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Studies on the Constituents of *Momordica charantia* L. III.[1,2] Characterization of New Cucurbitacin Glycosides of the Immature Fruits. (1). Structures of Momordicosides G, F_1, F_2 and I

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Several non-bitter cucurbitacin glycosides were isolated together with two bitter cucurbitacin glycosides from the immature fruits of *Momordica charantia* L. (Cucurbitaceae), and four of the non-bitter glycosides, momordicosides G, F_1, F_2 and I, were characterized from chemical and spectral evidence as folows; G, 3-*O*-β-D-allopyranoside of 5,19-epoxy-25-methoxy-5β-cucurbita-6,23-dien-3β-ol; F_1, 3-*O*-β-D-glucopyranoside of 5,19-epoxy-25-methoxy-5β-cucurbita-6,23-dien-3β-ol; F_2, 3-*O*-β-D-allopyranoside of 5,19-epoxy-5β-cucurbita-6,23-diene-3β,25-diol; I, 3-*O*-β-D-glucopyranoside of 5,19-epoxy-5β-cucurbita-6,23-diene-3β,25-diol.

Keywords——*Momordica charantia*; Cucurbitaceae; tetracyclic triterpene glycoside; cucurbitacin; momordicosides G, F_1, F_2 and I; allopyranoside; 5,19-epoxy-25-methoxy-5β-cucurbita-6,23-dien-3β-ol; 5,19-epoxy-5β-cucurbita-6,23-diene-3β,25-diol

In the preceding papers[1,3] of this series, we have reported the isolation and characterization of five novel-type cucurbitacin glycosides from the seeds of *Momordica charantia* L. As a continuation of our studies on this plant, we examined the constituents of the immature fruits, which have been taken as a vegetable and are also claimed to have a use as a bitter stomachic in the southern part of Japan. We have isolated several non-bitter glycosides and two bitter glycosides named momordicosides K and L, and this paper deals with the structures of four of the non-bitter glycosides, momordicosides G, F_1, F_2 and I.

The immature fruits were chopped and homogenized in MeOH. The filtrate was concentrated under reduced pressure to 1/10 volume and successively extracted with $CHCl_3$ and BuOH. The $CHCl_3$ extract was separated into the less polar fraction (Fr. C-I) and the more polar fraction (Fr. C-II). The BuOH extract was also separated to the less polar (Fr. B-I) and the more polar (Fr. B-II) fractions, Fr. C-II and Fr. B-I showed almost the same thin-layer chromatography (TLC) patterns although the areas and color intensities of the corresponding

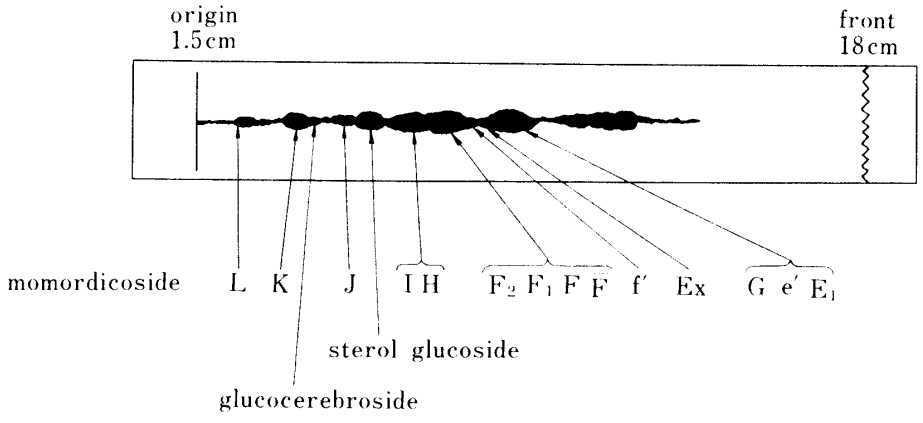


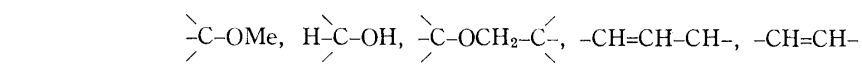
Fig. 1. TLC of Fr. C-II

Kieselgel 60 F_{254}: $CHCl_3$–MeOH–H_2O (7: 3: 1, bottom).

spots were different, and Fr. C-II contained a considerable quantity of non-glycosidic materials. A typical TLC pattern and designation are shown in Fig. 1.

Fr. C-II and Fr. B-I were repeatedly chromatographed on silica gel to separate them into thin-layer-chromatographically homogeneous materials; some of these were later proved to be mixtures of two or more compounds, and they were separated by column chromatography on silica gel after conversion into their acetates.

Momordicoside F_1 acetate, $C_{45}H_{68}O_{12}\cdot 1/2H_2O$, gave the free glycoside, $C_{37}H_{60}O_8\cdot 2.5H_2O$, on treatment with MeONa. Enzymatic hydrolysis of F_1 with crude hesperidinase gave F_1-aglycone, $C_{31}H_{50}O_3$. The ^1H nuclear magnetic resonance (^1H-NMR) spectrum of F_1-aglycone showed the presence of at least six quaternary methyl groups, a methoxyl group (δ 3.22), an oxymethine (δ 3.56) group, an oxymethylene group (δ 3.55, d, J=9 Hz; δ 3.67, d, J=9 Hz) on a quaternary carbon and two disubstituted double bonds (δ 5.60, 2H, br s; δ 5.61, H, dd, J=10, 4 Hz; δ 6.14, H, dd, J=10, 2 Hz), one of which is a *cis* double bond. The ^{13}C nuclear magnetic resonance (^{13}C-NMR) spectrum showed the signals of four C–C bonded quaternary carbons (δ 37.5, 45.4, 45.6 and 48.7), four olefinic carbons (δ 128.3 d, 131.2 d, 132.4 d and 137.6 d) each having one hydrogen, and five oxygen-bearing carbons (δ 52.1 q, 74.7 s, 76.2 d, 79.8 t and 87.5 s). Based on these spectral data, F_1-aglycone was considered to be a tetracyclic triterpene having functional groups shown below.



In the ^{13}C-NMR spectrum of F_1, four of five oxygenated carbon signals of the aglycone moiety were at almost the same positions as those of F_1-algycone, but the doublet signal of F_1-aglycone at δ 76.2 was shifted downfield by *ca.* 9 ppm in F_1, indicating that the sugar moiety in F_1 is linked to the secondary hydroxyl group.

When F_1 acetate was hydrogenated over PdO, two compounds (F_1–AcH-1 and -2) having no methoxyl group and one compound (F_1–AcH-3) with a methoxyl group were obtained.

F_1–AcH-1, $C_{44}H_{70}O_{11}$, was treated with MeONa to give a free glycoside (F_1H–1), $C_{36}H_{62}O_7\cdot 1/2H_2O$, which gave, on methanolysis, an aglycone (F_1H-1-ag), $C_{30}H_{52}O_2\cdot H_2O$. Its ^1H-NMR spectrum (in $CDCl_3$) showed signals of oxymethylene protons (δ 3.53, H, d, J=8 Hz, δ 3.76, H, d, J=8 Hz) and a hydroxymethine proton (δ 3.37, H, dt, J=9, 3 Hz) coupled with a hydroxyl proton (δ 3.98, H, d, J=9 Hz).[4] No methoxyl group or olefinic proton signals were observed. The ^{13}C-NMR spectrum exhibited three oxygenated carbon signals (δ 89.9 s, 78.5 t and 76.8 d). These spectral data indicated that F_1H-1-ag is a saturated secondary alcoholic compound which retains an ether ring. Elimination of the methoxyl group by catalyitc hydrogenation indicated that the methoxyl group exists on the carbon allylic to the double bond in the side chain,[5] and therefore the partial structure of the side chain is extended to –CH=CH–C(OMe)Me_2.

On treatment with MeONa, F_1–AcH-2, $C_{44}H_{70}O_{11}$, gave the corresponding free glycoside (F_1H-2), $C_{36}H_{62}O_7\cdot 1/2H_2O$. F_1H-2 was methanolyzed to give two aglycones, the less polar one (F_1H-2-ag-1) of which was identical with F_1H-1-ag. The more polar one (F_1H-2-ag), $C_{30}H_{52}O_2\cdot H_2O$, showed the ^1H-NMR signals of a hydroxymethylene group (δ 3.70, H, d, J=10 Hz; δ 3.93, H, d, J=10 Hz), a hydroxymethine proton (δ 3.75, H, br s) and an olefinic proton (δ 5.76, H, br d, J=6 Hz). The ^{13}C-NMR spectrum showed the signals of trisubstituted olefinic carbons (δ 120.4 d and 142.9 s), a secondary carbinyl carbon (δ 76.0 d) and a primary carbinyl carbon (δ 65.5 t). These data indicated that F_1H-2-ag is a diol having a primary hydroxyl group and a trisubstituted double bond which have been derived by reductive cleavage of the ether ring and migration of the disubstituted double bond. This also indicated that the ether oxygen of F_1-aglycone is attached to the carbon allylic to the disubstituted double bond.[6] The ^1H-NMR signals of a hydroxymethine and olefinic protons of F_1H-2-ag were similar to those of 3β-hydroxy-23,24,25,26,27-pentanorcucurbit-5-en-22-al[3] (δ 3.74, H_3, br s; δ 5.61, H_6, br d, J=5.5 Hz). The ^{13}C-NMR spectrum of F_1H-2-ag showed signals of a

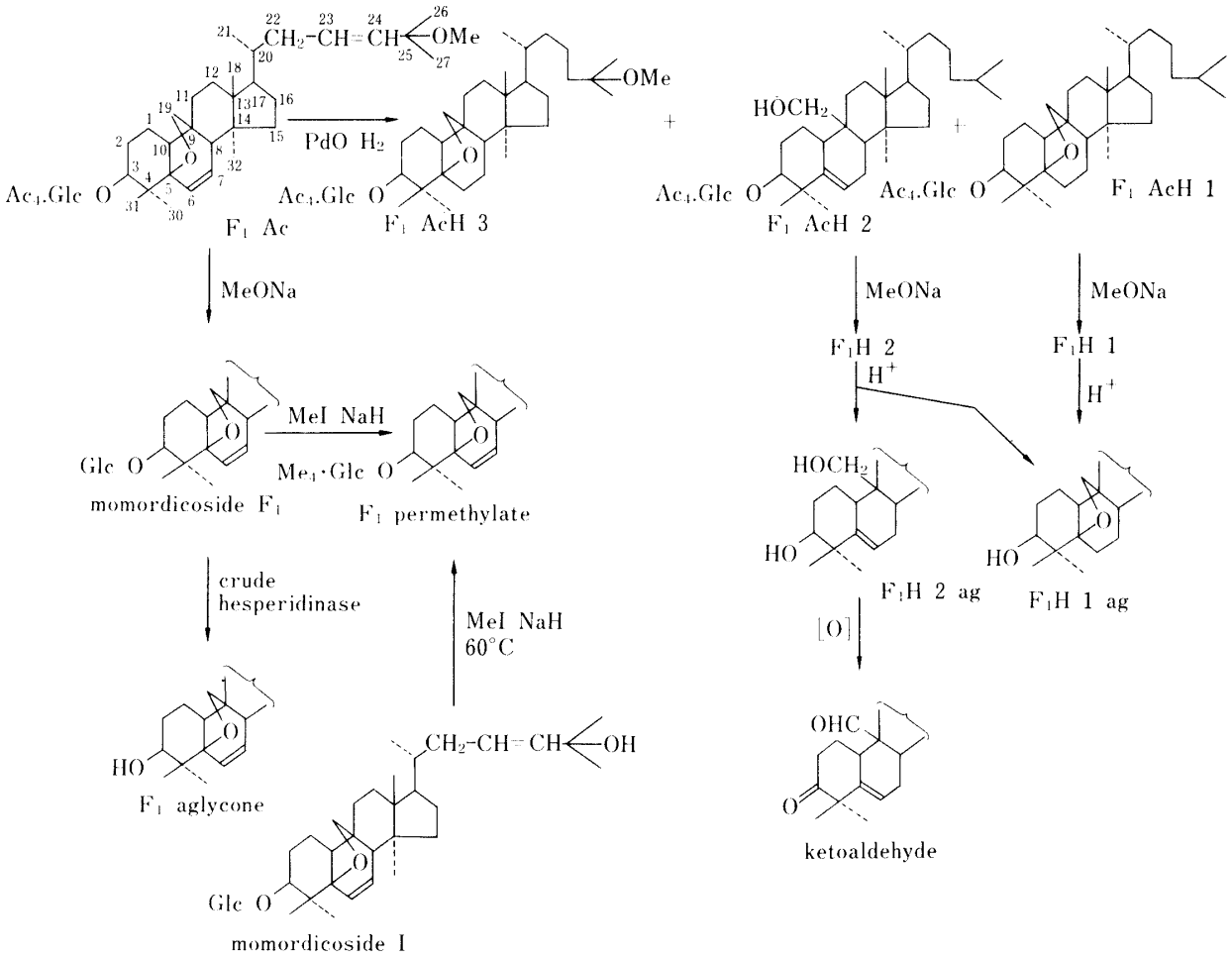


Chart 1

hydroxymethine carbon (δ 76.0 d), olefinic carbons (δ 120.4 d and 142.9 s) and C–C bonded quaternary carbons (δ 39.6, 41.7, 46.4 and 49.4). These signals were also similar to those of the above-mentioned aldehyde[3] (oxygenated C: δ 75.8d and 204.5 d. olefinic C: δ 119.0 d and 142.8 s. C–C bonded quaternary C: δ 34.9, 41.5, 46.9 and 48.9) except for the chemical shift of one quaternary carbon (δ 39.6) which might have a hydroxymethylene group.[7]

The similarity of the spectral data suggested that F_1H-2-ag is cucurbit-5-ene-3β,19-diol.

When F_1H-2-ag was oxidized with pyridinium chlorochromate in dichloromethane ,a ketoaldehyde was obtained, and it showed a negative circular dichroism (CD) spectrum ($[\theta]_{280}$ $-3400°$ (dioxane)), clearly indicating that the ketoaldehyde has a cucurbit-5-en-3-one structure,[8] and therefore, F_1H-1-ag and F_1-aglycone are 5,19-epoxy-5β-cucurbitan-3β-ol and 5,19-epoxy-25-methoxy-5β-cucurbita-6,23-dien-3β-ol, respectively.

The ^{1}H-NMR spectrum of F_1–AcH-3 showed signals of a methoxyl (δ 3.18), oxymethylene protons (δ 3.48, H, d, J=8 Hz; δ 3.86, H, d, J=8 Hz), and a hydroxymethine proton (δ 3.51, H, br s). The ^{13}C-NMR spectrum showed five oxygenated carbon signals due to the aglycone moiety, and no olefinic carbon signal was observed. From these spectra data, F_1–AcH-3 was concluded to be the acetylated glycoside of 5,19-epoxy-25-methoxy-5β-cucurbitan-3β-ol.

When F_1 was methanolyzed, methyl α-D-glucopyranoside was obtained (checked by TLC). The ^{1}H-NMR spectrum of F_1 permethylate showed the anomeric proton signal at δ 4.24 as a doublet (J=7 Hz). The molecular rotation difference between F_1 and F_1-aglycone was $-276°$. Accordingly, F_1 is a 3-*O*-β-D-glucopyranoside of 5,19-epoxy-25-methoxy-5β-cucurbita-6,23-dien-3β-ol.

Momordicoside G was isolated as an acetate, $C_{45}H_{68}O_{12}\cdot H_2O$, treatment of which with MeONa regenerated the free glycoside, $C_{37}H_{60}O_8\cdot 2H_2O$. The ^{1}H-NMR and ^{13}C-NMR spectra of G and its acetate were quite similar to those of F_1 and its acetate, respectively, except for the signals due to the sugar moiety, suggesting that G has the same aglycone as F_1. G permethylate was hydrogenated over PdO to afford two products. Methanolysis of the less polar one (GMH-1), $C_{40}H_{70}O_7$, gave F_1H-1-ag and a methylated sugar.

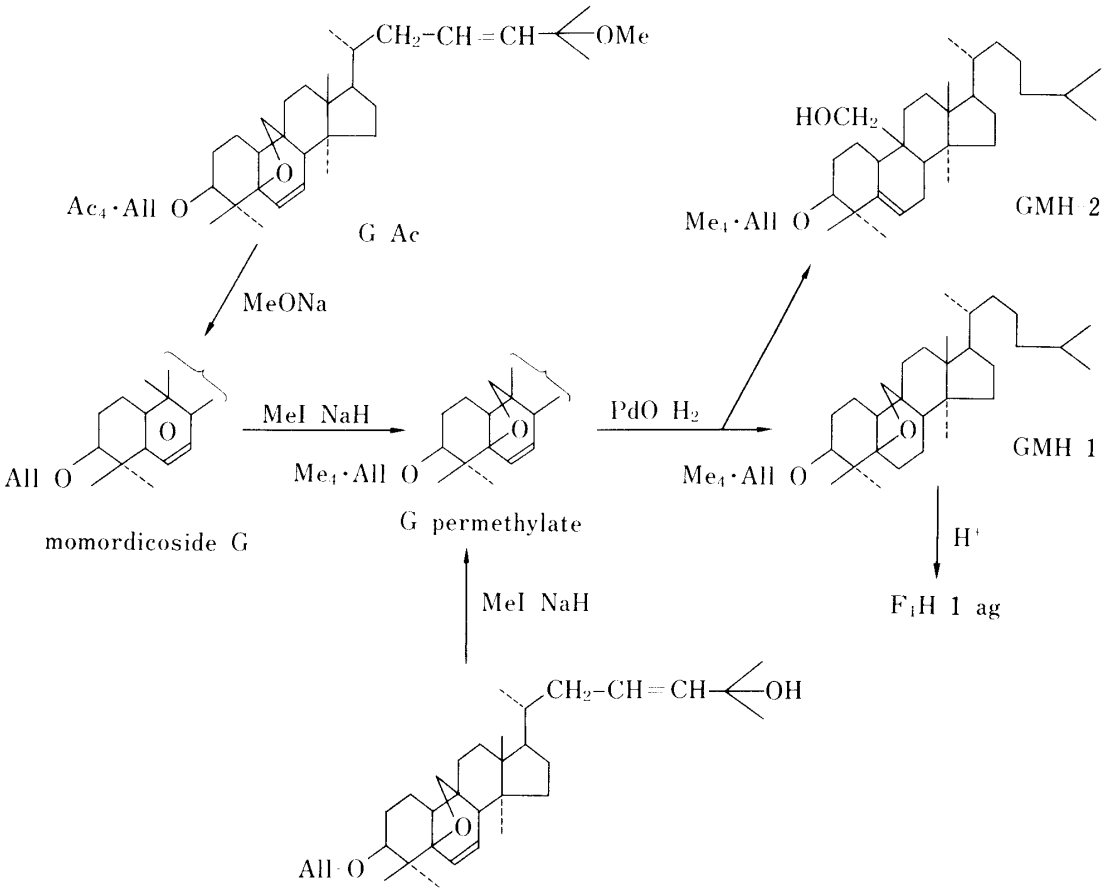


Chart 2

The methylated sugar was obtained as an oil ($[\alpha]_D$ −14.7°). The optical rotation and ^{1}H-NMR signals of the methylated sugar (H_1: δ 4.60, d, J=8 Hz. H_2: δ 2.99, dd, J=8, 3 Hz. H_3: δ 4.00, t, J=3, 2 Hz. H_4: δ 3.22, dd, J=2, 12 Hz. H_5: δ 3.80, H, m) suggested it to be methyl 2,3,4,6-tetra-*O*-methyl β-D-allopyranoside.[10] The ^{1}H-NMR spectrum of the methylated sugar was superimposable on that of an authentic sample.

Another hydrogenation product (GMH-2) is a primary alcohol having a trisubstituted double bond; its aglycone seems to be the same as F_1H-2-ag, because the ^{13}C-NMR spectrum of GMH-2 was almost the same as that of F_1–AcH-2 except for the signals due to the sugar moiety.

From these results, momoridicoside G was concluded to be a 3-*O*-β-D-allopyranoside of 5,19-epoxy-25-methoxy-5β-cucurbita-6,23-dien-3β-ol. The mode of the sugar linkage was determined from the J-value (8 Hz) of the anomeric proton signal of G permethylate.

Momordicoside F_2, $C_{36}H_{58}O_8\cdot H_2O$, was also isolated as a tetra-*O*-acetate, $C_{44}H_{66}O_{12}$. The *IR* spectrum of the acetate showed the absorption of a hydroxyl group, suggesting the presence of a hardly acetylable hydroxyl group in F_2. The ^{1}H-NMR spectra of F_2 and its

acetate showed no methoxyl signal. The signal of two equivalent methyl groups on an oxygenated carbon atom, which appeared at δ 1.30 in the case of G, was shifted downfield to δ 1.53, and other spectral features of F_2 and its acetate were similar to those of G and its acetate, respectively, suggesting F_2 to be the C_{25}–OH derivative of G. The ^{13}C-NMR spectra of F_2 and its acetate were consistent with the proposed structure. When F_2 was methylated, a penta-*O*-methylate was formed and its IR spectrum was superimposable on that of G permethylate. From this, it follows that momordicoside F_2 is a 3-*O*-β-D-allopyranoside of 5,19-epoxy-5β-cucurbita-6,23-diene-3β,25-diol.

Momordicoside I, $C_{36}H_{58}O_8 \cdot H_2O$, was obtained by MeONa treatment of its acetate, $C_{44}H_{66}O_{12} \cdot 1/2H_2O$. Enzymatic hydrolysis of I with crude hesperidinase gave I-aglycone, $C_{30}H_{48}O_3$. The ^{1}H-NMR spectrum of I-aglycone suggested it to be the C_{25}–OH derivative of F_1-aglycone. The ^{13}C-NMR spectrum supported this structure. When I acetate was hydrogenated over PdO, two hydrogenation products (I–AcH-1 and -2) having no hydroxyl group were obtained. I–AcH-1 and -2 were identical with F_1–AcH-1 and -2, respectively. Methylation of I provided a product which was identical in all respects with F_1 permethylate. Thus, momordicoside I is a 3-*O*-β-D-glucopyranoside of 5,19-epoxy-5β-cucurbita-6,23-diene-3β,25-diol.

Momoricosides G, F_1, F_2 and I are the first cucurbitacins having the 5β-cucurbitane nucleus to be found in nature, and G and F_2 are the first triterpenoid glycosides having D-allose as a component sugar.

Experimental[11]

Extraction and Isolation of Momordicosides——*Momordica charantia* L. was cultivated in the herbal garden of this university in 1978. The immature fruits (*ca.* 70 kg) were harvested during the period from July to September, and the harvested fruits were chopped and soaked in MeOH (2 l/kg) in tin cans until the end of the harvesting season. The soaked fruits were homogenized and filtered. The filtrate (*ca.* 300 l) was concentrated under reduced pressure at 50°C to 30 l (turbid aqueous solution containing a resinous material stuck on the wall of the container). The concentrated aqueous solution and the resinous material were first extracted with $CHCl_3$ (45 l), and the $CHCl_3$ solution was concentrated under reduced pressure to give a dark resinous material (164 g). The aqueous solution after extraction with $CHCl_3$ was then extracted with BuOH (30 l), and the BuOH solution was concentrated to give a dark resin (153 g). The $CHCl_3$ extract was dissolved in hot MeOH (2 l) and treated with active charcoal (25 g). After refluxing of the solution for 30 min, the charcoal powder was filtered off and washed with MeOH (1 l). The MeOH solution was concentrated under reduced pressure to give a brown resin (Fr. C) (142 g). Fr. C was passed through a polystyrene resin (HP 20Ag, 50—100 mesh) column to separate it into the less polar (Fr. C-I) and the more polar (Fr. C-II) fractions. A typical run was as follows.

Fr. C (10 g) was dissolved in 70% MeOH (500 ml) and passed through the resin column (100 ml). The resin column was washed with MeOH (500 ml). The 70% MeOH and MeOH eluates were combined and concentrated to give Fr. C-II (8.6 g) as a brown resin. The resin column was then washed with AcOEt (300 ml). The AcOEt solution was concentrated to give Fr. C-I (1.8 g). Fr. C-I contained compounds less polar than momordicoside E_1, and this fraction was stored for further examination.

The BuOH extract was dissolved in hot EtOH (1.5 l). The solution was cooled to room temperature, and the precipitates were removed by centrifugation and then washed with EtOH. The supernatant and washings were combined and concentrated under reduced pressure to give Fr. B (a dark brown resinous material, *ca.* 100 g). Fr. B was separated into the more polar (Fr. B-II) and the less polar (Fr. B-I) fractions on an HP 20Ag column. A typical run was as follows.

Fr. B (10 g) was dissolved in 40% EtOH (500 ml) and applied to the column (100 ml). The column was washed with 70% EtOH (500 ml) and then EtOH (500 ml). All fractions were monitored by TLC. The eluate with 40% EtOH and the initial portion of the 70% EtOH eluate were combined and concentrated to give Fr. B-II (5 g). The remaining portion of the 70% EtOH eluate and the EtOH eluate were combined and concentrated to give Fr. B-I (5 g). Fr. B-II contained materials more polar than momordicoside L, and was stored for further examination.

Fr. C-II and Fr. B-I were combined and subjected to repeated column chromatography on silica gel using MeOH–$CHCl_3$ (5→15%) and AcOEt–MeOH–H_2O (50: 2: 0.5, 40: 2: 0.5) systems to yield thin-layer-chromatographically homogeneous fractions. The fractions less polar than momordicoside E_1 and the fractions more polar than momordicoside L were set aside for further examination. The sterol glucoside, barely soluble in MeOH and $CHCl_3$, was deposited as a white precipitate during the process. Glucocerebroside was deposited as white precipitates when the fraction containing momordicoside K was dissolved in MeOH

and stored in a refrigerator. The mother liquor, after removal of glucocerebroside, was concentrated and cooled in a refrigerator to give crude momordicoside K (1.2 g).

Other fractions could not be crystallized although they were thin-layer-chromatographically homogeneous. They were separately acetylated with Ac_2O–pyridine at room temperature and the acetates were chromatographed on silica gel (30—100 times the weight of materials) using acetone in benzene (5—10%). The approximate yields and physical and chemical data are as follows: momordicoside E_1 acetate, 3.78 g; e′ acetate, 52 mg; G acetate, 618 mg; Ex acetate, 63 mg; f′ acetate, 30 mg; $\bar{F}$ acetate, 360 mg; F acetate, 1.47 g; F_1 acetate, 2.17 g; F_2 acetate, 200 mg; H acetate, 370 mg; I acetate, 409 mg; J acetate, 40 mg; L acetate, 180 mg.

Momordicoside G Acetate: Colorless needles from MeOH. mp 195—199°C. $[\alpha]_D^{19°}$ −70.6° ($c=1.00$, $CHCl_3$). CD $[\theta]_{202}^{16°}$: −96600° ($c=5.8\times10^{-5}$ g/ml, MeOH). *Anal.* Calcd for $C_{45}H_{68}O_{12}\cdot H_2O$, C: 66.01, H, 8.56. Found: C, 65.59; H, 8.43. ^{1}H-NMR: 0.78, 0.93, 1.30, 1.33 (×2) (CH_3), 1.98, 2.08 (×2), 2.22 (OAc), 3.23 (3H, s, OCH_3), 3.52 (H, d, $J=8$ Hz, C_{19}–H), 3.56 (H, br s, C_3–H), 3.77 (H, d, $J=8$ Hz, C_{19}–H), 5.60 (2H ?, br s, C_{23}–H, C_{24}–H), 6.12 (H, t, $J=3$ Hz, C_3–H of allopyranosyl group), 6.21 (H, d, $J=9$ Hz, C_6–H). ^{13}C-NMR: quaternary C; 38.7, 45.2, 45.4, 48.8. Oxygenated C; sugar moiety; 62.9t, 67.4d, 69.3d, 69.7d, 70.5d 101.1d, aglycone moiety; 50.1q (OCH_3), 74.8s (C_{25}), 80.0t (C_{19}), 85.0s (C_5), 85.5d (C_3). Olefinic C; 128.4d, 129.8d, 134.3d, 137.5d. Acetyl carbonyl C; 169.2, 169.4, 170.5.

Momordicoside F_1 Acetate: Colorless needles from MeOH. mp 207—209°C. $[\alpha]_D^{20°}$: −75.6° ($c=1.00$, $CHCl_3$). CD $[\theta]_{203}^{16°}$: −80000° ($c=1\times10^{-4}$ g/ml, MeOH). *Anal.* Calcd for $C_{45}H_{68}O_{12}\cdot 1/2H_2O$: C, 66.74; H, 8.53. Found: C, 66.74; H, 8.39. ^{1}H-NMR: 0.76, 0.88, 1.28, 1.32 (×2) (CH_3), 1.98, 2.02, 2.08, 2.15 (OAc), 3.20 (3H, s, OCH_3), 3.50 (H, d, $J=8$ Hz, C_{19}–H), 3.54 (H, br s, C_3–H), 3.70 (H, d, $J=8$ Hz, C_{19}–H), 5.60 (2H ?, br s, C_{23}–H, C_{24}–H), 6.20 (H, br d, $J=10$ Hz, C_6–H). ^{13}C-NMR: quaternary C; 38.7, 45.3, 45.4, 48.8. Oxygenated C; sugar moiety; 62.5t, 69.5d, 72.0d, 72.1d, 73.3d, 102.8d. Aglycone moiety; 50.1q (OCH_3), 74.8s (C_{25}), 80.0t (C_{19}), 85.0s (C_5), 85.0d (C_3), olefinic C; 128.4d, 129.8d, 134.3d, 137.6d. Acetyl carbonyl C; 169.5, 169.7, 170.2, 170.4.

Momordicoside F_2 Acetate: Colorless needles from hexane–acetone. mp 221—223°C. $[\alpha]_D^{20°}$: −68.8° ($c=1.23$, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH). EI-MS *m/z*: 786.453 (M^+). Calcd for $C_{44}H_{66}O_{12}$: 786.452. ^{1}H-NMR: 0.75, 0.84, 0.92, 1.29, 1.53 (×2) (CH_3), 1.97, 2.06 (×2), 2.21 (OAc), 3.50 (H, d, $J=9$ Hz, C_{19}–H), 3.55 (H, br s, C_3–H), 3.70 (H, d, $J=9$ Hz, C_{19}–H), 5.92 (2H, br s, C_{23}–H, C_{24}–H), 6.12 (H, t, $J=3$ Hz, C_3–H of allopyranosyl group), 6.20 (H, br d, $J=10$ Hz, C_6–H). ^{13}C-NMR: quaternary C; 38.7, 45.2, 45.3, 48.8. Oxygenated C; sugar moiety; 62.9t, 67.4d, 69.3d, 69.8d, 70.5d, 101.1d. Aglycone moiety; 69.8s (C_{25}), 79.9t (C_{19}), 85.0s (C_5). Olefinic C; 124.1d, 129.9d, 134.2d, 141.6d. Acetyl carbonyl C; 169.5, 170.4, 170.6.

Momordicoside I Acetate: Colorless needles from hexane–acetone. mp 203—206°C. $[\alpha]_D^{20°}$ −79.2° ($c=1.20$, $CHCl_3$). CD $[\theta]_{202}^{16°}$: −87700° ($c=1.12\times10^{-4}$ g/ml, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH). *Anal.* Calcd for $C_{44}H_{66}O_{12}\cdot 1/2H_2O$: C, 66.42; H, 8.43. Found: C, 66.65; H, 8.64. ^{1}H-NMR: 0.78, 0.86, 0.91, 1.29, 1.54 (×2) (CH_3), 2.01, 2.06, 2.11, 2.18 (OAc), 3.55 (H, d, $J=10$ Hz, C_{19}–H), 3.60 (H, br s, C_3–H), 3.76 (H, d, $J=10$ Hz, C_{19}–H), 5.97 (2H, br s, C_{23}–H, C_{24}–H), 6.23 (H, br d, $J=10$ Hz, C_6–H). ^{13}C-NMR: quaternary C; 38.7, 45.2, 45.3, 48.8. Oxygenated C; sugar moiety; 62.4t, 69.4d, 72.0d, 73.3d 102.8d. Aglycone moiety: 69.7s (C_{25}), 80.0t (C_{19}), 85.0s (C_5), 85.0d (C_3). Olefinic C; 124.1d, 129.9d, 134.2d, 141.6d. Acetyl carbonyl C; 169.5, 169.8, 170.3, 170.4. The data of acetates and free momordicosides E_1, e′, Ex, f′, $\bar{F}$, F, H, J, K and L will be given in subsequent papers.

MeONa Treatment of Momordicoside Acetates——The acetate (100 mg) was dissolved in MeOH (3 ml). A 1 N MeONa solution (40 μl) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was acidified by adding AcOH (10 μl) then concentrated. The residue was passed through a silica gel column (20 g). Elution with MeOH in $CHCl_3$ (5%, 10%) yielded homogeneous products, which were crystallized.

Momordicoside G: Colorless needles from CH_3CN–H_2O. mp 183—187°C. $[\alpha]_D^{28°}$: −107.3° ($c=1.00$, MeOH). CD $[\theta]_{202}^{16°}$: −93200° ($c=0.61\times10^{-4}$ g/ml, MeOH). *Anal.* Calcd for $C_{37}H_{60}O_8\cdot 2H_2O$: C, 66.47; H, 9.58. Found: C, 66.08; H, 9.25. ^{1}H-NMR: 0.80, 0.90, 1.33 (×2), 1.47 (CH_3), 3.22 (3H, s, OCH_3), 3.60 (H, d, $J=8$ Hz, C_{19}–H), 3.64 (H, br s, C_3–H), 3.78 (H, d, $J=8$ Hz, C_{19}–H), 3.93 (H, dd, $J=8$, 3 Hz, C_2–H of allopyranosyl group), 4.69 (H, t, $J=3$ Hz, C_3–H of allopyranosyl group), 5.38 (H, d, $J=8$ Hz, C_1–H of allopyranosyl group), 5.60 (br s, C_{23}–H, C_{24}–H), 6.20 (H, dd, $J=10$, 2 Hz, C_6–H). ^{13}C-NMR: Table I.

Momordicoside F_1: Colorless needles from MeOH–H_2O (1: 1). mp 198—203°C. $[\alpha]_D^{28°}$: −111.0° ($c=1.10$, MeOH). CD: $[\theta]_{201}^{16°}$: −82800° ($c=0.58\times10^{-4}$ g/ml, MeOH). *Anal.* Calcd for $C_{37}H_{60}O_8\cdot 2.5H_2O$: C, 65.58; H, 9.60. Found: C, 65.77; H, 9.18. ^{1}H-NMR: 0.78, 0.88, 0.92, 1.32 (×2), 1.50 (CH_3), 3.22 (3H, s, OCH_3), 3.58 (d, $J=9$ Hz, C_{19}–H), 3.74 (d, $J=9$ Hz, C_{19}–H), 4.87 (d, $J=7$ Hz, C_1–H of glucopyranosyl group), 5.59 (br s, C_{23}–H, C_{24}–H), 6.20 (br d, $J=10$ Hz, C_6–H). ^{13}C-NMR: Table I.

Momordicoside F_2: Colorless platelets from acetone-H_2O. mp 155—158°C. $[\alpha]_D^{20°}$: −96.5° ($c=0.87$, $CHCl_3$–MeOH (1: 1)). *Anal.* Calcd for $C_{36}H_{58}O_8\cdot H_2O$: C, 67.92; H, 9.43. Found: C, 68.00; H, 9.53. ^{1}H-NMR: 0.77, 0.86, 0.90, 1.47, 1.54 (×2) (CH_3), 3.61 (d, $J=8$ Hz, C_{19}–H), 3.66 (br s, C_3–H), 3.79 (d, $J=8$ Hz, C_{19}–H), 3.93 (H, dd, $J=3$, 8 Hz, C_2–H of allopyranosyl group), 4.69 (H, t, $J=3$ Hz, C_3–H of allopyranosyl group), 5.39 (H, d, $J=8$ Hz, C_1–H of allopyranosyl group), 5.57 (H, dd, $J=4$, 10 Hz, C_7–H), 5.94 (2H, br s, C_{23}–H, C_{24}–H), 6.19 (H, br d, $J=10$ Hz, C_6–H). ^{13}C-NMR: Table I.

Table I. ^{13}C-NMR Chemical Shifts of Momordicosides

Momordicosides	Quat. C	Oxygenated C	Olefinic C
G	38.9, 45.1	(a) 52.1q, 74.7s, 79.9t, 84.9d, 85.7s	128.0d, 129.6d
	45.3, 48.7	(s) 63.1t, 69.0d, 72.3d, 72.8d, 75.8d	133.8d, 137.3d
F_1	39.0, 45.2	(a) 52.2q, 74.8s, 80.0t, 85.4d, 85.8s	128.3d, 129.9d
	45.4, 48.8	(s) 63.0t, 71.7d, 75.7d, 78.3d(x2?)	134.1d, 137.6d
		106.8d	
F_1-aglycone	37.5, 45.4	(a) 52.1q, 74.7s, 76.2d, 79.8t, 87.5s	128.3d, 131.2d
	45.6, 48.7		132.4d, 137.6d
F_2	39.0, 45.2	(a) 69.7s, 80.1t, 85.1d, 85.9s	124.1d, 129.9d
	45.4, 48.8	(s) 63.3t, 69.2d, 72.4d, 73.0d, 76.1d	134.1d, 141.7d
		103.8d	
I	39.0, 45.2	(a) 69.7s, 80.0t, 85.4d, 85.8s	124.1d, 129.9d
	45.3, 48.8	(s) 63.0t, 71.8d, 75.7d, 78.3d(x2?)	134.1d, 141.6d
		106.8d	
I-aglycone	37.6, 45.4	(a) 69.7s, 76.2d, 79.8t, 87.6s	124.1d, 131.3d
	45.6, 48.8		132.4d, 141.7d

(a): aglycone moiety, (s): sugar moiety.

Momordicoside I: White powder from 50% MeOH. mp 210—216°C. $[\alpha]_D^{28°}$: −110.2° (c=1.00, MeOH). CD $[\theta]_{201}^{16°}$: −120200° ($c=0.54\times10^{-4}$ g/ml, MeOH). *Anal.* Calcd for $C_{36}H_{58}O_8\cdot H_2O$: C, 67.89; H, 9.50. Found: C, 67.63; H, 9.28. ^{1}H-NMR: 0.76, 0.84, 0.92, 1.51, 1.53 (×2) (CH_3), 3.58 (d, J=8 Hz, C_{19}–H), 3.69 (br s, C_3–H), 3.74 (d, J=8 Hz, C_{19}–H), 4.89 (H, d, J=8 Hz, C_1–H of glucopyranosyl group), 5.54 (H, dd, J=10, 4 Hz, C_7–H), 5.92 (2H, br s, C_{23}–H, C_{24}–H), 6.19 (H, br d, J=10 Hz, C_6–H). ^{13}C-NMR: Table I.

Enzymatic Hydrolysis of F_1——F_1 (340 mg) was dissolved in 30% EtOH (10 ml), and crude hesperidinase (500 mg) was added to the solution. The mixture was shaken at 38°C for 2 d. The solvent was evaporated off under reduced pressure and the residue was extracted with EtOH (5 ml×2). The EtOH-soluble fraction was chromatographed on silica gel (70 g) using 2% MeOH in $CHCl_3$ to give crude F_1-aglycone (109 mg). Crystallization from hexane gave colorless leaflets. mp 139—140°C. $[\alpha]_D^{20°}$: −90.6° (c=1.95, $CHCl_3$). CD $[\theta]_{199}^{16°}$: −43500° ($c=0.4\times10^{-4}$ g/ml, MeOH). EI-MS m/z: 470.379 (M^+). Calcd for $C_{31}H_{50}O_3$: 470.376. FD-MS m/z: 470 (M^+), 455. ^{1}H-NMR: 0.80, 0.87, 0.90, 1.31 (×2) (CH_3), 3.22 (3H, s, OCH_3), 3.56 (br s, C_3–H), 3.55 (H, d, J=9 Hz, C_{19}–H), 3.67 (H, d, J=9 Hz, C_{19}–H), 5.60 (2H, br s, C_{23}–H, C_{24}–H), 5.61 (H, dd, J=10, 4 Hz, C_7–H), 6.14 (H, dd, J=10, 2 Hz, C_6–H). ^{13}C-NMR: quaternary C; 37.5, 45.4, 45.6, 48.7. Oxygenated C; 52.1q (OCH_3), 74.7s (C_{25}), 76.2d (C_3), 79.8t (C_{19}), 87.5s (C_5). Olefinic C; 128.3d, 131.2d, 132.4d, 137.6d.

Catalytic Hydrogenation of F_1 Acetate——F_1 acetate (1 g) was dissolved in EtOAc–EtOH (1: 2) (60 ml) and PdO (1 g) was added. The mixture was shaken in an H_2 atmosphere for 2 h. PdO was removed by filtration and the filtrate was concentrated to dryness. The TLC (Kieselgel, acetone–benzene (15: 85)) showed 3 spots (*Rf* 0.58, F_1–AcH-1; 0.50, F_1–AcH-3; 0.33, F_1–AcH-2). The reaction product was subjected to column chromatography on silica gel (80 g) using 5% acetone in benzene to give thin-layer-chromatographically homogeneous compounds.

F_1–AcH-1: 467 mg. Colorless needles from MeOH. mp 225°C. $[\alpha]_D^{20°}$: −12.0° (c=0.5, $CHCl_3$). *Anal.* Calcd for $C_{44}H_{70}O_{11}$: C, 68.22; H, 9.04. Found: C, 68.01; H, 9.07. ^{1}H-NMR: 0.79, 0.87, 0.93, 1.22 (CH_3), 2.00, 2.02, 2.07, 2.21 (OAc), 3.49 (H, d, J=8 Hz, C_{19}–H), 3.53 (H, br s, C_3–H), 3.87 (H, d, J=8 Hz, C_{19}–H), 4.97 (H, d, J=7 Hz, C_1–H of glucopyranosyl group). ^{13}C-NMR: quaternary C; 40.0, 46.2, 48.1, 50.1. Oxygenated C; sugar moiety; 62.5t, 69.5d, 72.0d, 73.3d, 102.7d. Aglycone moiety; 78.8t (C_{19}), 85.4d (C_3), 86.7s (C_5). Acetyl carbonyl C; 169.6, 169.8, 170.3, 170.5.

F_1H-1: F_1AcH-1 was treated with MeONa. mp 251—254°C (dec.). $[\alpha]_D^{20°}$: −0.9° (c=1.05, $CHCl_3$–MeOH (1: 1)). *Anal.* Calcd for $C_{36}H_{62}O_7\cdot1/2H_2O$: C, 70.24; H, 10.24. Found: C, 69.96; H, 10.16. ^{1}H-NMR: 0.78, 0.82, 0.88, 0.93, 1.42 (CH_3), 3.59 (d, J=8 Hz, C_{19}–H), 3.63 (br s, C_3–H), 3.91 (d, J=8 Hz, C_{19}–H), 4.93 (H, d, J=7 Hz, C_1–H of glucopyranosyl group). ^{13}C-NMR: quaternary C; 40.2, 46.1, 48.2, 50.0. Oxygenated C; sugar moiety; 63.0t, 71.8d, 76.1d, 78.0d, 78.4d, 105.8d. Aglycone moiety; 78.8t (C_{19}), 85.0d (C_3), 88.0s (C_5).

F_1–AcH-2: 255 mg. Colorless needles from MeOH. mp 226°C. $[\alpha]_D^{20°}$: +11.8° (c=1.00, $CHCl_3$). *Anal.* Calcd for $C_{44}H_{70}O_{11}$: C, 68.22; H, 9.04. Found: C, 67.92; H, 8.85. ^{1}H-NMR: 0.87, 0.93, 0.96, 1.11, 1.13, 1.24, 1.33 (CH_3), 1.96, 2.01, 2.07, 2.08 (OAc), 3.56 (br s, C_3–H), 3.64 (d, J=10 Hz, C_{19}–H), 3.86 (d, J=10 Hz, C_{19}–H), 4.92 (d, J=7 Hz, C_1–H of glucopyranosyl group). ^{13}C-NMR: quaternary C; 39.5, 41.2, 46.3, 49.3. Oxygenated C; sugar moiety; 62.4t, 69.3d, 72.0d, 72.2d, 73.3d, 102.2d. Aglycone moiety; 65.2t (C_{19}), 87.2d (C_3). Olefinic C; 120.2d, 142.0s. Acetyl carbonyl C; 169.3, 169.7, 170.2, 170.4.

F_1H-2: F_1–AcH-2 was similarly deacetylated with MeONa. White powder (MeOH), mp 235—237°C. $[\alpha]_D^{20°}$: −0.4° (c=1.00, $CHCl_3$–MeOH (1: 1)). *Anal.* Calcd for $C_{36}H_{62}O_7\cdot1/2H_2O$: C, 70.24; H, 10.24. Found:

C, 70.45; H, 10.43. ^{1}H-NMR: 0.86, 0.92, 0.93, 1.13, 1.54 (CH_3), 4.87 (H, d, J=8 Hz, C_1–H of glucopyranosyl group), 5.58 (H, br d, J=5 Hz, C_6–H). ^{13}C-NMR: quaternary C: 39.5, 41.8, 46.3, 49.3. Oxygenated C: sugar moiety; 63.0t, 71.7d, 75.3d, 78.1d, 78.6d, 107.5d. Aglycone moiety, 65.6t (C_{19}), 87.8d (C_3). Olefinic C; 119.9d, 142.7s.

F_1–AcH-3: 89 mg. Colorless needles from MeOH. mp 198—199°C. EI-MS m/z (relative intensity, %): 804 (0.6) (M^+), 772 (1.5) (M^+−MeOH), 523 (59.4), 331 (68.3), 271 (40.6), 175 (95.0), 169 (100). ^{1}H-NMR: 0.78, 0.92, 1.16, 1.21, 1.45 (CH_3), 1.99, 2.01, 2.06, 2.20 (OAc), 3.18 (3H, s, OCH_3), 3.48 (d, J=8 Hz, C_{19}–H), 3.51 (br s, C_3–H), 3.86 (d, J=8 Hz, C_{19}–H), 4.94 (d, J=7 Hz, C_1–H of glucopyranosyl group). ^{13}C-NMR: quaternary C; 39.9, 46.1, 48.1, 50.0. Oxygenated C; sugar moiety; 62.4t, 69.4d, 71.9d, 72.0d, 73.2d, 102.6d. Aglycone moiety; 48.9q (OCH_3), 74.4s (C_{25}), 78.7t (C_{19}), 85.3d (C_3), 86.6s (C_5). Acetyl carbonyl C; 169.5, 169.7, 170.2, 170.4.

Methanolysis of F_1H-1——F_1H-1 (140 mg) was dissolved in 1 N HCl (MeOH) (2 ml) and the solution was stirred at room temperature for 2 h. The reaction mixture was neutralized with Ag_2CO_3 and filtered. The filtrate was bubbled through with H_2S and concentrated. The residue was treated with benzene and the benzene-soluble material (56 mg) was chromatographed on silica gel (30 g) with 2% acetone in benzene to give F_1H-1-ag (40 mg). Crystallization from MeOH gave long colorless needles. mp 133—134°C. $[\alpha]_D^{21°}$ +31.4° (c=1.40, $CHCl_3$). *Anal.* Calcd for $C_{30}H_{52}O_2 \cdot H_2O$: C, 80.72; H, 12.11. Found: C, 80.91; H, 11.74. ^{1}H-NMR: 0.80, 0.84, 0.88, 0.93, 1.32 (CH_3), 3.45—3.60 (m, C_3–H), 3.57 (d, J=8 Hz, C_{19}–H), 3.78 (H, d, J=8 Hz, C_{19}–H), 4.25 (H, d, J=9 Hz, C_3–OH). ^{1}H-NMR ($CDCl_3$): 0.81, 0.86, 0.89, 0.96, 1.13 (CH_3), 3.37 (H, dt, J=9, 3 Hz, C_3–H), 3.53 (H, d, J=8 Hz, C_{19}–H), 3.76 (H, d, J=8 Hz, C_{19}–H), 3.98 (H, d, J=9 Hz, C_3–OH). ^{13}C-NMR: quaternary C; 38.6, 46.1, 48.5, 49.9. Oxygenated C; 76.9d (C_3), 78.5t (C_{19}), 89.9s (C_5).

Methanolysis of F_1H-2——F_1H-2 (98 mg) was dissolved in 1 N HCl (MeOH) (4 ml) and the solution was refluxed for 1 h. The reaction mixture was worked up as described above. The product showed two spots on TLC (Kieselgel, 15% acetone in benzene: Rf, 0.57 (F_1H-2-ag-1); 0.11 (F_1H-2-ag)). Silica gel column chromatography (10 g, $CHCl_3$) of the product gave F_1H-2-ag-1 (18 mg) and F_1H-2-ag (44 mg).

F_1H-2-ag-1: Colorless needles from MeOH. mp 132—134°C. IR and ^{1}H-NMR spectra were superimposable on those of F_1H-1-ag.

F_1H-2-ag: Colorless platelets from MeOH–H_2O. mp 169—170°C. $[\alpha]_D^{31°}$: +40.5° (c=1.55, $CHCl_3$–MeOH (1: 1)). *Anal.* Calcd for $C_{30}H_{52}O_2 \cdot H_2O$: C, 80.65; H, 11.70. Found: C, 80.72; H, 12.11. ^{1}H-NMR: 0.86, 0.93, 1.00, 1.16, 1.18, 1.41 (CH_3), 3.70 (H, d, J=10 Hz, C_{19}–H), 3.75 (H, br s, C_3–H), 3.93 (H, d, J=10 Hz, C_{19}–H), 5.76 (H, br d, J=6 Hz, C_6–H). ^{13}C-NMR: quaternary C; 39.6, 41.7, 46.4, 49.4. Oxygenated C; 65.5t (C_{19}), 76.0d (C_3). Olefinic C; 120.4d (C_6), 142.9s (C_5).

Oxidation of F_1H-2-ag——F_1H-2-ag (37 mg) and pyridinium chlorochromate (70 mg) were added to CH_2Cl_2 (1.5 ml) and the mixture was stirred at room temperature for 3 h, then passed through a silica gel column (5 g). The column was washed with CH_2Cl_2 (50 ml). The eluate was concentrated *in vacuo*, and the residue was chromatographed on silica gel (30 g) with 1% acetone in benzene. The thin-layer-chromatographically homogeneous product (16 mg) was crystallized from MeOH to give colorless needles of a ketoaldehyde (8 mg). mp 123—125°C. CD $[\theta]_{280}^{17°}$: −3400° (c=0.9×10^{-3} g/ml, dioxane). EI-MS m/z (relative intensity %): 440 (13) (M^+), 425 (20), 422 (25), 411 (12), 407 (23), 393 (72), 171 (70), 95 (79), 43 (100). ^{1}H-NMR: 0.82, 0.84, 0.97, 0.93, 1.30, 1.39 (CH_3), 5.74 (H, br s, $W_{1/2}$=10 Hz, C_6–H), 9.47 (H, s, -CHO).

Methanolysis of F_1——F_1 (10 mg) was heated in 1 N HCl (MeOH) (0.5 ml) in a water bath (60°C) for 1 h. The reaction mixture was checked by TLC (Kieselgel, $CHCl_3$–MeOH–H_2O (7: 3: 0.5)) and showed one spot (Rf: 0.40, Methyl α-D-glucopyranoside: 0.40).

Methylation of F_1——F_1 (170 mg) was dissolved in freshly distilled THF (1.5 ml) and NaH (330 mg) was added portionwise. The mixture was sonicated for a few minutes, then MeI (1 ml) was added. The reaction mixture was stirred at room temperature for 1 h and then poured dropwise into MeOH (10 ml). The MeOH solution was neutralized with AcOH and concentrated. The residue was chromatographed on silica gel (50 g) using 6% acetone in benzene as the eluting solvent to give F_1 permethylate (105 mg): colorless needles from MeOH. mp 160—161°C. $[\alpha]_D^{23°}$: −77.5° (c=1.00, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.86, 0.88, 1.18, 1.24 (CH_3), 3.16, 3.41, 3.51, 3.62, 3.64 (OCH_3), 4.24 (d, J=7 Hz, C_1–H of glucopyranosyl group), 5.40 (br s, C_{23}–H, C_{24}–H), 5.54 (dd, J=10, 4 Hz, C_7–H), 6.09 (dd, J=10, 2 Hz, C_6–H). ^{13}C-NMR: quaternary C; 38.8, 45.3 (×2), 48.8. Oxygenated C (methoxyl Cs are omitted): 72.0t, 74.8s (C_{25}), 75.0d, 79.9t (C_{19}), 84.7d, 85.2s (C_5), 105.8d. Olefinic C; 128.3d, 129.7d, 134.2d, 137.5d.

Methylation of G——G (540 mg) was methylated in the same way as described above to give G permethylate (500 mg): colorless needles from MeOH. mp 206—207°C. $[\alpha]_D^{12°}$: −68.9° (c=1.70, $CHCl_3$). ^{1}H-NMR: 0.79, 0.89, 1.32 (×2), 1.37 (CH_3), 3.22, 3.39, 3.42, 3.67, 3.79 (OCH_3), 5.06 (H, d, J=8 Hz, C_1–H of allopyranosyl group), 5.59 (br s mounted on C_7–H signal, C_{23}–H, C_{24}–H), 6.21 (H, dd, J=10, 2 Hz, C_6–H). ^{13}C-NMR: quaternary C; 38.8, 45.3, 45.4, 48.8. Oxygenated C (methoxyl Cs are omitted); 72.6t, 72.9d, 74.8s (C_{25}), 77.4d, 78.2d, 79.9t (C_{19}), 81.9d, 85.2d, 85.3s (C_5), 103.8d. Olefinic C; 128.3d, 129.6d, 134.4d, 137.6d.

Catalytic Hydrogenation of G Permethylate——G permethylate (169 mg) was dissolved in 20 ml of AcOEt–EtOH (1: 1). PdO (286 mg) was added to the solution and the mixture was shaken in an H_2 atmosphere for 2 h. PdO was removed by filtration and the filtrate was concentrated to dryness under reduced

pressure. The residue was chromatographed on silica gel (40 g). Elution with 5% acetone in benzene gave GMH-1 (29 mg), and elution with 7% acetone in benzene gave GMH-2 (80 mg).

GMH-1: Colorless needles from MeOH. mp 177—178°C $[\alpha]_D^{20°}$: +20.1° (c=1.45, $CHCl_3$). EI-MS m/z: 662.512 (M^+). Calcd for $C_{40}H_{70}O_7$: 662.511. ^{1}H-NMR: 0.79, 0.80, 0.86, 0.90, 1.30 (CH_3), 3.38, 3.41, 3.66, 3.82 (OCH_3), 5.06 (H, d, J=8 Hz, C_1–H of allopyranosyl group). ^{13}C-NMR: quaternary C; 39.7, 46.1, 48.2, 50.0. Oxygenated C (methoxyl Cs are omitted): 72.6t, 72.8d, 77.5d, 78.2, 78.6t (C_{19}), 82.0d, 85.8d, 87.1s (C_5), 103.8d.

GMH-2: Colorless needles from hexane. mp 138°C. $[\alpha]_D^{24°}$: +27.7° (c=1.00, $CHCl_3$). EI-MS m/z: 662.512 (M^+). Calcd for $C_{40}H_{70}O_7$: 662.512. ^{1}H-NMR: 0.87, 0.93, 0.97, 1.09, 1.14, 1.34 (CH_3), 3.38, 3.41, 3.56, 3.67 (OCH_3), 5.07 (H, d, J=8 Hz, C_1–H of allopyranosyl group), 5.71 (br d, J=6 Hz, C_6–H). ^{13}C-NMR: quaternary C; 39.7, 41.6, 46.3, 49.3. Oxygenated C; (methoxyl Cs are omitted); 65.4t (C_{19}), 72.5t, 72.9d, 76.8d, 78.1d, 82.0d, 86.1d, 102.7d. Olefinic C; 120.1d (C_6), 142.5s (C_5).

Methanolysis of GMH-1——GMH-1 (45 mg) was dissolved in 0.5 N HCl (MeOH) (1 ml) and the solution was refluxed for 2 h. Long needles (16 mg) were deposited on cooling to room temperature. The needles were filtered off and the filtrate was worked up as described above. The residue was chromatographed on silica gel (15 g). The aglycone (25 mg) was eluted with 5% acetone in benzene, and the sugar (10 mg) was eluted with 15% acetone in benzene. The aglycone was crystallized from MeOH to give colorless needles (GMH-1-aglycone). mp 135°C. The IR spectrum was superimposable on that of F_1H-1-ag.

The Methylated Sugar: $[\alpha]_D^{23°}$: −14.7° (c=1.15, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 3.39, 3.42, 3.50, 3.51, 3.61 (OCH_3), δ 4.60 (d, J=8 Hz, H_1), δ 2.99 (dd, J=8, 3 Hz, H_2), δ 4.00 (t, J=3, 2 Hz, H_3), δ 3.22 (dd, J=2, 12 Hz, H_4), δ 3.71—3.93 (m, H_5).

Methylation of F_2——F_2 (60 mg) was methylated essentially in the same manner as described for the methylation of G. The product showed two spots on TLC. The less polar and predominant one (30 mg) was obtained by column chromatography on silica gel (15 g) using 5% acetone in benzene as an eluent. Crystallization from MeOH gave colorless needles. mp 205.5—206.5°C. The IR spectrum was superimposable on that of G permethylate.

Enzymatic Hydrolysis of I——I (124 mg) was dissolved in 30% EtOH (8.5 ml). Crude hesperidinase (300 mg) was added and the mixture was shaken at 38°C for 3 d. EtOH (30 ml) was added to the reaction mixture and the whole was concentrated to dryness under reduced pressure. The residue was extracted with hot EtOH and the EtOH extract was crystallized from MeOH to give colorless platelets. mp 205—210°C. $[\alpha]_D^{21°}$: −89.3° (c=1.05, $CHCl_3$). CD $[\theta]_{202}^{16°}$: −59500° (c=0.46×10^{-4} g/ml, MeOH). EI-MS m/z: 456.359 (M^+). Calcd for $C_{30}H_{48}O_3$: 456.360. ^{1}H-NMR: 0.78, 0.82, 0.90, 0.97 (d, J=5 Hz), 1.37, 1.52 (×2) (CH_3), 3.53 (d, J=8 Hz, C_{19}–H), 3.66 (d, J=8 Hz, C_{19}–H), 4.20 (H, d, J=10 Hz, C_3–OH), 5.60 (H, dd, J=10, 4 Hz, C_7–H), 5.92 (2H, br s, C_{23}–H, C_{24}–H), 6.12 (H, dd, J=10, 2 Hz, C_6–H). The signal of C_3–H was overlapped by the signal of C_{19}-protons. ^{13}C-NMR: quaternary C; 37.6, 45.4, 45.6, 48.8. Oxygenated C; 69.7s (C_{25}), 76.2d (C_3), 79.8t (C_{19}), 87.6s (C_5). Olefinic C; 124.1d, 131.3d, 132.4d, 141.7d.

Catalytic Hydrogenation of I Acetate——I acetate (110 mg) was dissolved in EtOH–AcOEt (1: 1) (20 ml). PdO (117 mg) was added to the solution and the mixture was shaken in an H_2 atmosphere for 2 h. PdO was filtered off and the filtrate was concentrated to dryness under reduced pressure. The residue was chromatographed on silica gel (40 g). Elution with 2% acetone in benzene gave I-AcH-1 (55 mg). Elution with 7% acetone in benzene gave I-AcH-2 (16 mg).

I-AcH-1: Colorless needles from MeOH. mp 225—226°C. The IR and ^{1}H-NMR spectra were superimposable on those of F_1-AcH-1.

I-AcH-2: Colorless needles from MeOH. mp 231—232°C. The IR spectrum was superimposable on that of F_1-AcH-2.

Methylation of I——I (43 mg) was dissolved in THF (0.5 ml), NaH (52 mg) was added to the solution, and the mixture was sonicated for a few minutes. MeI (0.5 ml) was added to the mixture and the whole was heated in a sealed tube for 2 h at 60°C. The reaction mixture was worked up in the usual manner. The product was chromatographed on silica gel (10 g). Elution with 5% acetone in benzene gave thin-layer-chromatographically homogeneous I permethylate (40 mg). Crystallization from MeOH gave colorless needles: mp 161—162°C. The IR spectrum was identical with that of F_1 permethylate.

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References and Notes

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10) β-anomer, $-19.0°$; α-anomer, $+148.5°$ (unpublished data reported by K. Mihashi *et al.* of this Faculty at the 101st Annual Meeting of The Pharmaceutical Society of Japan, Kumamoto, April 1981).
11) Instruments and materials used in this work were as follows: Yanako micromelting apparatus (melting points), Hitachi grating infrared spectrophotometer Model EPI-G3 (IR spectra), JASCO DIP-4 digital polarimeter (specific rotations), JASCO J-2 automatic recording spectropolarimeter (CD spectra), JEOL JNM FX-100 (25 MHz) spectrometer (^{13}C-NMR spectra), Hitachi R-22 (90 MHz) spectrometer (^{1}H-NMR spectra), JEOL D-300 mass spectrometer (MS), Kiesel gel 60 (70—230 mesh) (E. Merck) (column chromatography), precoated Kieselgel 60 F_{254} plates (E. Merck) (TLC). Melting points are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were measured in pyridine-d_5 unless otherwise stated, and chemical shifts are expressed on the δ-scale using tetramethylsilane as an internal standard (s, singlet; br, broad; d, doublet; dd, double doublet; t, triplet; dt, double triplet; q, quartet; m, multiplet).