Medicinal Foodstuffs. XXI.[1] Structures of New Cucurbitane-Type Triterpene Glycosides, Goyaglycosides-a, -b, -c, -d, -e, -f, -g, and -h, and New Oleanane-Type Triterpene Saponins, Goyasaponins I, II, and III, from the Fresh Fruit of Japanese *Momordica charantia* L.

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Received July 7, 2000; accepted September 19, 2000

Eight cucurbitane-type triterpene glycosides called goyaglycosides-a, -b, -c, -d, -e, -f, -g, and -h and three oleanane-type triterpene saponins termed goyasaponins I, II, and III were isolated from the fresh fruit of Japanese *Momordica charantia* L. (Cucurbitaceae) together with five known cucurbitane-type triterpene glycosides momordicosides A, C, F_1, I, and K. The structures of goyaglycosides and goyasaponins were elucidated on the basis of chemical and physicochemical evidence.

Key words *Momordica charantia*; goyaglycoside; goyasaponin; nigauri; cucurbitane-type triterpene glycoside; oleanane-type triterpene saponin

The Cucurbitaceae plant *Momordica* (*M.*) *charantia* L. (Japanese name "Tsurureishi") is cultivated as a vegetable in Asian countries. In Chinese, Indian Ayurvedic, and Indonesian Jamu traditional medicines, the fruit of this plant has been used as a bitter stomachic, a laxative, an antidiabetic, and an anthelmintic for children. Recently, the alcoholic extract from the fruit of *M. charantia* originated in Sri Lanka was reported to inhibit the increase of serum glucose in glucose-loaded rats.[2] As chemical constituents of the fruit, many cucurbitane-type triterpene glycosides were reported,[3] but the constituents responsible for the inhibition of glucose absorption have not been identified. In the course of our studies on the bioactive constituents of medicinal foodstuffs,[1,4] we have also characterized many triterpene glycosides from the fruit of *M. charantia* originated in Japan, Thailand, Indonesia, India, and Sri Lanka. In this paper, we present the isolation and structure elucidation of goyaglycosides-a (**1**), -b (**2**), -c (**3**), -d (**4**), -e (**5**), -f (**6**), -g (**7**), and -h (**8**) and goyasaponins I (**9**), II (**10**), and III (**11**) from the fresh fruit of Japanese *M. charantia*, which is commonly called "nigauri" or "goya".

The cucurbitane- and oleanene-type triterpene glycosides of the fresh fruit of Japanese *M. charantia* were separated by the procedures shown in Chart 1. The methanolic extract obtained from the fresh fruit of *M. charantia* was partitioned into an ethyl acetate and a water mixture to give an ethyl acetate extract and an aqueous phase. The aqueous phase was extracted with 1-butanol to furnish a 1-butanol extract and an aqueous extract. The 1-butanol extract was subjected to normal- and reversed-phase silica gel column chromatography and finally HPLC to give goyaglycosides-a (**1**), -b (**2**), -c (**3**), -d (**4**), -e (**5**), -f (**6**), -g (**7**), and -h (**8**), goyasaponins I (**9**), II (**10**), and III (**11**), and momordicosides A[3a] (**12**), C[3b] (**13**), F_1[3c] (**14**), I[3c] (**15**), and K[3d] (**16**).

Structures of Cucurbitane-Type Triterpene Glycosides (1—8) Goyaglycoside-a (**1**) was obtained as a white pow-

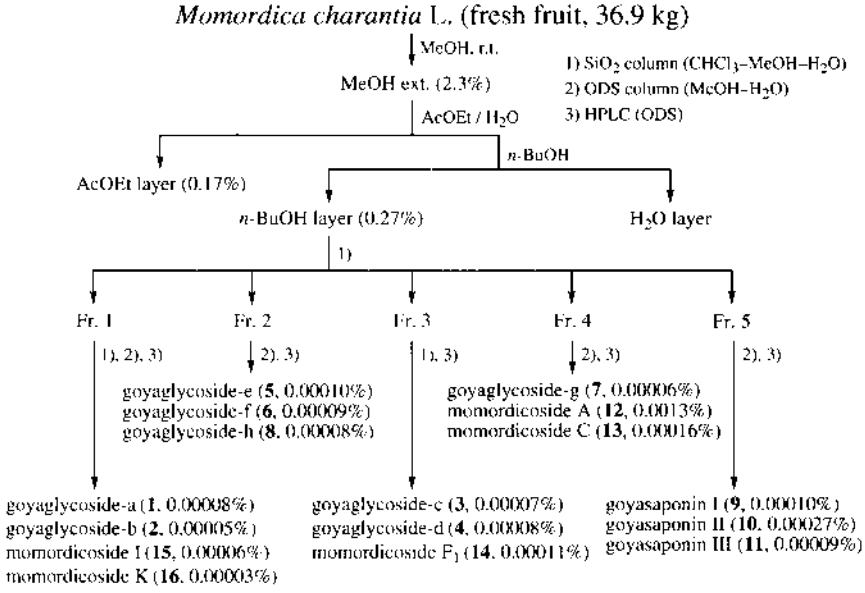

Chart 1

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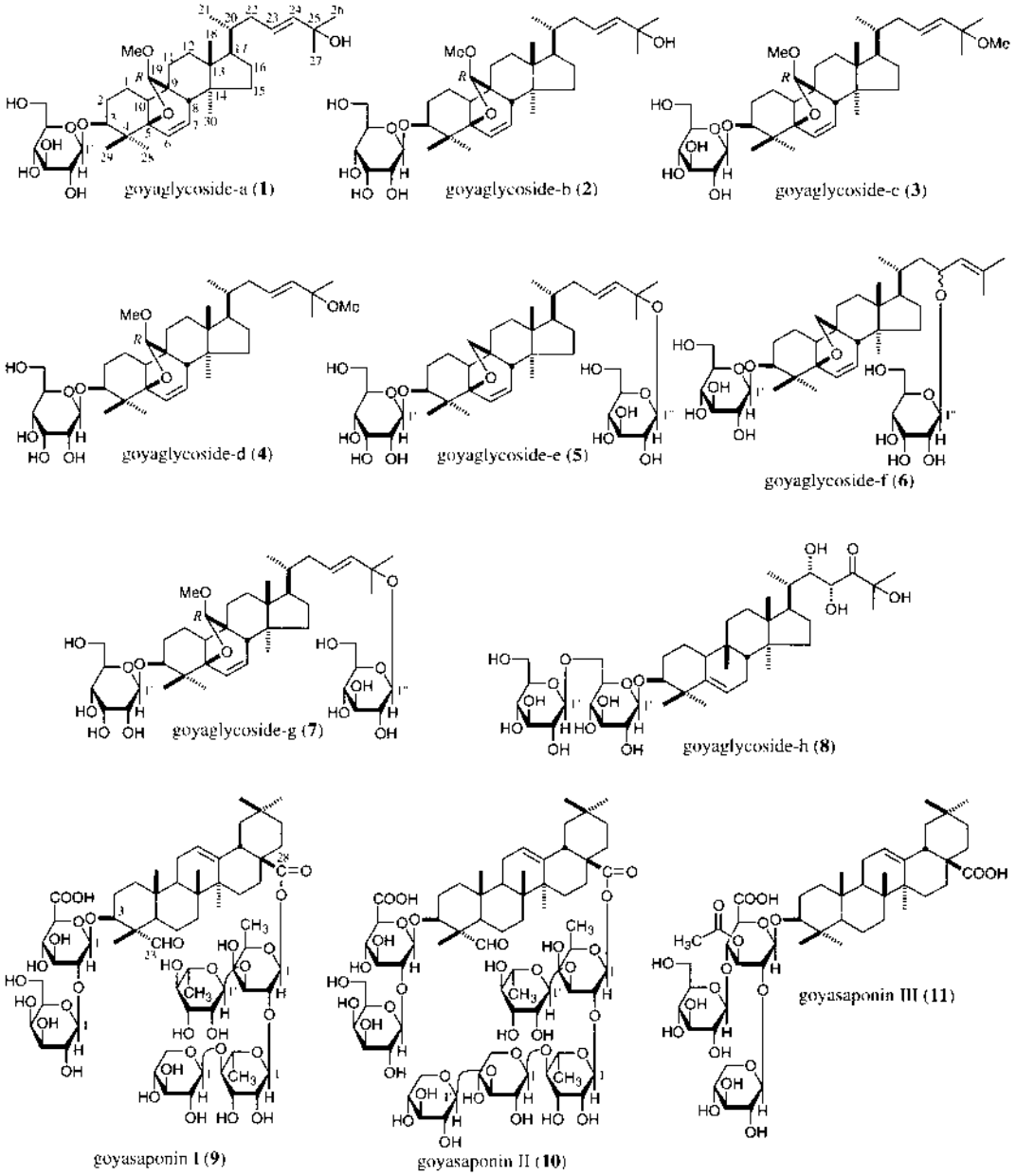

Chart 2

der with negative optical rotation ($[\alpha]_D^{26}$ −101.4°). The IR spectrum of **1** showed strong absorption bands at 3423 and 1080 cm^{-1} suggestive of a glycosidic function. In the negative- and positive-ion FAB-MS of **1**, quasimolecular ion peaks were observed at *m/z* 647 $(M-H)^-$ and *m/z* 649 $(M+H)^+$ and the molecular formula $C_{37}H_{60}O_9$ was determined by high-resolution MS measurement. Furthermore, fragment ion peaks of **1** were observed at *m/z* 617 $(M-CH_3O)^-$ and *m/z* 455 $(M-CH_3O-C_6H_{10}O_5)^-$. Acid hydrolysis of **1** with 5% aqueous sulfuric acid (H_2SO_4)–1,4-dioxane (1 : 1, v/v) furnished D-glucose, which was identified by GLC analysis of the thiazolidine derivative,[5] while enzymatic hydrolysis of **1** with naringinase furnished 19(*R*)-methoxy-5β,19-epoxycucurbita-6,23-diene-3β,25-diol (**17**).[6] The ^{1}H-NMR and ^{13}C-NMR spectra of **1**, which were assigned by various NMR experiments,[7] showed signals due to the aglycone moiety [δ 0.86, 0.89, 0.90, 1.47 (all s, 29, 30, 18, 28-H_3), 0.97 (d, J=5.3 Hz, 21-H_3), 1.54 (s, 26, 27-H_3), 3.12 (dd-like, 8-H), 3.44 (s, 19-OMe), 3.73 (br s, 3-H), 4.84 (s, 19-H), 5.62 (dd, J=3.6, 9.6 Hz, 7-H), 5.92 (m, 23, 24-H), 6.16 (dd, J=2.0, 9.6 Hz, 6-H)] and a β-D-glucopyranosyl moiety [δ 4.95 (d, J=7.6 Hz, 1′-H)]. The bonding position of the β-D-glucopyranosyl moiety in **1** was clarified by HMBC experiment, which showed a long-range correlation between the 1′-proton of the glucopyranosyl moiety and the 3-carbon of the aglycone moiety. Consequently, the structure of goyaglycoside-a was determined to be 19(*R*)-methoxy-5β,19-epoxycucurbita-6,23-diene-3β,25-diol 3-*O*-β-D-glucopyranoside (**1**).[8]

Goyaglycoside-b (**2**), obtained as a white powder with negative optical rotation, liberated D-allose by acid hydrolysis, which was also identified by GLC analysis of the thiazolidine derivative.[5] The molecular formula $C_{37}H_{60}O_9$ of **2** was determined from quasimolecular ion peaks [*m/z* 647 $(M-H)^-$ and 649 $(M+H)^+$] in the negative- and positive-ion FAB-MS and

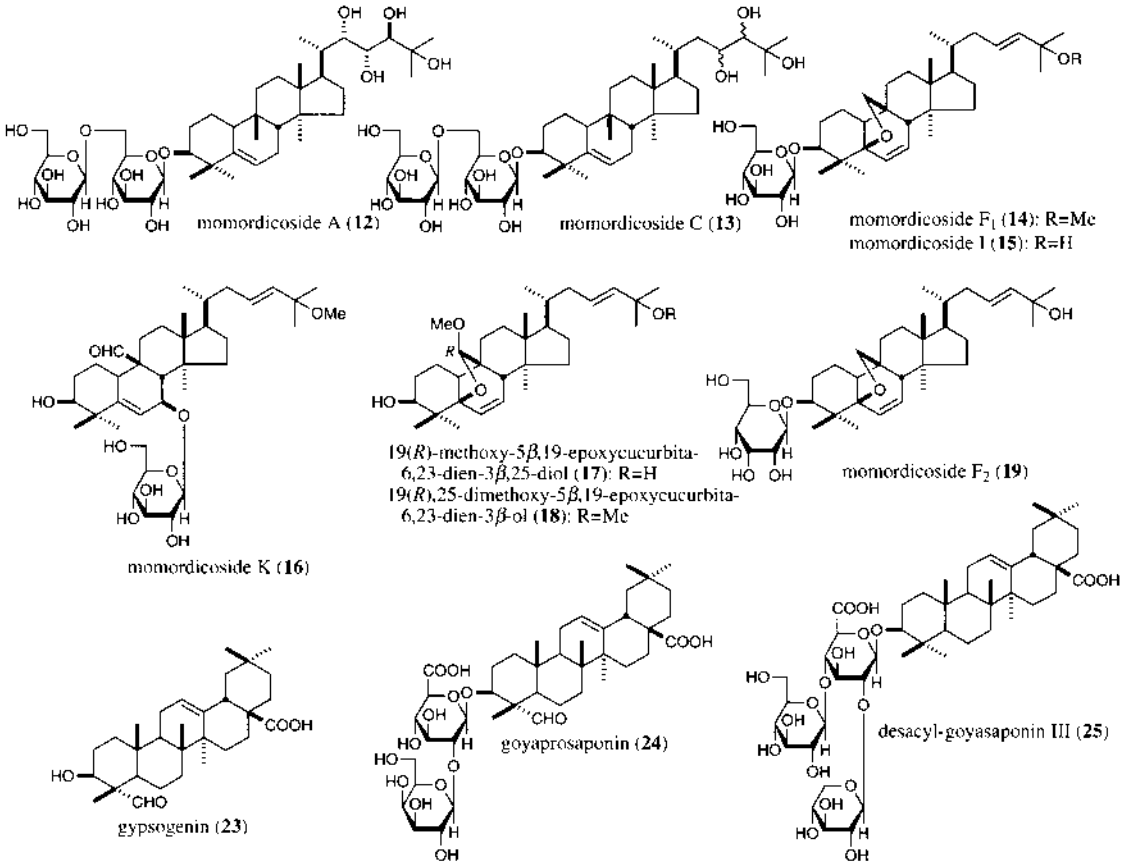

Chart 3

by high-resolution MS measurement. The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[7] of **2** showed signals due to a 19(*R*)-methoxy-5β,19-epoxycucurbita-6,23-diene-3β,25-diol moiety [δ 0.83, 0.89, 0.90, 1.44 (all s, 29, 30, 18, 28-H$_3$), 0.98 (d, J=5.3 Hz, 21-H$_3$), 1.54 (s, 26, 27-H$_3$), 3.13 (dd-like, 8-H), 3.50 (s, 19-OMe), 3.70 (br s, 3-H), 4.88 (s, 19-H), 5.61 (dd, J=3.3, 9.6 Hz, 7-H), 5.92 (m, 23, 24-H), 6.15 (dd, J=2.0, 9.6 Hz, 6-H)] together with an β-D-allopyranosyl moiety [δ 5.44 (d, J=7.6 Hz, 1′-H)]. In the HMBC experiment of **2**, a long-range correlation was observed between the 1′-proton of the allopyranosyl moiety and the 3-carbon of the aglycone. Finally, comparison of the NMR data for **2** with those for **1** led us to formulate the structure of goyaglycoside-b as 19(*R*)-methoxy-5β,19-epoxycucurbita-6,23-diene-3β,25-diol 3-*O*-β-D-allopyranoside (**2**).[8]

Goyaglycosides-c (**3**) and -d (**4**), obtained as a white powder with negative optical rotation, were found to have the same molecular formula, $C_{38}H_{62}O_9$, which was determined from the quasimolecular ion peaks [*m/z* 661 $(M-H)^-$, *m/z* 685 $(M+Na)^+$] in the negative- and positive-ion FAB-MS and by high-resolution MS measurement. Acid hydrolysis of **3** furnished D-glucose, while D-allose was obtained by acid hydrolysis of **4**.[5] Enzymatic hydrolysis of **3** with naringinase furnished 19(*R*),25-dimethoxy-5β,19-epoxycucurbita-6,23-dien-3β-ol (**18**).[6]

The carbon and proton signals in the ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[7] of **3** and **4** were superimposable on those of **1** and **2**, except for signals due to the 25-methoxyl group, respectively. The ^{1}H-NMR spectra of **3** and **4** showed two methoxyl signals to the 19- [**3**: δ 3.44 (s); **4**: δ 3.50 (s)] and 25-positions [**3**, **4**: δ 3.22 (s)]. Furthermore, in the HMBC experiments on **3** and **4**, long-range correlations were observed between the 25-methoxyl protons and the 25-carbon and between the 1′-proton [**3**: δ 4.95 (d, J=7.6 Hz); **4**: δ 5.43 (d, J=7.7 Hz)] and the 3-carbon. Consequently, the structures of goyaglycosides-c and -d were characterized as 19(*R*),25-dimethoxy-5β,19-epoxycucurbita-6,23-dien-3β-ol 3-*O*-β-D-glucopyranoside (**3**)[8] and 19(*R*),25-dimethoxy-5β,19-epoxycucurbita-6,23-dien-3β-ol 3-*O*-β-D-allopyranoside (**4**).[8]

Goyaglycoside-e (**5**) was obtained as a white powder with negative optical rotation ($[\alpha]_D^{28}$ −75.6°). The molecular formula $C_{42}H_{68}O_{13}$ was determined from the negative- [*m/z* 779 $(M-H)^-$] and positive- [*m/z* 781 $(M+H)^+$] ion FAB-MS and by high-resolution MS measurement. Furthermore, a fragment ion peak was observed at *m/z* 617 $(M-C_6H_{11}O_5)^-$ in the negative-ion FAB-MS of **5**. Acid hydrolysis of **5** with 5% aqueous H_2SO_4–1,4-dioxane (1 : 1, v/v) furnished D-allose and D-glucose.[5] Enzymatic hydrolysis of **5** with naringinase furnished momordicoside F$_2$ (**19**).[3c] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[7] of **5** showed signals assignable to a β-D-glucopyranosyl moiety [δ 4.98 (d, J=7.6 Hz, 1″-H)] together with a momordicoside F$_2$ moiety [δ 0.98 (d, J=5.6 Hz, 21-H$_3$), 2.31 (br s, 8-H), 3.64 (br s, 3-H), 3.65, 3.71 (ABq, J=7.9 Hz, 19-H$_2$), 5.35 (d, J=8.5 Hz, 1′-H), 5.56 (dd, J=3.3, 9.9 Hz, 7-H), 5.79 (ddd-like, 23-H), 6.01 (d, J=15.8 Hz, 24-H), 6.18 (d, J=9.9 Hz, 6-H)]. In the HMBC experiment of **5**, long-range correlations were observed between the 1′-proton of the D-allopyranosyl moiety and the 3-carbon and between the 1″-proton of the D-glu-

Table 1. ^{13}C-NMR Data for Goyaglycosides-a (**1**), -b (**2**), -c (**3**), -d (**4**), -e (**5**), -f (**6**), -g (**7**), and -h (**8**) and Goyagenin A (**20**)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**20**
C- 1	18.7	18.7	18.6	18.7	18.9	18.9	18.7	22.7	17.4
2	27.4	27.4	27.3	27.3	27.6	27.6	27.4	29.6	27.2
3	83.8	83.6	83.6	83.4	85.1	85.3	83.7	87.3	76.2
4	39.2	39.1	39.1	39.0	39.0	39.1	39.1	41.8	39.1
5	85.5	85.6	85.4	85.4	86.0	85.9	85.6	143.4	86.8
6	133.2	133.2	133.1	132.9	134.1	134.1	133.2	118.7	132.8
7	131.6	131.6	131.5	131.3	130.0	130.0	131.6	24.7	131.0
8	42.3	42.3	42.2	42.2	52.3	52.3	42.3	43.9	41.7
9	48.2	48.3	48.1	48.1	45.3	45.3	48.2	34.8	48.3
10	41.7	41.7	41.6	41.6	40.2	40.2	41.7	38.6	40.5
11	23.3	23.4	23.2	23.3	23.8	23.9	23.3	32.6	23.2
12	30.9	30.9	30.9	30.9	31.1	31.2	31.0	30.9	30.6
13	45.3	45.3	45.3	45.3	45.5	45.6	45.4	47.1	45.1
14	48.4	48.4	48.2	48.3	48.9	48.9	48.4	49.2	48.0
15	33.9	33.9	33.8	33.9	33.5	33.5	33.9	35.4	33.5
16	28.2	28.2	28.1	28.1	28.2	28.3	28.2	25.3	28.0
17	50.4	50.4	50.3	50.4	50.5	51.3	50.6	48.2	47.6
18	14.9	14.9	14.8	14.9	15.1	15.0	14.9	15.4	15.2
19	112.4	112.5	112.3	112.2	80.2	80.2	112.5	28.1	28.0
20	36.6	36.6	36.3	36.3	36.5	32.7	36.5	43.7	42.4
21	18.9	18.9	18.8	18.9	19.1	19.4	19.1	15.3	15.2
22	39.6	39.6	39.6	39.6	39.8	43.7	39.9	72.8	72.6
23	124.4	124.4	128.3	128.2	128.4	75.2	128.4	75.2	27.6
24	141.7	141.7	137.6	137.4	138.5	129.3	138.5	217.6	18.0
25	69.7	69.7	74.7	74.7	77.6	132.0	77.6	77.3	74.4
26	30.9	30.8	26.0	26.1	28.7	25.8	28.7	28.1	216.1
27	30.9	30.8	26.4	26.5	27.7	18.2	27.7	28.9	77.8
28	21.2	21.2	21.1	21.2	21.1	21.1	21.2	25.9	27.3
29	24.9	24.9	24.8	24.9	25.6	25.6	24.9	28.5	28.9
30	20.0	20.0	19.9	20.0	20.3	20.3	20.0	18.2	25.5
19-OMe	57.6	57.7	57.5	57.6			57.7		
25-OMe			50.0	50.0					
Glc or All-1′	105.3	102.5	105.2	102.3	103.8	106.6	102.5	106.9	
2′	76.2	73.7	76.1	73.6	73.1	75.8	73.7	75.4	
3′	78.6	71.8	77.8	71.6	72.4	78.3	71.8	78.5	
4′	72.1	69.3	72.0	69.2	69.3	72.0	69.3	71.9	
5′	78.0	76.4	78.5	76.3	76.1	78.3	76.4	77.4	
6′	63.1	63.3	63.0	63.2	63.4	63.1	63.3	70.3	
Glc or All-1″					99.8	101.5	99.8	105.3	
2″					75.3	72.7	75.3	75.3	
3″					78.8	73.2	78.8	78.5	
4″					71.9	69.4	71.9	71.9	
5″					78.0	75.7	78.0	78.6	
6″					63.0	63.3	63.0	62.9	

The spectra were taken in pyridine-d_5 at 68 MHz.

copyranosyl moiety and the 25-carbon. Consequently, the structure of goyaglycoside-e was determined as 25-*O*-β-D-glucopyranosyl-5β,19-epoxycucurbita-6,23-diene-3β,25-diol 3-*O*-β-D-allopyranoside (**5**).

Goyaglycoside-f (**6**) was isolated as a white powder with negative optical rotation ($[\alpha]_D^{27}$ −51.9°). In the negative- and positive-ion FAB-MS of **6**, quasimolecular ion peaks were observed at *m*/*z* 779 $(M-H)^-$ and *m*/*z* 781 $(M+H)^+$ and the molecular formula $C_{42}H_{68}O_{13}$ was determined by high-resolution MS measurement. Acid hydrolysis of **6** with 5% aqueous H_2SO_4–1,4-dioxane (1 : 1, v/v) furnished D-allose and D-glucose.[5] Furthermore, a fragment ion peak of **6** was observed at *m*/*z* 617 $(M-C_6H_{11}O_5)^-$. The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[7] of **6** showed a β-D-glucopyranosyl moiety [δ 4.87 (d, J=7.6 Hz, 1′-H)], a β-D-allopyranosyl moiety [δ 5.34 (d, J=7.9 Hz, 1″-H)], and an aglycone moiety [δ 2.31 (br s, 8-H), 3.61, 3.67 (ABq, J= 8.2 Hz, 19-H_2), 3.69 (br s, 3-H), 5.56 (d-like, 24-H), 5.61 (dd-like, 7-H), 6.19 (d, J=9.2 Hz, 6-H)]. The carbon and proton signals due to the tetracyclic carbon skeleton structure (C-1—21, C-28—30) of the aglycone moiety were superimposable on those of **5**, whereas the signals due to the side chain structure (C-22—27) were similar to those of protojujubosides[9] having the 23-*O*-glycosyl-24-ene structure. The plane structure of the aglycone moiety in **6** was determined by a detailed HMBC experiment. Namely, long-range correlations were observed between the following protons and carbons: 19-H_2 and 5, 8, 9, 10-C; 21-H_3 and 17, 20, 22-C; 26, 27-H_3 and 24, 25-C; 28, 29-H_3 and 3, 4, 5-C; 18-H_3 and 12, 13, 14, 17-C; 30-H_3 and 8, 13, 14, 15-C; 1′-H and 3-C; 1″-H and the 23-C (Fig. 1). The stereostructure of the aglycone moiety was characterized by NOESY experiment, which were observed between the following protons and protons: 28-H_3 and 3-H, 30-H_3; 30-H_3 and 17-H; 19-H_2 and 8-H, 29-H_3; 8-H and 18-H_3 (Fig. 1). Consequently, the structure of goyaglycoside-f was determined to be 23-*O*-β-D-allopyra-

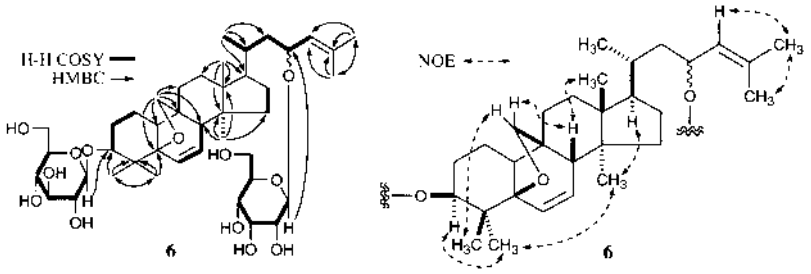

Fig. 1

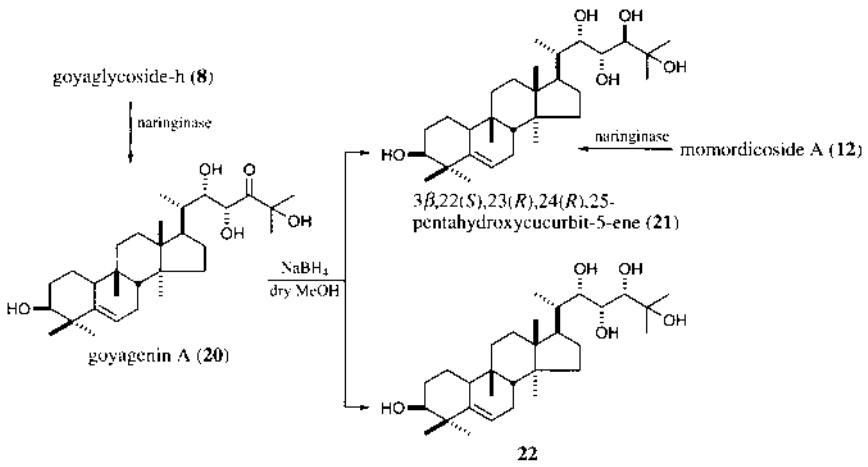

Fig. 2

nosyl 5β,19-epoxycucurbita-6,24-diene-3β,23ξ-diol 3-*O*-β-D-glucopyranoside (**6**).

Goyaglycoside-g (**7**), obtained as a white powder, liberated D-allose and D-glucose by acid hydrolysis. The molecular formula $C_{43}H_{70}O_{14}$ of **7** was obtained from quasimolecular ion peaks [*m/z* 809 $(M-H)^-$ and 833 $(M+Na)^+$] in the negative- and positive-ion FAB-MS. Enzymatic hydrolysis of **7** with cellulase furnished goyaglycoside-b (**2**). The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[7] of **7** showed signals due to a goyaglycoside-b moiety [δ 0.83, 0.91, 0.92, 1.44, 1.54, 1.60 (all s, 29, 18, 30, 28, 26, 27-H_3), 1.00 (d, J=5.3 Hz, 21-H_3), 3.12 (dd-like, 8-H), 3.50 (s, 19-OMe), 3.69 (br s, 3-H), 4.89 (s, 19-H), 5.43 (d, J=7.6 Hz, 1′-H), 5.61 (dd, J=3.3, 9.9 Hz, 7-H), 5.79 (ddd, J=5.6, 7.9, 15.8 Hz, 23-H), 6.01 (d, J=15.8 Hz, 24-H), 6.15 (dd, J=2.3, 9.9 Hz, 6-H)] together with an β-D-glucopyranosyl moiety [δ 4.99 (1H, d, J=7.9 Hz, 1″-H)]. In the HMBC experiment of **7**, a long-range correlation was observed between the 1″-proton of the glucopyranosyl moiety and the 25-carbon. Consequently, the structure of goyaglycoside-g was determined to be 25-*O*-β-D-glucopyranosyl-19(*R*)-methoxy-5β,19-epoxycucurbita-6,23-diene-3β,25-diol 3-*O*-β-D-allopyranoside (**7**).[8]

Goyaglycoside-h (**8**) was isolated as a white powder with positive optical rotation ($[\alpha]_D^{24}$ +0.7°). In the negative- and positive-ion FAB-MS of **8**, quasimolecular ion peaks were observed at *m/z* 813 $(M-H)^-$ and *m/z* 837 $(M+Na)^+$, and high-resolution MS analysis revealed the molecular formula of **8** to be $C_{42}H_{70}O_{15}$. By acid hydrolysis with 5% aqueous H_2SO_4–1,4-dioxane (1 : 1, v/v), **8** liberated D-glucose.[5] Enzymatic hydrolysis of **8** with naringinase furnished a new triterpene aglycone called goyagenin A (**20**), whose molecular formula $C_{30}H_{50}O_5$ was determined from the positive-ion FAB-MS [*m/z* 513 $(M+Na)^+$] and by high-resolution MS measurement. The IR spectrum of **20** showed absorption bands at 3567 and 1717 cm^{-1} suggestive of hydroxyl and carbonyl functions. The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[7] of **8** showed signals due to six tertiary methyls [δ 0.80, 0.88, 0.91, 1.06, 1.48, 1.63, 1.72 (all s, 30, 19, 28, 18, 29, 27, 26-H_3)], three methines bearing a hydroxyl group [δ 3.73 (br s, 3-H), 4.81 (dd-like, 22-H), 5.53 (d-like, 23-H)], a secondary methyl [δ 1.50 (d, J=6.3 Hz, 21-H_3)], a olefin [δ 5.45 (dd-like, 6-H)], and two β-D-glucopyranosyl moieties [δ 4.80 (d, J=7.6 Hz, 1′-H), 5.17 (d, J=7.6 Hz, 1″-H)] together with a carbonyl and four quaternary carbons. The proton and carbon signals of **8** in ^{1}H- and ^{13}C-NMR spectra were superimposable on those of a known cucurbitane-type triterpene saponin, momordicoside A (**12**),[3a] except for those around the 24-position. In the HMBC spectrum of **8**, long-range correlations were observed between the following protons and carbons: Glc-1′-H and 3-C; Glc-1″-H and Glc-6′-C; 26-, 27-H_3 and 24-C. These findings and comparisons of the ^{1}H- and ^{13}C-NMR spectra of **8** with those of known momordicosides[3] led us to formulate the structure of **8** as 3,22,23,25-tetrahydroxycucurbit-5-ene-24-one 3-*O*-β-D-glucopyranosyl(1→6)-β-D-glucopyranoside.

In order to learn the absolute stereostructure of **8**, the aglycone, goyagenin A (**20**) was treated with sodium borohydride ($NaBH_4$) to furnish 3β,22(*S*),23(*R*),24(*R*),25-pentahydroxycucurbit-5-ene (**21**)[3a] and its 24-diastereomar (**22**) as shown in Fig. 2. On the basis of the evidence, goyaglycoside-h was determined to be 3β,22(*S*),23(*R*),25-tetrahydroxycucurbit-5-en-24-one 3-*O*-β-D-glucopyranosyl(1→6)-β-D-glucopyrano-

Table 2. ^{13}C-NMR Data for Goyasaponins I (**9**), II (**10**), and III (**11**), Goyaprosaponin (**24**), and Desacyl-goyasaponin III (**25**)

	9	**10**	**24**	**11**	**25**		**9**	**10**	**24**		**11**	**25**
C-1	38.2	38.2	38.1	38.6	38.7	Gal-1	106.4	106.2	106.3	Xyl-1	105.5	106.2
2	25.1	25.1	24.9	26.5	26.6	2	74.5	74.3	74.4	2	75.1	76.5
3	83.6	83.7	83.5	90.0	89.5	3	74.9	74.9	74.9	3	78.4	78.1
4	55.0	55.0	55.0	39.6	39.6	4	70.2	70.2	70.2	4	71.1	71.1
5	48.6	48.5	48.4	55.8	55.9	5	77.1	78.1	77.1	5	67.2	67.4
6	20.5	20.4	20.4	18.5	18.5	6	62.2	62.2	62.2	Glc-1	104.6	104.7
7	32.6	32.6	32.5	33.2	33.3	Fuc-1	93.8	93.8		2	75.2	74.9
8	40.2	40.2	40.0	39.8	39.8	2	76.7	76.8		3	78.2	78.0
9	47.8	47.8	47.9	48.0	48.1	3	83.7	83.4		4	71.8	71.6
10	36.3	36.3	36.3	37.1	37.0	4	72.6	72.5		5	78.2	78.0
11	23.3	23.3	23.7	23.8	23.8	5	74.4	74.4		6	63.0	62.5
12	122.6	122.6	122.2	122.6	122.6	6	18.9	18.9		Ac-1	170.8	
13	144.1	144.0	144.9	144.9	144.9	Rha-1	100.9	100.9		2	21.6	
14	42.2	42.2	42.2	42.2	42.2	2	71.7	71.7				
15	28.2	28.2	28.3	28.4	28.4	3	72.6	72.6				
16	23.7	23.7	23.8	23.8	23.8	4	84.3	83.9				
17	47.1	47.0	46.6	46.7	46.7	5	68.8	68.7				
18	42.0	42.0	42.0	42.0	42.1	6	18.5	18.5				
19	46.3	46.3	46.5	46.5	46.6	Rha-1′	101.7	101.6				
20	30.8	30.8	30.9	31.0	31.0	2′	72.4	72.4				
21	34.0	34.0	34.2	34.3	34.3	3′	72.9	72.9				
22	32.4	32.4	33.2	33.2	33.3	4′	70.5	70.4				
23	209.6	209.6	209.3	27.8	27.9	5′	73.8	73.8				
24	11.0	11.0	10.9	16.4	16.4	6′	18.4	18.4				
25	15.7	15.7	15.6	15.4	15.5	Xyl-1	107.2	106.4				
26	17.6	17.6	17.3	17.4	17.4	2	76.0	75.0				
27	26.1	26.0	26.2	26.2	26.2	3	78.6	86.9				
28	176.2	176.2	180.1	180.1	180.1	4	70.9	69.0				
29	33.1	33.1	33.3	33.3	33.3	5	67.5	66.8				
30	23.8	23.8	23.8	23.8	23.8	Xyl-1′		105.8				
GlcA-1	103.4	103.4	103.3	104.9	105.0	2′		75.2				
2	82.5	82.3	82.5	78.3	81.6	3′		78.1				
3	77.7	77.7	77.7	75.1	76.1	4′		70.9				
4	72.6	72.6	72.8	78.0	82.0	5′		67.3				
5	77.3	77.4	77.4	76.1	78.4							
6	172.6	172.2	172.2	171.8	172.0							

The spectra were taken in pyridine-d_5 at 125 MHz.

side (**8**).

Structures of Oleanene-Type Triterpene Saponins (9—11) Goyasaponin I (**9**) was obtained as a white powder with negative optical rotation ($[\alpha]_D^{24}$ −13.5°). The IR spectrum of **9** showed absorption bands at 3410, 1717, 1684, 1078, and 1046 cm^{-1} due to hydroxyl, carbonyl, and carboxyl functions. In the negative- and positive-ion FAB-MS of **9**, quasi-molecular ion peaks were observed at *m/z* 1377 $(M-H)^-$ and *m/z* 1401 $(M+Na)^+$ and the molecular formula $C_{65}H_{102}O_{31}$ was determined by high-resolution MS measurement. Furthermore, fragment ion peaks were observed at *m/z* 1231 $(M-C_6H_{11}O_4)^-$, 1215 $(M-C_6H_{11}O_5)^-$, 1099 $(M-C_{11}H_{19}O_8)^-$, 1039 $(M-C_{12}H_{19}O_{11})^-$, and 807 $(M-C_{23}H_{39}O_{16})^-$ in the negative-ion FAB-MS of **9**. Acid hydrolysis of **9** with 5% aqueous H_2SO_4–1,4-dioxane (1 : 1, v/v) furnished D-xylose, L-rhamnose, D-fucose, D-galactose, and D-glucuronic acid,[5] while methanolysis of **9** with 9% HCl–dry methanol liberated gypsogenin (**23**).[10] Alkaline hydrolysis of **9** with 5% aqueous NaOH provided goyaprosaponin (**24**).

By acid hydrolysis with 5% aqueous H_2SO_4–1,4-dioxane (1 : 1, v/v), goyaprosaponin (**24**) liberated D-glucuronic acid and D-galactose.[5] The molecular formula $C_{42}H_{64}O_{15}$ of **24** was also determined from the negative- and positive-ion FAB-MS [*m/z* 807 $(M-H)^-$, *m/z* 831 $(M+Na)^+$] and by high-resolution MS measurement. The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 2) spectra[7] of **24** showed signals due to the gypsogenin moiety [δ 3.26 (dd-like, 18-H), 4.06 (dd-like, 3-H), 5.43 (br s, 12-H), 9.92 (s, 23-H)] and the disaccharide moiety consisted of a β-D-glucopyranosiduronic acid [δ 4.90 (d, J=7.3 Hz, GlcA-1-H)] and a β-D-galactopyranosyl [δ 5.18 (d, J=7.6 Hz, Gal-1-H)] part. The disaccharide structure bonding to the 3-position of **24** was determined by HMBC experiment. Thus, long-range correlations were observed between the 1-proton of the glucuronic acid part and the 3-carbon of the gypsogenin part and between the 1-proton of the galactopyranosyl moiety and the 2-carbon of the glucuronic acid part. Based on this evidence, the structure of goyaprosaponin (**24**) was elucidated.

The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 2) spectra[7] of **9** indicated the presence of a β-D-fucopyranosyl moiety [δ 1.53 (d, J=6.1 Hz, Fuc-6-H$_3$), 6.27 (d, J=5.5 Hz, Fuc-1-H)], two α-L-rhamnopyranosyl moiety [δ 1.61 (d, J=6.1 Hz, Rha-6′-H$_3$), 1.71 (d, J=5.2 Hz, Rha-6-H$_3$), 5.65 (br s, Rha-1′-H), 5.74 (br s, Rha-1-H)], and a β-D-xylopyranosyl moiety [δ 5.05 (1H, d, J=7.3 Hz, Xyl-1-H)] together with a goyaprosaponin moiety [δ 3.11 (dd, J=3.0, 13.3 Hz, 18-H), 4.04 (dd-like, 3-H), 5.38 (br s, 12-H), 9.92 (s, 23-H), 4.89 (d, J=7.3 Hz, GlcA-1-H), 5.18 (d, J=7.6 Hz, Gal-1-H)]. The tetrasaccharide structure bonding to the 28-carboxyl group of gypsogenin in **9** was characterized by a HMBC experiment.

Namely, long-range correlations were observed between the following protons and carbons [Fuc-1-H and 28-C; Rha-1-H and Fuc-2-C; Rha-1′-H and Fuc-3-C; Xyl-1-H and Rha-4-C]. Consequently, the structure of goyasaponin I has been elucidated as 28-*O*-*β*-D-xylopyranosyl(1→4)-*α*-L-rhamnopyranosyl(1→2)-[*α*-L-rhamnopyranosyl(1→3)]-*β*-D-fucopyranosyl gypsogenin 3-*O*-*β*-D-galactopyranosyl(1→2)-*β*-D-glucopyranosiduronic acid (**9**).

Goyasaponin II (**10**), isolated as a white powder, furnished goyaprosaponin (**24**) upon alkaline hydrolysis. The molecular formula $C_{70}H_{110}O_{35}$ was determined from the negative- [*m/z* 1509 $(M-H)^-$] and positive- [*m/z* 1533 $(M+Na)^+$] ion FAB-MS and by high-resolution MS measurement. Furthermore, fragment ion peaks were observed at *m/z* 1363 $(M-C_6H_{11}O_4)^-$, 1347 $(M-C_6H_{11}O_5)^-$, 1245 $(M-C_{10}H_{17}O_8)^-$, 1171 $(M-C_{12}H_{19}O_{11})^-$, and 1099 $(M-C_{16}H_{27}O_{12})^-$ were observed in the negative-ion FAB-MS of **10**. Acid hydrolysis of **10** with 5% aqueous H_2SO_4–1,4-dioxane (1 : 1, v/v) furnished D-xylose, L-rhamnose, D-fucose, D-galactose, and D-glucuronic acid.[5] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 2) spectra[7] of **10** showed signals assignable to a *β*-D-glucopyranosiduronic acid moiety [*δ* 4.89 (d, *J*=7.3 Hz, GlcA-1-H)], a *β*-D-galactopyranosyl moiety [*δ* 5.20 (d, *J*=7.3, Gal-1-H)], a *β*-D-fucopyranosyl moiety [*δ* 1.54 (d, *J*=5.8 Hz, Fuc-6-H$_3$), 6.28 (d, *J*=5.5 Hz, Fuc-1-H)], two *α*-L-rhamnopyranosyl moieties [*δ* 1.61 (d, *J*=6.1 Hz, Rha-6′-H$_3$), 1.68 (d, *J*=5.5 Hz, Rha-6-H$_3$), 5.65 (br s, Rha-1′-H), 5.73 (br s, Rha-1-H)], two *β*-D-xylopyranosyl moieties [*δ* 5.07 (d, *J*=7.0 Hz, Xyl-1-H), 5.18 (d, *J*=7.3 Hz, Xyl-1′-H)], and a gypsogenin moiety [*δ* 3.11 (dd-like, 18-H), 4.04 (dd, *J*=5.8, 15.0 Hz, 3-H), 5.44 (br s, 12-H), 9.93 (s, 23-H)]. The oligoglycoside structure of **10** was characterized by a HMBC experiment, which showed long-range correlations between the following protons and carbons: GlcA-1-H and 3-C, Gal-1-H and GlcA-2-C, Fuc-1-H and 28-C, Rha-1-H and Fuc-2-C, Rha-1′-H and Fuc-3-C, Xyl-1-H and Rha-4-C, Xyl-1′-H and Xyl-3-C. The carbon signals in the ^{13}C-NMR spectrum of **10** were very similar to those of **9**, except for the signals due to an additional xylopyranosyl moiety of **10**. Consequently, goyasaponin II was determined to be 28-*O*-*β*-D-xylopyranosyl(1→3)-*β*-D-xylopyranosyl(1→4)-*α*-L-rhamnopyranosyl(1→2)-[*α*-L-rhamnopyranosyl(1→3)]-*β*-D-fucopyranosyl gypsogenin 3-*O*-*β*-D-galactopyranosyl(1→2)-*β*-D-glucopyranosiduronic acid (**10**).

Goyasaponin III (**11**), isolated as a white powder with negative optical rotation ($[\alpha]_D^{24}$ −1.9°), liberated D-glucuronic acid, D-xylose, and D-glucose on acid hydrolysis,[5] and its IR spectrum showed absorption bands due to hydroxyl, carboxyl, and carbonyl functions. Here again, the molecular formula $C_{49}H_{76}O_{19}$ of **11** was identified from the negative- and positive-ion FAB-MS [quasimolecular ion peaks: *m/z* 967 $(M-H)^-$, *m/z* 991 $(M+Na)^+$] and by high-resolution MS measurement.

Treatment of **11** with 1% sodium methoxide in methanol at room temperature furnished desacyl-goyasaponin III (**25**), whose molecular formula $C_{47}H_{74}O_{18}$ was determined by high-resolution MS measurement of the quasimolecular ion peaks in the negative- [*m/z* 925 $(M-H)^-$] and positive- [*m/z* 949 $(M+Na)^+$] ion FAB-MS. Acid hydrolysis of **25** with 5% aqueous H_2SO_4–1,4-dioxane (1 : 1, v/v) liberated oleanolic acid, D-glucuronic acid, D-xylose, and D-glucose.[5] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 2) spectra[7] of **25** showed signals assignable to an oleanolic acid part [*δ* 3.25 (dd, *J*=4.0, 11.6 Hz, 3-H), 3.29 (dd, *J*=3.7, 13.7 Hz, 18-H), 5.45 (br s, 12-H)], a *β*-D-glucopyranosiduronic acid part [*δ* 5.27 (d, *J*=7.3 Hz, GlcA-1-H)], a *β*-D-xylopyranosyl part [*δ* 4.94 (d, *J*=7.6 Hz, Xyl-1-H)], and a *β*-D-glucopyranosyl part [*δ* 5.15 (d, *J*=7.6 Hz, Glc-1-H)]. The triglycoside structure bonding to the 3-hydroxyl group of an oleanolic acid moiety in **11** was characterized by a HMBC experiment. Namely, long-range correlations were observed between the following protons and carbons: GlcA-1-H and 3-C; Xyl-1-H and GlcA-2-C; Glc-1-H and GlcA-4-C; GlcA-3-H and Ac-1-C.

The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 2) spectra[7] of **11** showed signals assignable to an acetyl group [*δ* 2.45 (3H, s, Ac-2)] together with the desacyl-goyasaponin III moiety. Comparison of the ^{1}H- and ^{13}C-NMR data for **11** with those for **25** revealed an acylation shift around the 3-position of the D-glucopyranosiduronic acid moiety in the triglycoside part of **11**. In the HMBC experiment of **11**, a long-range correlation was observed between the 3-proton of the D-glucopyranosiduronic acid moiety and the acetyl carbonyl carbon. Consequently, the structure of goyasaponin III has been elucidated as oleanolic acid 3-*O*-[*β*-D-xylopyranosyl(1→2)][*β*-D-glucopyranosyl(1→4)]-3′-*O*-acetyl-*β*-D-glucopyranosiduronic acid (**11**).

Experimental

The instruments used to obtain physical data and the experimental conditions for chromatography were described previously.[1]

Isolation of Goyaglycosides-a (1), -b (2), -c (3), -d (4), -e (5), -f (6), -g (7), and -h (8), Goyasaponins I (9), II (10), and III (11) and Five Known Glycosides (12—16) from the Fresh Fruit of *M. charantia* L. The fresh whole fruit of *M. charantia* L. (36.9 kg, cultivated in Okinawa prefecture, Japan), which included the immature seeds, was cut and extracted three times with MeOH under reflux. Evaporation of the solvent under reduced pressure provided the MeOH extract (846.0 g, 2.3%), and the extract (828.0 g) was partitioned into the AcOEt–H_2O (1 : 1) mixture. The water phase was further extracted with the *n*-BuOH. Removal of the solvent under reduced pressure from the AcOEt- and *n*-BuOH-soluble portions yielded 64.5 g (0.17%) and 98.3 g (0.27%) of residues, respectively. The *n*-BuOH-soluble portion (88.3 g) was subjected to normal-phase silica gel column chromatography [BW-200 (Fuji Silysia Co., Ltd., 4.5 kg), $CHCl_3$–MeOH–H_2O (15 : 3 : 1, lower layer→10 : 3 : 1, lower layer→65 : 35 : 10, lower layer→6 : 4 : 1, v/v)→MeOH] to give five fractions [Fr. 1 (2.5 g), Fr. 2 (4.0 g), Fr. 3 (6.1 g), Fr. 4 (21.4 g), Fr. 5 (50.2 g)].

Fraction 1 (2.5 g) was subjected to normal-phase silica gel column chromatography [140 g, $CHCl_3$–MeOH–H_2O (30 : 3 : 1, lower layer→20 : 3 : 1, lower layer, v/v)→MeOH] to give Fr. 1-1 (218.9 mg), Fr. 1-2 (1.5 g), Fr. 1-3 (553.9 mg), Fr. 1-4 (187.3 mg). Fraction 1-2 (1.5 g) was separated by reversed-phase silica gel column chromatography [Chromatorex ODS DM1020T (Fuji Silysia Chemical Ltd., 30 g), MeOH–H_2O (70 : 30→80 : 20→90 : 10, v/v)] and HPLC [YMC-Pack ODS-A (YMC Co., Ltd.), 1) MeOH–H_2O (85 : 15, v/v), 2) CH_3CN–H_2O (50 : 50, v/v)] to give goyaglycosides-a (**1**, 28.5 mg, 0.00008%) and -b (**2**, 20.0 mg, 0.00005%) and momordicoside I (**15**, 23.0 mg, 0.00006%). Fraction 1-3 (553.9 mg) was separated by reversed-phase silica gel column chromatography [11 g, MeOH–H_2O (50 : 50→75 : 25→85 : 15, v/v)→MeOH] and HPLC [CH_3CN–H_2O (50 : 50, v/v)] to give momordicoside K (**16**, 9.9 mg, 0.00003%).

Fraction 2 (2.5 g) was subjected to reversed-phase silica gel column chromatography [100 g, MeOH–H_2O (50 : 50→85 : 15→90 : 10→95 : 5, v/v)→MeOH] to give Fr. 2-1 (2.0 g), Fr. 2-2 (193.8 mg), Fr. 2-3 (133.9 mg), Fr. 2-4 (706.2 mg), Fr. 2-5 (415.6 mg), Fr. 2-6 (234.3 mg), Fr. 2-7 (185.9 mg). Fraction 2-4 was purified by HPLC [MeOH–H_2O (85 : 15, 70 : 30, v/v), CH_3CN–H_2O (35 : 65, v/v)] to give goyaglycosides-e (**5**, 37.2 mg, 0.00010%), -f (**6**, 32.0 mg, 0.00009%), and -h (**8**, 27.7 mg, 0.00008%).

Fraction 3 was separated by normal-phase silica gel column chromatography [305 g, $CHCl_3$–MeOH–H_2O (20 : 3 : 1, lower layer→15 : 3 : 1, lower layer→10 : 3 : 1, lower layer→7 : 3 : 1, lower layer, v/v)→MeOH] to give Fr.

3-1 (132.0 mg), Fr. 3-2 (359.9 mg), Fr. 3-3 (609.5 mg), Fr. 3-4 (327.2 mg), Fr. 3-5 (597.3 mg), Fr. 3-6 (3.8 g). Fraction 3-2 (359.9 mg) was purified by HPLC [1) MeOH–H_2O (85 : 15, v/v), 2) CH_3CN–H_2O (75 : 25, v/v)] to give goyaglycoside-d (**4**, 29.9 mg, 0.00008%). Fraction 3-3 (609.5 mg) was purified by HPLC [MeOH–H_2O (85 : 15, v/v)] to give goyaglycoside-c (**3**, 24.2 mg, 0.00007%) and momordicoside F_1 (**14**, 40.5 mg, 0.00011%).

Fraction 4 (21.4 g) was separated by reversed-phase silica gel column chromatography [520 g, MeOH–H_2O (50 : 50→65 : 35→80 : 20, v/v)→MeOH] and HPLC [MeOH-1% aq. AcOH (65 : 45, v/v)] to give goyaglycoside-g (**7**, 23.8 mg, 0.00006%) and momordicosides A (**12**, 473.2 mg, 0.0013%) and C (**13**, 59.3 mg, 0.00016%).

Fraction 5 (49.0 g) was subjected to reversed-phase silica gel column chromatography [900 g, MeOH–H_2O (50 : 50→80 : 20, v/v)→MeOH] to give Fr. 5-1 (35.6 g), Fr. 5-2 (1.2 g), Fr. 5-3 (442.9 mg), Fr. 5-4 (2.4 g), Fr. 5-5 (2.5 g). Fraction 5-4 (327.3 mg) was purified by HPLC [MeOH-1% aq. AcOH (80 : 20, v/v)] to give goyasaponins I (**9**, 37.4 mg, 0.00010%), II (**10**, 101.1 mg, 0.00027%). Fraction 5-5 (2.5 g) was separated by reversed-phase silica gel column chromatography [MeOH–H_2O (70 : 30→80 : 20, v/v)→MeOH] and HPLC [MeOH–1% aq. AcOH (80 : 20, v/v)] to give goyasaponin III (**11**, 32.6 mg, 0.00009%).

The known compounds (**12**—**16**) were identified by comparison of their physical data ($[\alpha]_D$, IR, ^{1}H-NMR, ^{13}C-NMR) with reported values.[3)]

Goyaglycoside-a (**1**): A white powder, $[\alpha]_D^{26}$ −101.4° (c=0.5, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{37}H_{61}O_9$ $(M+H)^+$: 649.4316. Found: 649.4307. IR (KBr): 3423, 1080 cm^{-1}. ^{1}H-NMR (270 MHz, pyridine-d_5) δ: 0.86, 0.89, 0.90, 1.47 (3H each, all s, 29, 30, 18, 28-H_3), 0.97 (3H, d, J=5.3 Hz, 21-H_3), 1.54 (6H, s, 26, 27-H_3), 3.12 (1H, dd-like, 8-H), 3.44 (3H, s, 19-OMe), 3.73 (1H, br s, 3-H), 4.84 (1H, s, 19-H), 4.95 (1H, d, J=7.6 Hz, 1′-H), 5.62 (1H, dd, J=3.6, 9.6 Hz, 7-H), 5.92 (2H, m, 23, 24-H), 6.16 (1H, dd, J=2.0, 9.6 Hz, 6-H). ^{13}C-NMR (68 MHz, pyridine-d_5) δc: given in Table 1. Negative-ion FAB-MS: m/z 647 $(M-H)^-$, 617 $(M-CH_3O)^-$, 455 $(M-CH_3O-C_6H_{10}O_5)^-$. Positive-ion FAB-MS: m/z 649 $(M+H)^+$.

Goyaglycoside-b (**2**): A white powder, $[\alpha]_D^{23}$ −110.7° (c=0.5, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{37}H_{61}O_9$ $(M+H)^+$: 649.4316. Found: 649.4320. IR (KBr): 3428, 1086, 1032 cm^{-1}. ^{1}H-NMR (270 MHz, pyridine-d_5) δ: 0.83, 0.89, 0.90, 1.44 (3H each, all s, 29, 30, 18, 28-H_3), 0.98 (3H, d, J=5.3 Hz, 21-H_3), 1.54 (6H, s, 26, 27-H_3), 3.13 (1H, dd-like, 8-H), 3.50 (3H, s, 19-OMe), 3.70 (1H, br s, 3-H), 4.88 (1H, s, 19-H), 5.44 (1H, d, J=7.6 Hz, 1′-H), 5.61 (1H, dd, J=3.3, 9.6 Hz, 7-H), 5.92 (2H, m, 23, 24-H), 6.15 (1H, dd, J=2.0, 9.6 Hz, 6-H). ^{13}C-NMR (68 MHz, pyridine-d_5) δc: given in Table 1. Negative-ion FAB-MS: m/z 647 $(M-H)^-$, 455 $(M-CH_3O-C_6H_{10}O_5)^-$. Positive-ion FAB-MS: m/z 649 $(M+H)^+$.

Goyaglycoside-c (**3**): A white powder, $[\alpha]_D^{26}$ −110.8° (c=0.5, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{38}H_{62}O_9Na$ $(M+Na)^+$: 685.4292. Found: 685.4296. IR (KBr): 3410, 1078 cm^{-1}. ^{1}H-NMR (270 MHz, pyridine-d_5) δ: 0.86, 1.48 (3H each, both s, 29, 28-H_3), 0.92, 1.33 (6H each, all s, 18, 30, 26, 27-H_3), 3.13 (1H, dd-like, 8-H), 3.22, 3.44 (3H each, both s, 25, 19-OMe), 3.73 (1H, br s, 3-H), 4.85 (1H, s, 19-H), 4.95 (1H, d, J=7.6 Hz, 1′-H), 5.55 (1H, d, J=15.8 Hz, 24-H), 5.65 (2H, m, 7, 23-H), 6.17 (1H, dd, J=1.7, 9.6 Hz, 6-H). ^{13}C-NMR (68 MHz, pyridine-d_5) δc: given in Table 1. Negative-ion FAB-MS: m/z 661 $(M-H)^-$, 647 $(M-CH_3)^-$, 499 $(M-C_6H_{11}O_5)^-$. Positive-ion FAB-MS: m/z 685 $(M+Na)^+$.

Goyaglycoside-d (**4**): A white powder, $[\alpha]_D^{26}$ −141.1° (c=0.1, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{38}H_{62}O_9Na$ $(M+Na)^+$: 685.4292. Found: 685.4298. IR (KBr): 3434, 1082, 1034 cm^{-1}. ^{1}H-NMR (270 MHz, pyridine-d_5) δ: 0.83, 1.44 (3H each, both s, 29, 28-H_3), 0.93, 1.33 (6H each, both s, 18, 30, 26, 27-H_3), 0.99 (3H, d, J=5.4 Hz, 21-H_3), 3.14 (1H, dd-like, 8-H), 3.22, 3.50 (3H each, both s, 25, 19-OMe), 3.69 (1H, br s, 3-H), 4.89 (1H, s, 19-H), 5.43 (1H, d, J=7.7 Hz, 1′-H), 5.55 (1H, d, J=15.8 Hz, 24-H), 5.62 (1H, dd, J=3.7, 9.7 Hz, 7-H), 5.66 (1H, ddd, J=5.6, 8.6, 15.8 Hz, 23-H), 6.15 (1H, dd, J=1.8, 9.8 Hz, 6-H). ^{13}C-NMR (68 MHz, pyridine-d_5) δc: given in Table 1. Negative-ion FAB-MS: m/z 661 $(M-H)^-$, 499 $(M-C_6H_{11}O_5)^-$. Positive-ion FAB-MS: m/z 685 $(M+Na)^+$.

Goyaglycoside-e (**5**): A white powder, $[\alpha]_D^{28}$ −75.6° (c=0.7, EtOH). High-resolution positive-ion FAB-MS: Calcd for $C_{42}H_{69}O_{13}$ $(M+H)^+$: 781.4739. Found: 781.4744. IR (KBr): 3410, 1082, 1032 cm^{-1}. ^{1}H-NMR (270 MHz, pyridine-d_5) δ: 0.77, 0.89, 0.90, 1.45, 1.54, 1.60 (3H each, all s, 18, 30, 29, 28, 26, 27-H_3), 0.98 (3H, d, J=5.6 Hz, 21-H_3), 2.31 (1H, br s, 8-H), 3.64 (1H, br s, 3-H), 3.65, 3.71 (1H each, ABq, J=7.9 Hz, 19-H_2), 4.98 (1H, d, J=7.6 Hz, 1″-H), 5.35 (1H, d, J=8.5 Hz, 1′-H), 5.56 (1H, dd, J=3.3, 9.9 Hz, 7-H), 5.79 (1H, ddd-like, 23-H), 6.01 (1H, d, J=15.8 Hz, 24-H), 6.18 (1H, d, J=9.9 Hz, 6-H). ^{13}C-NMR (68 MHz, pyridine-d_5) δc: given in Table 1. Negative-ion FAB-MS: m/z 779 $(M-H)^-$, 617 $(M-C_6H_{11}O_5)^-$. Positive-ion FAB-MS: m/z 781 $(M+H)^+$.

Goyaglycoside-f (**6**): A white powder, $[\alpha]_D^{27}$ −51.9° (c=0.5, EtOH), High-resolution positive-ion FAB-MS: Calcd for $C_{42}H_{69}O_{13}$ $(M+H)^+$: 781.4739. Found: 781.4733. IR (KBr): 3410, 1082, 1032 cm^{-1}. ^{1}H-NMR (270 MHz, pyridine-d_5) δ: 0.79, 0.89, 0.92, 1.49, 1.68, 1.71 (3H each, all s, 18, 30, 29, 28, 26, 27-H_3), 1.12 (3H, d, J=6.3 Hz, 21-H_3), 2.31 (1H, br s, 8-H), 3.61, 3.67 (1H each, ABq, J=8.2 Hz, 19-H_2), 3.69 (1H, br s, 3-H), 4.87 (1H, d, J=7.6 Hz, 1′-H), 5.34 (1H, d, J=7.9 Hz, 1″-H), 5.56 (1H, d-like, 24-H), 5.61 (1H, dd-like, 7-H), 6.19 (1H, d, J=9.2 Hz, 6-H). ^{13}C-NMR (68 MHz, pyridine-d_5) δc: given in Table 1. Negative-ion FAB-MS: m/z 779 $(M-H)^-$, 617 $(M-C_6H_{11}O_5)^-$. Positive-ion FAB-MS: m/z 781 $(M+H)^+$.

Goyaglycoside-g (**7**): A white powder, $[\alpha]_D^{27}$ −79.2° (c=0.5, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{43}H_{70}O_{14}Na$ $(M+Na)^+$: 833.4663. Found: 833.4695. IR (KBr): 3434, 1655, 1080, 1034 cm^{-1}. ^{1}H-NMR (270 MHz, pyridine-d_5) δ: 0.83, 0.91, 0.92, 1.44, 1.54, 1.60 (3H each, all s, 29, 18, 30, 28, 26, 27-H_3), 1.00 (3H, d, J=5.3 Hz, 21-H_3), 3.12 (1H, dd-like, 8-H), 3.50 (3H, s, 19-OMe), 3.69 (1H, br s, 3-H), 4.89 (1H, s, 19-H), 4.99 (1H, d, J=7.9 Hz, 1″-H), 5.43 (1H, d, J=7.6 Hz, 1′-H), 5.61 (1H, dd, J=3.3, 9.9 Hz, 7-H), 5.79 (1H, ddd, J=5.6, 7.9, 15.8 Hz, 23-H), 6.01 (1H, d, J=15.8 Hz, 24-H), 6.15 (1H, dd, J=2.3, 9.9 Hz, 6-H). ^{13}C-NMR (68 MHz, pyridine-d_5) δc: given in Table 1. Negative-ion FAB-MS: m/z 809 $(M-H)^-$, 647 $(M-C_6H_{11}O_5)^-$. Positive-ion FAB-MS: m/z 833 $(M+Na)^+$.

Goyaglycoside-h (**8**): A white powder, $[\alpha]_D^{24}$ +0.7° (c=0.5, pyridine). High-resolution positive-ion FAB-MS: Calcd for $C_{42}H_{70}O_{15}Na$ $(M+Na)^+$: 837.4612. Found: 837.4623. IR (KBr): 3432, 1717, 1076, 1038 cm^{-1}. ^{1}H-NMR (270 MHz, pyridine-d_5) δ: 0.80, 0.88, 0.91, 1.06, 1.48, 1.63, 1.72 (3H each, all s, 30, 19, 28, 18, 29, 27, 26-H_3), 1.50 (3H, d, J=6.3 Hz, 21-H_3), 1.65 (1H, br s, 8-H), 3.73 (1H, br s, 3-H), 4.80 (1H, d, J=7.6 Hz, 1′-H), 4.81 (1H, dd-like, 22-H), 5.17 (1H, d, J=7.6 Hz, 1″-H), 5.45 (1H, dd-like, 6-H), 5.53 (1H, d-like, 23-H). ^{13}C-NMR (68 MHz, pyridine-d_5) δc: given in Table 1. Negative-ion FAB-MS: m/z 813 $(M-H)^-$, 491 $(M-C_{12}H_{21}O_{10})^-$. Positive-ion FAB-MS: m/z 837 $(M+Na)^+$.

Goyasaponin I (**9**): A white powder, $[\alpha]_D^{24}$ −13.5° (c=0.5, pyridine). High-resolution positive-ion FAB-MS: Calcd for $C_{65}H_{102}O_{31}Na$ $(M+Na)^+$: 1401.6303. Found: 1401.6290. IR (KBr): 3410, 1717, 1684, 1078, 1046 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.81, 0.90, 0.96, 0.98, 1.21, 1.41 (3H each, all s, 25, 29, 26, 30, 27, 24-H_3), 1.53 (3H, d, J=6.1 Hz, Fuc-6-H_3), 1.61 (3H, d, J=6.1 Hz, Rha-6′-H_3), 1.71 (3H, d, J=5.2 Hz, Rha-6-H_3), 3.11 (1H, dd, J=3.0, 13.3 Hz, 18-H), 4.04 (1H, dd-like, 3-H), 4.89 (1H, d, J=7.3 Hz, GlcA-1-H), 5.05 (1H, d, J=7.3 Hz, Xyl-1-H), 5.18 (1H, d, J=7.6 Hz, Gal-1-H), 5.38 (1H, br s, 12-H), 5.65 (1H, br s, Rha-1′-H), 5.74 (1H, br s, Rha-1-H), 6.27 (1H, d, J=5.5 Hz, Fuc-1-H), 9.92 (1H, s, 23-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δc: given in Table 2. Negative-ion FAB-MS: m/z 1377 $(M-H)^-$, 1231 $(M-C_6H_{11}O_4)^-$, 1215 $(M-C_6H_{11}O_5)^-$, 1099 $(M-C_{11}H_{19}O_8)^-$, 1039 $(M-C_{12}H_{19}O_{11})^-$, 807 $(M-C_{23}H_{39}O_{16})^-$. Positive-ion FAB-MS: m/z 1401 $(M+Na)^+$.

Goyasaponin II (**10**): A white powder, $[\alpha]_D^{24}$ −18.5° (c=1.0, pyridine). High-resolution positive-ion FAB-MS: Calcd for $C_{70}H_{110}O_{35}Na$ $(M+Na)^+$: 1533.6725. Found: 1533.6735. IR (KBr): 3432, 1726, 1655, 1080, 1047 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.81, 0.90, 0.96, 0.98, 1.21, 1.41 (3H each, all s, 25, 29, 26, 30, 27, 24-H_3), 1.54 (3H, d, J=5.8 Hz, Fuc-6-H_3), 1.61 (3H, d, J=6.1 Hz, Rha-6′-H_3), 1.68 (3H, d, J=5.5 Hz, Rha-6-H_3), 3.11 (1H, dd-like, 18-H), 4.04 (1H, dd, J=5.8, 15.0 Hz, 3-H), 4.89 (1H, d, J=7.3 Hz, GlcA-1-H), 5.07 (1H, d, J=7.0 Hz, Xyl-1-H), 5.18 (1H, d, J=7.3 Hz, Xyl-1′-H), 5.20 (1H, d, J=7.3, Gal-1-H), 5.44 (1H, br s, 12-H), 5.65 (1H, br s, Rha-1′-H), 5.73 (1H, br s, Rha-1-H), 6.28 (1H, d, J=5.5 Hz, Fuc-1-H), 9.93 (1H, s, 23-H). ^{13}C-NMR (pyridine-d_5, 125 MHz) δc: given in Table 2. Negative-ion FAB-MS: m/z 1509 $(M-H)^-$, 1363 $(M-C_6H_{11}O_4)^-$, 1347 $(M-C_6H_{11}O_5)^-$, 1245 $(M-C_{10}H_{17}O_8)^-$, 1171 $(M-C_{12}H_{19}O_{11})^-$, 1099 $(M-C_{16}H_{27}O_{12})^-$. Positive-ion FAB-MS: m/z 1533 $(M+Na)^+$.

Goyasaponin III (**11**): A white powder, $[\alpha]_D^{24}$ −1.9° (c=0.5, pyridine). High-resolution positive-ion FAB-MS: Calcd for $C_{49}H_{76}O_{19}Na$ $(M+Na)^+$: 991.4879. Found: 991.4882. IR (KBr): 3422, 1734, 1715, 1076, 1048 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.80, 0.95, 0.97, 1.00, 1.03, 1.14, 1.30 (3H each, all s, 25, 29, 26, 30, 24, 23, 27-H_3), 2.45 (3H, s, Ac), 3.18 (1H, dd, J=4.3, 11.9 Hz, 3-H), 3.27 (1H, dd, J=4.6, 14.0 Hz, 18-H), 4.90 (1H, d, J=7.3 Hz, GlcA-1-H), 4.97 (1H, d, J=7.3 Hz, Xyl-1-H), 5.20 (1H, d, J=7.6 Hz, Glc-1-H), 5.44 (1H, br s, 12-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δc: given in Table 2. Negative-ion FAB-MS: m/z 967 $(M-H)^-$, 925 $(M-C_2H_3O)^-$, 835 $(M-C_6H_{11}O_4)^-$, 805 $(M-C_6H_{11}O_5)^-$, 455 $(M-C_{19}H_{29}O_{16})^-$. Positive-ion FAB-MS: m/z 991 $(M+Na)^+$.

Acid Hydrolysis of Goyaglycosides (1—8), Goyasaponins (9—11), 24, and 25 A solution of **1**—**11**, **24** and **25** (3 mg each) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Amber-

lite IRA-400 (OH^- form) and the resin was removed by filtration. After removal of the solvent from the filtrate *in vacuo*, the residue was transferred to a Sep-Pak C18 cartridge with H_2O and MeOH. The H_2O eluate was concentrated and the residue was treated with L-cysteine methyl ester hydrochloride (4 mg) in pyridine (0.5 ml) at 60 °C for 1 h. After reaction, the solution was treated with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (0.2 ml) at 60 °C for 1 h. The supernatant was then subjected to GLC analysis to identify the derivatives of D-glucose (i) from **1**, **3**, **5**, **6**, **7**, **8**, **11**, **25**; D-allose (ii) from **2**, **4**, **5**, **6**, **7**; D-glucuronic acid (iii) from **9**, **10**, **11**, **24**, **25**; D-galactose (iv) from **9**, **10**, **24**; D-fucose (v) from **9**, **10**; L-rhamnose (vi) from **9**, **10**; D-xylose (vii) from **9**, **10**, **11**, **25**; GLC conditions: column : Supeluco STB™-1, 30 m×0.25 mm (i.d.) capillary column, column temperature: 230 °C, He flow rate: 15 ml/min, t_R: i: 24.2 min, ii: 27.0 min, i: 24.4 min, ii: 25.5 min, iii: 17.2 min, iv: 15.4 min, v: 13.8 min.

Enzymatic Hydrolysis of Goyaglycosides-a (1) and -c (3) A solution of **1** (9.0 mg) or **3** (9.9 mg) in 0.1 M acetate buffer (pH 4.0, 3 ml) was treated with naringinase (Sigma Chemical Co., 30 mg) and was stirred at 40 °C for 10 days. After addition of EtOH to the reaction mixture, the solvent was removed *in vacuo*. The crude product was purified by reversed-phase (2 g, H_2O→MeOH) and normal-phase silica gel column chromatography [1 g, *n*-hexane–AcOEt (3 : 1, v/v)] to give 19(*R*)-methoxy-5β,19-epoxycucurbita-6,23-diene-3β,25-diol (**17**, 1.6 mg, 23.7%) or 19(*R*),25-dimethoxy-5β,19-epoxycucurbita-6,23-diene-3β-ol (**18**, 2.3 mg, 30.8%), which were identified by comparison with reported values[6] (^{1}H-NMR, IR, $[\alpha]_D$).

Enzymatic Hydrolysis of Goyaglycoside-e (5) A solution of **5** (9.9 mg) in 0.1 M acetate buffer (pH 4.0, 3 ml) was treated with naringinase (Sigma Chemical Co., 30 mg) and was stirred at 40 °C for 24 h. After addition of EtOH to the reaction mixture, the solvent was removed *in vacuo*. The crude product was purified by reversed- (2 g, H_2O→MeOH) and normal-phase silica gel column chromatography [1 g, $CHCl_3$–MeOH–H_2O (30 : 3 : 1, lower layer, v/v)] to give momordicoside F_2 (**19**, 3.0 mg, 38.1%), which was identified by a comparison with reported values[3c] (^{1}H-NMR, IR, $[\alpha]_D$).

Enzymatic Hydrolysis of Goyaglycoside-g (7) A solution of **7** (0.9 mg) in 0.1 M acetate buffer (pH 5.0, 2 ml) was treated with cellulase (Sigma Chemical Co., 10 mg) and was stirred at 37 °C for 10 days. After addition of EtOH to the reaction mixture, the solvent was removed *in vacuo*. The crude product was purified by reversed-phase (2 g, H_2O→MeOH) and normal-phase silica gel column chromatography [1 g, $CHCl_3$–MeOH–H_2O (7 : 3 : 1, lower layer, v/v)] to give goyaglycoside-b (**2**, 0.4 mg, 55.5%), which was identified by comparison with an authentic natural sample (^{1}H-NMR, IR, $[\alpha]_D$).

Enzymatic Hydrolysis of Goyaglycoside-h (8) A solution of **8** (9.9 mg) in 0.1 M acetate buffer (pH 4.0, 3 ml) was treated with naringinase (Sigma Chemical Co., 30 mg) and was stirred at 40 °C for 24 h. After addition of EtOH to the reaction mixture, the solvent was removed *in vacuo*. The crude product was purified by reversed-phase (2 g, H_2O→MeOH) and normal-phase silica gel column chromatography [1 g, *n*-hexane–AcOEt (2 : 1, v/v)] to give goyagenin A (**20**, 1.5 mg, 25%).

Goyagenin A (**20**): A white powder, $[\alpha]_D^{29}$ −0.4° (c=0.08, $CHCl_3$). High-resolution positive-ion FAB-MS: Calcd for $C_{30}H_{50}O_5Na$ $(M+Na)^+$: 513.3556. Found: 513.3593. IR (film): 3567, 1717 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.83, 0.90, 0.93, 1.02, 1.14, 1.44, 1.47, (3H each, all s, 30, 19, 18, 28, 29, 27, 26-H_3), 1.04 (3H, d, J=6.7 Hz, 21-H_3), 3.48 (1H, dd-like, 3-H), 4.74 (1H, dd-like, 22-H), 5.59 (1H, dd-like, 6-H), 5.60 (1H, d-like, 23-H). ^{13}C-NMR (125 MHz, $CDCl_3$) δc: given in Table 1. Positive-ion FAB-MS: m/z 513 $(M+Na)^+$.

Reduction of Goyagenin A (20) with $NaBH_4$ A solution of **20** (1.1 mg) in dry MeOH (0.5 ml) was treated with $NaBH_4$ (2 mg) and was stirred at 0 °C for 2 h. After addition of acetone to the reaction mixture, the mixture was neutralized with Dowex HCR W2 (H^+ form) and the resin was removed by filtration. After removal of the solvent from the filtrate *in vacuo*, the residue was separated by HPLC [MeOH–H_2O (75 : 25, v/v)] to give 3β,22(*S*),23(*R*),24(*R*),25-pentahydroxycucurbit-5-ene (**21**, 0.5 mg, 45.5%) and its 24-diastereomar (**22**, 0.3 mg, 27.3%), and **21** was identified by comparison with reported values[3a] (^{1}H-NMR, IR, $[\alpha]_D$).

22: ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.83, 0.89, 0.92, 1.03, 1.31, 1.33 (3H each, all s, *tert*-CH_3×7), 1.28 (3H, d-like, 21-H_3), 3.78 (1H, br s, 3-H), 3.97, 4.28, 4.44 (1H each, all m, 22, 23, 24-H), 5.61 (1H, dd-like, 6-H).

Enzymatic Hydrolysis of Momordicoside A (12) A solution of **12** (10.1 mg) in 0.1 M acetate buffer (pH 4.0, 3 ml) was treated with naringinase (Sigma Chemical Co., 30 mg) and was stirred at 40 °C for 24 h. After addition of EtOH to the reaction mixture, the solvent was removed *in vacuo*. The crude product was purified by reversed-phase (2 g, H_2O→MeOH) and normal-phase silica gel column chromatography [1 g, $CHCl_3$–MeOH–H_2O (30 : 3 : 1, lower layer, v/v)] to give 3β,22(*S*),23(*R*),24(*R*),25-pentahydroxycucurbit-5-ene (**21**, 2.3 mg, 37.7%), and was identified by comparison with reported values[3a] (^{1}H-NMR, IR, $[\alpha]_D$).

Methanolysis of Goyasaponins I (9) and II (10) A solution of goyasaponins (**9**: 10.1 mg; **10**: 12.6 mg) in 9% HCl–dry MeOH (2 ml) was stirred under reflux for 30 min. After reaction, the reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and the resin was removed by filtration. After removal of the solvent from the filtrate *in vacuo*, the residue was separated by reversed-phase silica gel column chromatography (H_2O→MeOH) to give gypsogenin (**23**, 0.5 mg 16% from **9**; 0.7 mg, 17.9% from **10**), which was identified by comparison with reported values[9] (^{1}H-NMR, IR, $[\alpha]_D$).

Alkaline Hydrolysis of Goyasaponins I (9) and II (10) A solution of goyasaponins (**9**: 12.3 mg; **10**: 9.7 mg) in 5% aq. NaOH (3 ml) was stirred under reflux for 6 h. After cooling, the reaction mixture was neutralized with Dowex HCR W2 (H^+ form) and the resin was removed by filtration. After removal of the solvent from the filtrate *in vacuo*, the residue was separated by reversed-phase (H_2O→MeOH) and normal-phase silica gel column chromatography [$CHCl_3$–MeOH–H_2O (65 : 35 : 10, lower layer, v/v)] to give goyaprosaponin (**24**, 4.3 mg, 59.3% from **1**; 3.2 mg, 61.5% from **2**).

Goyaprosaponin (**24**): A white powder, $[\alpha]_D^{27}$ +34.8° (c=0.1, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{42}H_{64}O_{15}Na$ $(M+Na)^+$: 831.4143. Found: 831.4139. IR (KBr): 3434, 1719, 1082, 1051 cm^{-1}. ^{1}H-NMR (270 MHz, pyridine-d_5) δ: 0.79, 0.93, 0.95, 1.01, 1.27, 1.40 (3H each, all s, 25, 26, 29, 30, 27, 24-H_3), 3.26 (1H, dd-like, 18-H), 4.06 (1H, dd-like, 3-H), 4.90 (1H, d, J=7.3 Hz, GlcA-1-H), 5.18 (1H, d, J=7.6 Hz, Gal-1-H), 5.43 (1H, br s, 12-H), 9.92 (1H, s, 23-H). ^{13}C-NMR (68 MHz, pyridine-d_5) δc: given in Table 2. Negative-ion FAB-MS: m/z 807 $(M-H)^-$, 645 $(M-C_6H_{11}O_5)^-$, 469 $(M-C_{12}H_{19}O_{11})^-$. Positive-ion FAB-MS: m/z 831 $(M+Na)^+$.

Alkaline Hydrolysis of Goyasaponin III (11) A solution of **11** (10 mg) in 1% NaOMe–MeOH (1 ml) was stirred at room temperature (25 °C). After cooling, the reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and the residue was removed by filtration. After removal of the solvent from the filtrate *in vacuo*, the residue was separated by normal-phase silica gel column chromatography [1 g, $CHCl_3$–MeOH–H_2O (65 : 35 : 10, lower layer, v/v)] to give desacyl-goyasaponin III (**25**, 8.7 mg, 90.6%).

Desacyl-goyasaponin III (**25**): A white powder, $[\alpha]_D^{27}$ −0.8° (c=0.2, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{47}H_{74}O_{18}Na$ $(M+Na)^+$: 949.4773. Found: 949.4765. IR (KBr): 3408, 1709, 1076, 1048 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.82, 0.96, 0.98, 1.01, 1.04, 1.25, 1.32 (3H each, all s, 25, 29, 26, 30, 24, 23, 27-H_3), 3.25 (1H, dd, J=4.0, 11.6 Hz, 3-H), 3.29 (1H, dd, J=3.7, 13.7 Hz, 18-H), 4.94 (1H, d, J=7.6 Hz, Xyl-1-H), 5.15 (1H, d, J=7.6 Hz, Glc-1-H), 5.27 (1H, d, J=7.3 Hz, GlcA-1-H), 5.45 (1H, br s, 12-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δc: given in Table 2. Negative-ion FAB-MS: m/z 925 $(M-H)^-$, 793 $(M-C_5H_9O_4)^-$, 763 $(M-C_6H_{11}O_5)^-$, 455 $(M-C_{17}H_{27}O_{15})^-$. Positive-ion FAB-MS: m/z 949 $(M+Na)^+$.

References and Notes

1) Part XX: Matsuda H., Murakami T., Nishida N., Kageura T., Yoshikawa M., *Chem. Pharm. Bull*., **48**, 1429—1435 (2000).
2) Karunanayake E. H., Welihinda J., Sirimanne S. R., Sinnadarai G., *J. Ethnopharmacol*., **11**, 223—231 (1984).
3) *a*) Okabe H., Miyahara Y., Yamauchi T., Miyahara K., Kawasaki T., *Chem. Pharm. Bull*., **28**, 2753—2762 (1980); *b*) Miyahara Y., Okabe H., Yamauchi T., *ibid*., **29**, 1561—1566 (1981); *c*) Okabe H., Miyahara Y., Yamauchi T., *ibid*., **30**, 3977—3986 (1982); *d*) *Idem*, *ibid*., **30**, 4334—4340 (1982); *e*) Yasuda M., Iwamoto M., Okabe H., Yamauchi T., *ibid*., **32**, 2044—2047 (1984); *f*) Fatope M. O., Takeda Y., Yamashita H., Okabe H., Yamauchi T., *J. Nat. Prod*., **53**, 1491—1497 (1990).
4) *a*) Matsuda H., Li Y., Murakami T., Yamahara J., Yoshikawa M., *Eur. J. Pharmacol*., **368**, 237—243 (1999); *b*) Matsuda H., Li Y., Yoshikawa M., *Life Sci*., **65**, PL27—32 (1999); *c*) Matsuda H., Li Y., Murakami T., Yamahara J., Yoshikawa M., *Bioorg. Med. Chem*., **7**, 323—327 (1999); *d*) Matsuda H., Li Y., Yamahara J., Yoshikawa M., *J. Pharmacol. Exp. Ther*., **289**, 729—734 (1999); *e*) Matsuda H., Li Y., Yoshikawa M., *Eur. J. Pharmacol*., **373**, 63—70 (1999); *f*) Matsuda H., Shimoda H., Yoshikawa M., *Bioorg. Med. Chem*., **7**, 1445—1450 (1999); *g*) Matsuda H., Li Y., Yoshikawa M., *ibid*., **7**, 1737—1741 (1999); *h*) Matsuda H., Shimoda H., Yamahara J., Yoshikawa M., *Biol. Pharm. Bull*., **22**, 870—872 (1999); *i*) Matsuda H., Murakami T., Yashiro K., Yamahara J., Yoshikawa M., *Chem. Pharm. Bull*., **47**,

1725—1729 (1999); *j*) Matsuda H., Shimoda H., Uemura T., Yoshikawa M., *Bioorg. Med. Chem. Lett*., **9**, 2647—2652 (1999); *k*) Murakami T., Matsuda H., Inadzuki M., Hirano K., Yoshikawa M., *Chem. Pharm. Bull*., **47**, 1717—1724 (1999); *l*) Murakami T., Nakamura J., Matsuda H., Yoshikawa M., *ibid*., **47**, 1759—1764 (1999); *m*) Matsuda H., Li Y., Yoshikawa M., *Life Sci*., **66**, PL41—46 (2000); *n*) Li Y., Wen S., Yamahara J., Yoshikawa M., *Eur. J. Pharmacol*., **387**, 339—344 (2000).

5) *a*) Hara S., Okabe H., Mihashi K., *Chem. Pharm. Bull*., **34**, 1843—1845 (1986); *b*) Zhang D., Miyase T., Kuroyanagi M., Umehara K., Ueno A., *ibid*., **43**, 966—970 (1995).

6) Mulholland D. A., Sewram V., Osborne R., Pegel K. H., Connolly J. D., *Phytochemistry*, **45**, 391—395 (1997).

7) The ^{1}H- and ^{13}C-NMR spectra of **1**—**11**, **20**, **24** and **25** were assigned with the aid of homo- and hetero- correlation spectroscopy (^{1}H–^{1}H, ^{1}H–^{13}C COSY), distortionless enhancement by polarization transfer (DEPT), nuclear Overhauser and exchange spectroscopy (NOESY) and heteonuclear multiple bond correlation (HMBC) experiments.

8) Goyaglycosides-a (**1**), -b (**2**), -c (**3**), -d (**4**), and -g (**7**) having one or two methoxyl groups in their structures were believed to be formed during the extraction or isolation procedure. The characterization of their genuine glycosides is an interesting subject for further investigation.

9) Matsuda H., Murakami T., Ikebata A., Yamahara J., Yoshikawa M., *Chem. Pharm. Bull*., **47**, 1744—1748 (1999).

10) Frechet D., Christ B., Sorbier B. M., Fischer H., Vuihorgne M., *Phytochemistry*, **30**, 927—931 (1991).