28}$ −23.1° (*c*=0.54, MeOH), was identified as CP_9 by direct comparison.[7]

Mild Alkaline-Hydrolysis of 1 A solution of **1** (70 mg) in 0.1 N KOH (5 ml), was left to stand for 1 h at room temperature. The reaction mixture was processed in a similar manner to that described above to give isoferulic acid and **1b** (50 mg). Compound **1b**, $[\alpha]_D^{30}$ −39.0° (*c*=0.70, MeOH), ^{1}H-NMR: 4.82 (1H, d, *J*=6 Hz, H-1 of Ara), 4.97 (1H, d, *J*=8 Hz, H-1 of Glc^3), 4.98 (1H, d, *J*=8 Hz, H-1 of Glc^2), 5.16 (1H, d, *J*=7.5 Hz, H-1 of Glc^4), 5.81 (1H, d, *J*=5 Hz, H-1 of Rib), 5.83 (1H, br s, H-1 of Rha^1), 6.22 (1H, d, *J*=8 Hz, H-1 of Glc^1), 6.25 (1H, br s, H-1 of Rha^2). ^{13}C-NMR: Table 3 (sugar moiety).

Clematernoside B (2) Amorphous powder, $[\alpha]_D^{28}$ −32.8° (*c*=0.61, MeOH). IR (KBr) cm^{-1}: 3452, 2940, 1710, 1634, 1516, 1266, 1060. FAB-MS (negative mode) *m/z*: 1835.8 [(M−H)$^-$], 1659.8 [(M−acyl−H)$^-$], 1365.7 [(M−Rha−Glc−Glc−H)$^-$], 1189.6, 1027.5, 865.5, 733.4. HR-FAB-MS: Table 1. UV λ_{max} nm (log ε): 216 (4.18), 243 (4.02), 296 (4.14), 325 (4.20). ^{1}H-NMR: 4.81 (1H, d, *J*=6 Hz, H-1 of Ara), 4.96 (1H, d, *J*=8 Hz, H-1 of Glc^3), 4.98 (1H, d, *J*=7.5 Hz, H-1 of Glc^2), 5.27 (1H, d, *J*=8 Hz, H-1 of Glc^4), 5.81 (1H, d, *J*=6 Hz, H-1 of Rib), 5.83 (1H, br s, H-1 of Rha^1), 5.99 (1H, dd, *J*=9, 8 Hz, H-3 of Glc^4), 6.21 (1H, d, *J*=8 Hz, H-1 of Glc^1), 6.25 (1H, br s, H-1 of Rha^2). ^{13}C-NMR: Tables 2—4.

Mild Alkaline-Hydrolysis of 2 A solution of **2** (10 mg) in 0.1 N KOH (5 ml) was left to stand at room temperature for 1 h and then passed through an Amberlite MB-3 column eluted with MeOH (10 ml). After concentrating the eluate, the residue was purified by preparative HPLC (column A, solv. 2) to give isoferulic acid and **1b** (7.5 mg).

Identification of Known Compounds 3 and 4 The ^{1}H- and ^{13}C-NMR data and optical rotation of **3** [amorphous powder, $[\alpha]_D^{28}$ −38.0° (*c*=0.64, MeOH)] and **4** [amorphous powder, $[\alpha]_D^{28}$ −45.5° (*c*=0.39, MeOH)] coincided with those of huzhangoside B[1, 5] and clematichinenoside C,[6] respectively.

Clematernoside C (5) Amorphous powder, $[\alpha]_D^{28}$ −43.1° (*c*=0.61, MeOH). IR (KBr) cm^{-1}: 3460, 2936, 1720, 1634, 1514, 1266, 1068. FAB-MS (negative mode) *m/z*: 1851.8 [(M−H)$^-$], 1675.8 [(M−isoferuloyl−H)$^-$], 1381.8 [(M−Rha−Glc−Glc−H)$^-$], 1205.9, 1043.8, 881.6, 749.5, 603.4. HR-FAB-MS: Table 1. UV λ_{max} nm (log ε): 216 (4.11), 243 (3.95), 297 (4.10), 326 (4.15). ^{1}H-NMR: 4.87 (1H, d, *J*=7.5 Hz, H-1 of Glc^3), 4.98 (1H, d, *J*=8 Hz, H-1 of Glc^2), 5.04 (1H, d, *J*=6.5 Hz, H-1 of Ara), 5.38 (1H, d, *J*=7.5 Hz, H-1 of Glc^4), 5.78 (1H, dd, *J*=8, 8 Hz, H-2 of Glc^4), 5.79 (1H, d, *J*=5.5 Hz, H-1 of Rib), 5.84 (1H, br s, H-1 of Rha^1), 6.21 (1H, d, *J*=8 Hz, H-1 of Glc^1), 6.29 (1H, br s, H-1 of Rha^2). ^{13}C-NMR: Tables 2—4.

Alkaline-Hydrolysis of 5 A solution of **5** (25 mg) in 0.5 N KOH (5 ml) was heated at 90 °C for 1 h. After cooling, the reaction mixture was passed through an Amberlite MB-3 column eluted with MeOH. After concentrating the eluate, the residue was purified by preparative HPLC (column A , solv. 1) to give **5a** (12 mg). Compound **5a**, amorphous powder, $[\alpha]_D^{30}$ −22.5° (*c*=0.73, MeOH) was identified as CP_{10} by direct comparison.[7]

Clematernoside D (6) Amorphous powder, $[\alpha]_D^{28}$ −50.2° (*c*=0.67, MeOH). IR(KBr)cm^{-1}: 3496, 2932, 1708, 1632, 1510, 1266, 1060. FAB-MS (negative mode) *m/z*: 2159.9 [(M−H)$^-$], 1689.7 [(M−Rha−Glc−Glc−H)$^-$], 1513.6, 1043.5, 881.4, 749.4. HR-FAB-MS: Table 1. UV λ_{max} nm (log ε): 215 (4.23), 244 (4.07), 298 (4.16), 326 (4.25). ^{1}H-NMR: 4.87 (1H, d, *J*=7.5 Hz, H-1 of Glc^3), 4.92 (1H, d, *J*=8 Hz, H-1 of Glc^5), 4.99 (1H, d, *J*=8 Hz, H-1 of Glc^2), 5.06 (1H, d, *J*=6.5 Hz, H-1 of Ara), 5.32 (1H, d, *J*=8.5 Hz, H-1 of Glc^4), 5.42 (1H, d, *J*=1.5 Hz, H-1 of Rha^3), 5.76 (1H, dd, *J*=8, 8 Hz, H-2 of Glc^4), 5.82 (1H, d, *J*=5.5 Hz, H-1 of Rib), 5.85 (1H, d, *J*=1.5 Hz, H-1 of Rha^1), 6.23 (1H, d, *J*=8 Hz, H-1 of Glc^1), 6.29 (1H, br s, H-1 of Rha^2). ^{13}C-NMR: Tables 2—4.

Clematernoside E (7) Amorphous powder, $[\alpha]_D^{28}$ −65.0° (*c*=0.10, MeOH). IR (KBr) cm^{-1}: 3456, 2928, 1714, 1634, 1514, 1262, 1050. FAB-MS (negative mode) *m/z*: 2143.9 [(M−H)$^-$], 1673.7 [(M−Rha−Glc−Glc−H)$^-$], 1189.6, 1027.5, 865.5, 733.5. HR-FAB-MS: Table 1. UV λ_{max} nm (log ε): 215 (4.09), 244 (3.94), 298 (4.08), 326 (4.16). ^{13}C-NMR: Tables 2—4. ^{1}H-NMR: Tables 5, 6.

Alkaline-Hydrolysis of 7 A solution of **7** (25 mg) in 0.5 N KOH (5 ml) was processed in the same way as for **1** to afford **7a** (15 mg). FAB-MS (negative mode) *m/z*: 1497.7 [(M−H)$^-$], 1351.6 [(M−Rha−H)$^-$], 1189.5 [(M−Glc−Rha−H)$^-$], 1027.5, 865.5, 733.5, 587.4 (Fig. 1). ^{1}H-NMR: 4.85 (1H, d, *J*=6 Hz, H-1 of Ara), 4.94 (1H, d, *J*=7.5 Hz, H-1 of Glc^3), 5.11 (1H, d, *J*=7.5 Hz, H-1 of Glc^4), 5.19 (1H, d, *J*=7.5 Hz, H-1 of Glc^5), 5.45 (1H, d, *J*=1.5 Hz, H-1 of Rha^3), 5.82 (1H, d, *J*=5.5 Hz, H-1 of Rib), 6.22 (1H, d, *J*=1.5 Hz, H-1 of Rha^2). ^{13}C-NMR: Table 3.

Clematernoside F (8) Amorphous powder, $[\alpha]_D^{30}$ −63.5° (*c*=0.57, MeOH). IR (KBr) cm^{-1}: 3468, 2940, 1716, 1632, 1516, 1262, 1064. FAB-MS (negative mode) *m/z*: 1849.8 [(M−H)$^-$], 1659.8 [(M−3,4-dimethoxycinnamoyl−H)$^-$], 1379.7 [(M−Rha−Glc−Glc−H)$^-$], 1189.6, 1027.5, 865.5, 733.4. HR-FAB-MS: Table 1. UV λ_{max} nm (log ε): 216 (4.45), 235 (4.36), 298 (4.45), 324 (4.56). ^{1}H-NMR: 4.82 (1H, d, *J*=6 Hz, H-1 of Ara), 4.93 (1H, d, *J*=7.5 Hz, H-1 of Glc^3), 4.99 (1H, d, *J*=7.5 Hz, H-1 of Glc^2), 5.39 (1H, d, *J*=8 Hz, H-1 of Glc^4), 5.81 (1H, dd, *J*=9, 8 Hz, H-2 of Glc^4), 5.81 (1H, d, *J*=5 Hz, H-1 of Rib), 5.85 (1H, s, H-1 of Rha^1), 6.21 (1H, d, *J*=8 Hz, H-1 of Glc^1), 6.25 (1H, br s, H-1 of Rha^2). ^{13}C-NMR : Tables 2—4.

Mild Alkaline-Hydrolysis of 8 A solution of **8** (20 mg) in 0.1 N KOH (5 ml) was processed in the same way as for **2** to afford 3,4-dimethoxycinnamic acid and a deacyl product (15 mg), the latter being identified as **1b** by direct comparison.

Clematernoside G (9) Amorphous powder, $[\alpha]_D^{30}$ −48.5° (*c*=0.84, MeOH). IR (KBr) cm^{-1}: 3436, 2928, 1708, 1630, 1512, 1262, 1066. FAB-MS (negative mode) *m/z*: 2306.0 ([M−H)$^-$], 1835.7 [(M−Rha−2Glc−H)$^-$], 1659.8, 1189.6, 1027.5, 865.5, 733.5. HR-FAB-MS: Table 1. UV λ_{max} nm (log ε): 216 (4.28), 244 (4.13), 297 (4.25), 326 (4.33). ^{13}C-NMR: Tables 2—4. ^{1}H-NMR: Tables 5, 6.

Alkaline-Hydrolysis of 9 A solution of **9** (43 mg) in 0.5 N KOH (5 ml) was processed in the same way as for **5** to give **9a** (14 mg). FAB-MS (negative mode) *m/z*: 1659.7 [(M−H)$^-$], 1513.6 [(M−Rha−H)$^-$], 1497.7 [(M−Glc−H)$^-$], 1189.5 [(M−2Glc−Rha−H)$^-$], 1027.5, 865.5, 733.5. ^{1}H-NMR: 4.85 (1H, d, *J*=6 Hz, H-1 of Ara), 4.96 (1H, d, *J*=8 Hz, H-1 of Glc^3), 4.97 (1H, d, *J*=7.5 Hz, H-1 of Glc^6), 5.10 (1H, d, *J*=7.5 Hz, H-1 of Glc^4), 5.20 (1H, d, *J*=8 Hz, H-1 of Glc^5), 5.56 (1H, d, *J*=1.5 Hz, H-1 of Rha^3), 5.83 (1H, d, *J*=5.5 Hz, H-1 of Rib), 6.25 (1H, d, *J*=1.5 Hz, H-1 of Rha^2). ^{13}C-NMR: Table 3.

Enzymatic Hydrolysis of 9 To a solution of **9** (30 mg) in H_2O (10 ml) was added cellulase (10 mg) and the mixture was allowed to stand at 38 °C for 1 h. The reaction mixture was applied on an ODS column (COSMOSIL 140C_{18}-OPN) eluted with H_2O and then with MeOH. The MeOH eluate was evaporated and the residue was purified by preparative HPLC (column A , solv. 1) to give **9c** (16 mg), which was identified as **7** by direct comparison.

Clematernoside H (10) Amorphous powder, $[\alpha]_D^{28}$ −42.5° (*c*=0.45,

MeOH). IR (KBr) cm^{-1}: 3500, 2900, 1710, 1630, 1050. FAB-MS (negative mode) *m/z*: 2289.9 [(M−H)$^-$], 1819.5 [(M−Rha−Glc−Glc−H)$^-$], 1659.5, 1027.5, 865.3, 733.2. HR-FAB-MS: Table 1. UV λ_{max} nm (log ε): 204 (4.08), 227 (4.00), 255 (3.97), 262 (3.90), 311 (4.25). ^{1}H-NMR: 4.83 (1H, d, J=6 Hz, H-1 of Ara), 4.91 (1H, d, J=7.5 Hz, H-1 of Glc^3), 4.91 (1H, d, J=8 Hz, H-1 of Glc^5), 4.93 (1H, d, J=7.5 Hz, H-1 of Glc^6), 4.99 (1H, d, J=8 Hz, H-1 of Glc^2), 5.31 (1H, d, J=7.5 Hz, H-1 of Glc^4), 5.49 (1H, d, J=1.5 Hz, H-1 of Rha^3), 5.76 (1H, dd, J=9, 7.5 Hz, H-2 of Glc^4), 5.82 (1H, d, J=5.5 Hz, H-1 of Rib), 5.86 (1H, d, J=1.5 Hz, H-1 of Rha^1), 6.23 (1H, d, J=8.5 Hz, H-1 of Glc^1), 6.25 (1H, br s, H-1 of Rha^2). ^{13}C-NMR: Tables 2—4.

Clematernoside I (11) Amorphous powder, $[\alpha]_D^{28}$ −32.3° (c=0.60, MeOH : H_2O=9 : 1). IR (KBr) cm^{-1}: 3500, 2950, 1740, 1610, 1510, 1265, 1060. FAB-MS (negative mode) *m/z*: 2468.0 [(M−H)$^-$], 1998.8 [(M−Rha−2Glc−H)$^-$], 1821.8, 1189.6, 1027.5, 865.5, 733.4. HR-FAB-MS: Table 1. UV λ_{max} nm (log ε): 215 (4.35), 243 (4.16), 298 (4.29), 326 (4.35). ^{13}C-NMR: Tables 2—4. ^{1}H-NMR: Tables 5, 6.

Enzymatic Hydrolysis of 11 To a solution of **11** (7 mg) in H_2O (5 ml) was added cellulase (10 mg) and the reaction mixture was processed in the same manner as for **9** to give **11c** (4 mg), which was identified as **13** by direct comparison.

Clematernoside J (12) Amorphous powder, $[\alpha]_D^{28}$ −37.6° (c=0.55, MeOH : H_2O=9 : 1). IR (KBr) cm^{-1}: 3500, 2950, 1720, 1610, 1510, 1265, 1060. FAB-MS (negative mode) *m/z*: 2468.0 [(M−H)$^-$], 1998.8 [(M−Rha−Glc−Glc−H)$^-$], 1821.8, 1189.6, 1027.5, 865.5, 733.4. HR-FAB-MS: Table 1. UV λ_{max} nm (log ε): 216 (4.45), 243 (4.28), 299 (4.41), 326 (4.47). ^{13}C-NMR: Tables 2—4. ^{1}H-NMR: Tables 5, 6.

Alkaline-Hydrolysis of 12 A solution of **12** (16 mg) in 0.5 N KOH (5 ml) was processed in the same way as for **5**, except for the HPLC conditions (column A, solv. 6), to give **12a** (7 mg). FAB-MS (negative mode) *m/z*: 1821.8 [(M−H)$^-$], 1675.8 [(M−Rha−H)$^-$], 1659.8 [(M−Glc−H)$^-$], 1497.8 [(M−2Glc−H)$^-$], 1335.7 [(M−3Glc−H)$^-$], 1189.6 [(M−3Glc−Rha−H)$^-$], 1027.6, 865.5, 733.5.

Clematernoside K (13) Amorphous powder, $[\alpha]_D^{28}$ −45.4° (c=0.48, MeOH). IR (KBr) cm^{-1}: 3500, 2920, 1740, 1610, 1510, 1270, 1060. FAB-MS (negative mode) *m/z*: 2305.9 [(M−H)$^-$], 1835.6 [(M−Rha−2Glc−H)$^-$], 1659.6, 1189.5, 1027.5, 865.5, 733.3. HR-FAB-MS: Table 1. UV λ_{max} nm (log ε): 214 (4.49), 243 (4.33), 299 (4.44), 326 (4.51). ^{13}C-NMR: Tables 2—4. ^{1}H-NMR: Tables 5, 6.

Alkaline-Hydrolysis of 13 A solution of **13** (31 mg) in 0.5 N KOH (5 ml) was processed in the same way as for **5** to give **13a** (15 mg). FAB-MS (negative mode) *m/z*: 1659.8 [(M−H)$^-$], 1497.7 [(M−Glc−H)$^-$], 1351.7 [(M−Glc−Rha−H)$^-$], 1189.6 [(M−Rha−2Glc−H)$^-$], 1027.6, 865.5, 733.5.

Acknowledgements The authors are grateful to members of the analytical center of this university for MS measurements. This work was supported in part by a Special Grant for Research from Hokuriku University.

References

1) Part VI: Kizu H., Shimana H., Tomimori T., *Chem. Pharm. Bull.*, **43**, 2187—2194 (1995).
2) Abstract of Papers, the 42nd Annual Meeting of Japanese Society of Pharmacognosy, Fukuyama, September 1995, p. 128; Abstract of Papers, the 116th Annual Meeting of the Pharmaceutical Society of Japan, Kanazawa, March 1996, Part 2, p. 147; Abstract of Papers, the 43rd Annual Meeting of Japanese Society of Pharmacognosy, Tokyo, September 1996, p. 241; Abstract of Papers, the 117th Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, March 1997, Part 2, p. 163.
3) Namba T., Mikage M., *Shoyakugaku Zasshi*, **37**, 307—316 (1983).
4) Fujita R., Itokawa H., Kumekawa Y., *Yakugaku Zasshi*, **94**, 189—193 (1974).
5) Mizutani K., Ohtani K., Wei J.-X., Kasai R., Tanaka O., *Planta Medica*, **50**, 327—331 (1984).
6) Shao B., Qin G., Xu R., Wu H., Ma K., *Phytochemistry*, **42**, 821—825 (1996).
7) Kizu H., Tomimori T., *Chem. Pharm. Bull.*, **28**, 3555—3560 (1980).
8) Kasai R., Okihara M., Asakawa J., Mizutani K., Tanaka O., *Tetrahedron*, **35**, 1427—1431 (1979).