Indonesian Medicinal Plants. XV.¹⁾ Chemical Structures of Five New Resin-Glycosides, Merremosides a, b, c, d, and e, from the Tuber of *Merremia mammosa* (Convolvulaceae)

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Five new resin-glycosides, named merremosides a (1), b (2), c (3), d (4), and e (5), were isolated from the tuber of *Merremia mammosa* (LOUR.) HALLIER f. (Convolvulaceae), an Indonesian medicinal plant. The structures of 1, 2, 3, 4, and 5 have been elucidated on the basis of chemical and physicochemical evidence, including syntheses of (1*S*)-(+)- and (1*R*)-(–)-jalapinolic acid (16b and 18b) and the glycosidic acid designated as merremoside i (6).

Key words Indonesian medicinal plant; Convolvulaceae; *Merremia mammosa*; resin-glycoside; merremoside; jalapinolic acid

Resin-glycosides, which are characteristic constituents²⁾ of convolvulaceous plants (e.g., *Pharbitis nil* CHOIS. and *Ipomoea purga* H.), have been studied since the last century.³⁾ However, structural studies have been mainly concerned with the alkaline hydrolysis products. Only recently have the structures of some resin-glycosides been fully characterized.⁴⁾

The tuber of *Merremia mammosa* (LOUR.) HALLIER f. (Convolvulaceae, Javanese name “Bidara upas”) is one of the so-called jamu raw materials⁵⁾ and is said to be useful for treating diabetes and illnesses involving the throat and respiratory system.⁵⁾ As a part of our chemical characterization of naturally occurring drug materials used in Indonesia,⁶⁾ we have been investigating the chemical constituents of the fresh tuber of *Merremia mammosa* and have isolated thirteen new resin-glycosides, named merremosides a, b, c, d, e, f, g, h₁ and h₂, and mammosides A, B, H₁ and H₂, from the chloroform-soluble portion of the methanol extract. This paper deals with the structure elucidation of merremosides a (1), b (2), c (3), d (4), and e (5).

The methanol extract of the fresh tuber was partitioned into a mixture of chloroform and water to give a chloroform-soluble portion (1.03% yield from the fresh tuber) and a water-soluble portion (5.07%). Repeated

separation of the chloroform-soluble portion by silica gel and reversed-phase silica gel chromatography provided merremosides a (1, 0.002% from the fresh tuber), b (2, 0.016%), c (3, 0.003%), d (4, 0.004%), e (5, 0.003%), f (0.001%), g (0.004%), h₁ (0.033%), h₂ (0.039%), and mammosides A (0.010%), B (0.072%), H₁ (0.097%), and H₂ (0.109%).^{4b-d)}

Merremoside d (4) Merremoside d (4), colorless fine crystals, C₄₈H₈₂O₂₀, showed absorption bands due to a hydroxyl (3420 cm⁻¹) group and an ester (1718 cm⁻¹) group in the infrared (IR) spectrum.

Hydrolysis of merremoside d (4) with 5% aqueous KOH yielded a glycosidic acid designated as merremoside i (6) and isobutyric acid, which was detected by gas-liquid chromatography (GLC) analysis. Treatment of 4 with 5% NaOMe–MeOH furnished merremoside i methyl ester (6a). Furthermore, on methanolysis with 9% HCl–MeOH, 6a gave methyl L-rhamnoside and methyl jalapinolate {7, [α]_D + 0.5° (CHCl₃)}, which was hydrolyzed with aqueous KOH to give jalapinolic acid {7a, [α]_D + 0.9° (CHCl₃)}.

In order to determine the absolute configuration of jalapinolic acid (7a), syntheses of (1*S*)- and (1*R*)-jalapinolic acid (16b and 18b) were tried as follows. The Baeyer–Villiger oxidation (giving 9) of cyclododecanone (8), followed by methanolysis and subsequent ethoxy-

merremoside a (1): R¹=R⁴= COCH(CH₃)C₂H₅; R²=R³= H

merremoside b (2): R¹=R⁴= COCH(CH₃)₂; R²=R³= H

merremoside c (3): R¹=R³= H; R²= COCH(CH₃)C₂H₅;
R⁴= COCH(CH₃)₂

merremoside d (4): R¹=R³= H; R²=R⁴= COCH(CH₃)₂

merremoside e (5): R¹=R⁴= H; R²=R³= COCH(CH₃)₂

Fig. 1

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Chart 1

Chart 2

ethylation, afforded an ω -hydroxydodecanoic acid derivative (**10**) in a satisfactory yield. Phenylselenation of **10**, followed by treatment with hydrogen peroxide, gave an α,β -unsaturated ester (**11**) in 74% yield, and this was converted into an allylic alcohol (**12**) by reduction with diisobutylaluminum hydride.

The Sharpless asymmetric epoxidation⁷⁾ using diethyl L-(+)-tartrate of the allylic alcohol (**12**) provided the (10*S*,11*S*)-epoxide (**13a**) in 83% yield, while the epoxidation of **12** using diethyl the D-(−)-tartrate gave the (10*R*,11*R*)-epoxide (**13b**) in 82% yield. The en-

antiomeric excess (ee) was determined by the proton nuclear magnetic resonance (^1H -NMR) analysis of the corresponding acetates (**13c** and **13d**) in the presence of tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium (III)⁸ to be both 92% in each asymmetric epoxidation.

The (10*S*,11*S*)-epoxide (**13a**) was converted in 63% yield into an (11*S*)-terminal epoxide (**14**) by successive treatments with diisobutylaluminum hydride, *p*-tosyl chloride–pyridine, and NaOMe in MeOH. Treatment of **14** with *n*-butylmagnesium chloride followed by benzoyl-

ation and acidic hydrolysis afforded an (11*S*)-diol 11-monobenzoate **15**, $[\alpha]_D +1.4^\circ$ in 40% yield. Finally, the Jones oxidation⁹⁾ of **15**, followed by diazomethane treatment and methanolysis, afforded methyl (11*S*)-(+)-jalapinate **16a**, $[\alpha]_D +0.9^\circ$ (CHCl_3), which was further converted by treatment with aqueous KOH into (11*S*)-(+)-jalapinic acid **16b**, $[\alpha]_D +0.7^\circ$ (CHCl_3) in a moderate yield.

Through a similar procedure to that from **13a** to **16b**, the (10*R*,11*R*)-epoxide (**13b**) was transformed into (11*R*)-(-)-jalapinic acid **18b**, $[\alpha]_D -0.8^\circ$ (CHCl_3) via the (11*R*)-diol 11-monobenzoate **17**, $[\alpha]_D -1.4^\circ$ (CHCl_3) and methyl (11*R*)-(-)-jalapinate **18a**, $[\alpha]_D -0.9^\circ$ (CHCl_3) in a fairly good yield.

Synthetic (11*S*)-(+)-jalapinic acid (**16b**) and methyl (11*S*)-(+)-jalapinate (**16a**) were respectively identical with **7a** and **7b** derived from merremoside d (**4**), based on comparisons of their physicochemical properties including the specific rotation. Thus, the absolute configuration at C-11 of natural jalapinic acid (**7a**) has been defined as *S*.

Next, we applied Horeau's method¹⁰⁾ to two synthetic methyl esters (**16a** and **18a**) and natural methyl jalapinate (**7**). In the cases of **16a** and **7**, the resulting 2-phenylbutanoic acid exhibited a positive specific rotation: $[\alpha]_D +0.13^\circ$ (benzene) for **16a** and $[\alpha]_D +0.18^\circ$ (benzene) for **7**. In contrast, when **18a** was submitted to the method, the specific rotation was negative: $[\alpha]_D -0.19^\circ$ (benzene). These findings would suggest an opposite assignment¹⁰⁾ to the above-determined 11*S*-configuration. This result may be explained by presuming that the optical yield in the phenylbutylation is low.¹¹⁾

The secondary ion mass spectroscopy (SIMS) of merremoside i methyl ester (**6a**) showed fragment ion peaks at m/z 585 (i), m/z 439 (ii), m/z 293 (iii), and m/z 147 (iv) derived from the oligosaccharide moiety, together with quasi-molecular ions m/z 909 ($\text{M}+\text{K}$)⁺ and m/z 893 ($\text{M}+\text{Na}$)⁺. The ¹H-NMR spectrum showed signals due to one *primary* methyl, one carbomethoxy methyl, four *secondary* methyls and four anomeric protons [δ 6.24,

6.25, 6.31 (2H), all brs]. The carbon-13 (¹³C)-NMR spectrum showed four anomeric carbon signals [δ_C 101.4, 102.8 (2C), 102.9] with ¹³C-¹H coupling constants of 169.9, 171.0, 171.5, and 171.6 Hz, respectively, indicating α -rhamnosyl linkage.¹²⁾ Complete methylation of **6a** with CH_3I -DMSO-NaH followed by methanolysis furnished methyl (11*S*)-(+)-jalapinate (**7**) and two methyl glycosides; methyl 2,3-di-*O*-methyl-L-rhamnopyranoside and methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside in a ratio of 3:1. Thus, the chemical structures of merremoside i (**6**) and merremoside i methyl ester (**6a**) have been proved to be as shown.

Furthermore, glycosidation of methyl (11*S*)-(+)-jalapinate (**7**) with *O*-(2,3,4-tri-*O*-acetyl-L-rhamnopyranosyl)trichloro-acetimidate (**19**)¹³⁾ in CH_2Cl_2 at -30°C in the presence of boron trifluoride etherate and molecular sieves 4 Å followed by alkaline hydrolysis afforded an α -glycoside (**20**). Treatment of **20** with 2,2-dimethoxypropane and camphor-10-sulfonic acid gave an acetonide (**21**) in a good yield. By repeated glycosidation and subsequent acetonization, the acetonide (**21**) was converted into merremoside i methyl ester (**6a**), which was identical with that derived from merremoside d (**4**).

In the SIMS, merremoside d (**4**) showed quasi-molecular ion peaks at m/z 1017 ($\text{M}+\text{K}$)⁺ and at m/z 1001 ($\text{M}+\text{Na}$)⁺, and the negative ion fast atom bombardment (negative FAB)-MS gave an ion peak at m/z 977 ($\text{M}-\text{H}$)⁻. A consideration of these findings and the result of elemental analysis indicated that merremoside d (**4**) possesses two isobutyryl moieties, and that a carboxyl function in jalapinic acid is attached to a hydroxyl group of the oligosaccharide moiety.

Fig. 2. SIMS for Merremoside i Methyl Ester (**6a**)

Chart 3

Fig. 3. SIMS and Negative FAB-MS of Merremoside d (**4**)

Chart 4

The ^1H -NMR spectrum of **4** exhibited signals due to one primary methyl, eight secondary methyls, four anomeric protons, and three methine protons attached to ester groups (isobutyroxy and lactone); δ 4.92 (dd, $J=9.5$, 9.5 Hz, 4'''-H), 4.99 (dd, $J=2.5$, 10.0 Hz, 3''-H), 5.11 (dd, $J=3.0$, 9.5 Hz, 3'''-H); the coupling patterns indicated that three ester linkages were attached to two 3-OH groups and one 4-OH in rhamnopyranose. Furthermore, the SIMS showed two characteristic fragment ions at m/z 433 (**v**) and m/z 217 (**vi**) and the negative FAB-MS showed fragment ions at m/z 907 (**vii**), m/z 761 (**viii**), m/z 545 (**ix**) and m/z 417 (**x+H**). These findings led us to conclude that the locations of two isobutyroxy moieties must be at 3'''-OH and 4'''-OH, while the lactone linkage is located at 3''-OH.

Further, in order to confirm the location of the lactone linkage in merremoside d (**4**), degradative reaction was carried out as follows: Acetonidation (giving **24**) of **4** followed by alkaline hydrolysis furnished a deisobutyroxy diacetonide derivative (**25**), which was subsequently treated with NaIO_4 and 5% NaOMe in MeOH to give a

monorhamnoside derivative (**26**). Finally, **26** was acetylated to afford a monoacetate (**27**). The ^1H -NMR spectrum of **27** showed signals assignable to one acetoxy methyl (δ 2.06, s) and 4'-H (δ 4.82, dd, $J=8.0$, 8.0 Hz). These findings show that the lactone linkage in **4** is located at 3''-OH, not at 3'-OH.

Consequently, the whole structure of merremoside d (**4**) has been determined to be as shown.

Merremoside b (2) Merremoside b (**2**), colorless fine crystals, $\text{C}_{48}\text{H}_{82}\text{O}_{20}$, showed absorption bands due to a hydroxyl (3350 cm^{-1}) group and an ester (1715 cm^{-1}) group in the IR spectrum.

Hydrolysis of merremoside b (**2**) with 5% aqueous KOH yielded merremoside i (**6**) and isobutyric acid. On the other hand, treatment with 5% NaOMe-MeOH gave merremoside i methyl ester (**6a**), which afforded methyl L-rhamnoside and methyl (11*S*)-(+)-jalapinolactate (**7**) on treatment with 9% HCl-MeOH .

In SIMS, merremoside b (**2**) showed quasi-molecular ion peaks at m/z 1017 ($\text{M}+\text{K}$) $^+$ and at m/z 1001 ($\text{M}+\text{Na}$) $^+$, together with fragment ion peaks at m/z 433

Fig. 4. SIMS and Negative FAB-MS of Merremoside b (2)

Fig. 5. Negative FAB-MS of **28**, **29**, **30**, and **31**

(**xi**) and m/z 217 (**vi**). The negative FAB-MS of **2** showed ion peaks at m/z 977 ($M-H$)⁻, 907 (**xii**), 761 (**xiii**), 545 (**ix**), and 417 ($x+H$). The ¹H-NMR spectrum showed signals of three methine protons on carbons bearing three ester functions; two isobutyroxy groups [δ 5.70, brs (2'''-H) and δ 5.73, dd, $J=9.8$, 9.8 Hz (4'''-H)] and one lactone moiety [δ 5.54, dd, $J=2.8$, 10.1 Hz (3''-H)].

Furthermore, treatment of merremoside b (**2**) with 2% NaOMe–MeOH at -10°C afforded merremoside d (**4**, 15%) and two monoisobutyryl derivatives [**28** (14%) and **29** (13%)]. Treatment of **2** with 4% NaOH–MeOH at 0°C yielded merremoside i methyl ester (**6a**, 39%), a deisobutyryl derivative (**30**, 20%) and a monoisobutyroxy derivative (**31**, 5%). Detailed analysis of the negative FAB-MS and ¹H-NMR spectra for **28**, **29**, **30**, and **31** led us to the structures shown.

Based on the above-mentioned evidence, the chemical structure of merremoside b (**2**) has been elucidated to be as shown. In addition, it has been found that the isobutyryl group at 2'''-OH in merremoside b (**2**) readily migrates to

the neighboring 3'''-OH.

Merremoside c (3) The IR spectrum of merremoside c (**3**), colorless fine crystals, $\text{C}_{49}\text{H}_{84}\text{O}_{20}$, showed a similar absorption pattern to those of merremosides b (**2**) and d (**4**). On hydrolysis with 5% aqueous KOH, merremoside c (**3**) gave merremoside i (**6**), isobutyric acid, and (2*S*)-(+)-methylbutyric acid (absolute configuration determined by HPLC analysis¹⁴) of the corresponding phenacyl ester **35**). Treatment of **3** with 5% NaOMe–MeOH afforded merremoside i methyl ester (**6a**). Furthermore, on methanolysis with 9% HCl–MeOH, merremoside c (**3**) gave methyl L-rhamnoside and methyl (1*S*)-(+)-jalapinolactate (**7**).

In SIMS, merremoside c (**3**) showed two quasi-molecular ion peaks at m/z 1015 ($M+Na$)⁺ and at m/z 993 ($M+H$)⁺, together with fragment ion peaks at m/z 447 (**xvii**) and at m/z 217 (**vi**). Further, the negative FAB-MS showed ion peaks at m/z 991 ($M-H$)⁻, m/z 921 (**xviii**), 775 (**xix**), 545 (**ix**), and 417 ($x+H$). In addition, the ¹H-NMR spectrum showed signals of three methine protons attached to one

Chart 5

SIMS

negative FAB-MS

Fig. 6. SIMS and Negative FAB-MS of Merremoside c (3)

SIMS

negative FAB-MS

Fig. 7. SIMS and Negative FAB-MS of Merremoside a (1)

isobutyroxy [δ 5.77, dd, $J=9.8$, 9.8 Hz ($4'''$ -H)], one methylbutyroxyl [δ 5.66, dd, $J=2.8$, 9.6 Hz ($3'''$ -H)] and one lactone moieties [δ 5.63, dd, $J=2.8$, 10.1 Hz ($3''$ -H)].

Based on the above-mentioned evidence, the chemical structure of merremoside c (3) was concluded to be as shown.

Merremoside a (1) The SIMS, negative FAB-MS and IR spectrum of merremoside a (1), colorless fine crystals, $C_{50}H_{86}O_{20}$, were similar to those of 2, 3, and 4. Hydrolysis of merremoside a (1) with 5% aqueous KOH gave merremoside i (6) and (2S)-(+)-methylbutyric acid. In addition, on methanolysis with 9% HCl-MeOH, 1 gave methyl L-rhamnoside and methyl (11S)-(+)-jalapinate (7).

The $^1\text{H-NMR}$ spectrum of 1 showed signals assignable

to three methine protons on carbons bearing three ester groups; δ 5.74, dd, $J=9.5$, 9.5 Hz ($4'''$ -H); δ 5.72, br s ($2'''$ -H); δ 5.54, dd, $J=2.8$, 10.1 Hz ($3''$ -H). The SIMS showed a quasi-molecular ion peak at m/z 1029 ($M + \text{Na}$) $^+$ together with fragment ion peaks at m/z 461 (xx) and m/z 231 (xxi), and the negative FAB-MS showed ion peaks at m/z 1005 ($M - \text{H}$) $^-$, m/z 921 (xix), m/z 775 (xxii), m/z 545 (ix), and m/z 417 ($x + \text{H}$).

From these findings, the chemical structure of merremoside a (1) was concluded to be as shown.

Merremoside e (5) The IR spectrum of merremoside e (5), colorless fine crystals, $C_{48}H_{82}O_{20}$, showed similar absorption bands to those for 1, 2, 3, and 4. Hydrolysis of merremoside e (5) with 5% aqueous KOH yielded merremoside i (6) and isobutyric acid. The $^1\text{H-NMR}$

Fig. 8. SIMS and Negative FAB-MS of Merremoside e (5)

spectrum showed signals due to three methine protons on carbons bearing three ester groups; δ 4.90, dd, $J=3.1$, 9.8 Hz; δ 5.00, dd, $J=2.9$, 9.3 Hz; δ 5.08, dd, $J=2.9$, 9.3 Hz ($3''$ -H, $3'''$ -H and $3''''$ -H).

Merremoside e (5) exhibited quasi-molecular ion peaks at m/z 1001 ($M+Na$)⁺ and m/z 979 ($M+H$)⁺ together with fragment ion peaks at m/z 433 (xxiv) and m/z 217 (xxv) in SIMS. Negative FAB-MS showed ion peaks at m/z 977 ($M-H$)⁻, m/z 907 (vii), m/z 761 (viii), m/z 545 (ix), and m/z 417 ($x+H$). Based on those findings, the chemical structure of merremoside e has been determined to be 5.

Finally, it should be mentioned that merremosides b (2) and d (4) exhibit antiserotonic activity [ED₅₀ (mice): 10 μ g/ml for 2 and 2 μ g/ml for 4], and merremosides a (1), b (2), c (3), and d (4) show ionophoretic activities against Na⁺, K⁺, and Ca²⁺ ions when assayed by the human erythrocyte membrane method.¹⁵⁾

In a parallel study, we have been investigating the constituents of the tuber. The results will be reported in the following paper.

Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-181 digital polarimeter in a 0.5 dm tube. EI-MS were taken on a JEOL JMS-D300 spectrometer. SIMS were taken on a Hitachi M-80 spectrometer. FAB-MS were taken on a JEOL JMS-DX300 spectrometer. ¹H- and ¹³C-NMR spectra were measured with a JEOL FX-90Q and a JEOL FX-500 spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ (ppm) and coupling constants (J values) are given in hertz (Hz). The following abbreviations are used: s=singlet, d=doublet, t=triplet, m=multiplet, and br.=broad. IR spectra were taken with a Hitachi EPI-G3 spectrometer. HPLC was carried out with a Shimadzu LC-7A. GLC was carried out with a Shimadzu GC-7A gas chromatograph. For column chromatography, Kieselgel 60 (70–230 mesh, Merck) was used. Thin layer chromatography (TLC) was conducted on precoated Kieselgel 60 F₂₅₄ plates (0.2 mm, Merck).

Plant Materials *Merremia mammosa* (LOUR.) HALLIER f. (Convolvulaceae) was collected at Pasar Beringharjo in Yogyakarta, Java Island, Indonesia, in August 1990, and identified at Herbarium Bogoriense, Research and Development Centre for Biology-LIPI, Indonesia.

Isolation of Merremosides a (1), b (2), c (3), d (4), and e (5) Fresh tubers (40 kg) of *Merremia mammosa* (LOUR.) HALLIER. f. (Convolvulaceae) were extracted three times with methanol (50 l each) with heating under reflux. The solvent was evaporated off under reduced pressure to yield the MeOH extract (2.44 kg, 6.1% from the fresh tuber). The MeOH extract was partitioned into a chloroform and water mixture

(1:1). The chloroform phase was concentrated under reduced pressure to give the CHCl₃ extract (412 g, 1.03%). The CHCl₃ extract (100 g) was purified by silica gel column chromatography [SiO₂ 2 kg, with CHCl₃:MeOH=15:1→10:1→7:1→6:1 and CHCl₃:MeOH:H₂O=7:3:1 (lower phase)] and reversed-phase HPLC (Shimpak Prep-ODS, 0.25 m × 20 mm, CH₃OH:H₂O=5:1 and CH₃OH:H₂O=4:1) to afford merremosides a (1, 194 mg, 0.002% from the fresh tuber), b (2, 1.55 g, 0.016%), c (3, 291 mg, 0.003%), d (4, 388 mg, 0.004%), e (5, 288 mg, 0.003%), f (95 mg, 0.001%), g (382 mg, 0.004%), h₁ (3.19 g, 0.033%), h₂ (3.77 g, 0.0039%), and mammosides A (982 mg, 0.010%), B (6.99 g, 0.072%), H₁ (9.40 g, 0.097%), and H₂ (10.5 g, 0.109%).

Merremoside a (1): Colorless fine crystals from EtOH, mp 125–126°C, [α]_D²⁰ –108° ($c=1.1$, in MeOH at 25°C). IR (KBr) cm⁻¹: 3360, 2938, 1717. ¹H-NMR (500 MHz, pyridine-*d*₅+D₂O) δ : 0.88 (3H, t, $J=7.3$ Hz), 0.95 (3H, t, $J=7.3$ Hz), 0.99 (3H, t, $J=7.3$ Hz) [ω -CH₃, –CH(CH₃)CH₂CH₃ × 2], 1.16 (3H, d, $J=7.0$ Hz), 1.21 (3H, d, $J=6.7$ Hz) [–CH(CH₃)CH₂CH₃ × 2], 1.42 (3H, d, $J=6.4$ Hz), 1.50 (3H, d, $J=6.4$ Hz), 1.57 (3H, d, $J=6.1$ Hz), 1.64 (12H, d, $J=6.1$ Hz) (6'-, 6''-, 6'''-, 6''''-H₃), 2.27 (1H, ddd, $J=3.0$, 6.9, 14.6 Hz, 2-H_a), 2.43, 2.52 (1H each, both m, –CH(CH₃)CH₂CH₃), 2.62 (1H, ddd, $J=3.0$, 6.9, 14.6 Hz, 2-H_b), 3.83 (1H, m, 11-H), 5.12 (1H, brs, 1'-H), 5.53 (1H, brs, 1'''-H), 5.54 (1H, dd, $J=2.8$, 10.1 Hz, 3''-H), 5.72 (1H, brs, 2''-H), 5.74 (1H, dd, $J=9.5$, 9.5 Hz, 4''''-H), 6.04 (1H, brs, 1'''-H), 6.31 (1H, brs, 1''-H). ¹³C-NMR (125 MHz, pyridine-*d*₅) δ : 99.5 (1''-C), 100.9 (1'-C), 101.9 (1'''-C), 103.1 (1''''-C), 174.3, 175.6, 176.0 (>C=O × 3). SIMS m/z : 1029 ($M+Na$)⁺, 461 (xx), 231 (xxi). Negative FAB-MS m/z : 1005 ($M-H$)⁻, 921 (xxi), 775 (xxii), 545 (ix), 417 ($x+H$). Anal. Calcd for C₅₀H₈₆O₂₀·2H₂O: C, 57.57; H, 8.70. Found: C, 57.82; H, 8.61.

Merremoside b (2): Colorless fine crystals from EtOH, mp 129–130°C, [α]_D²⁰ –90° ($c=2.0$, in MeOH at 25°C). IR (KBr) cm⁻¹: 3350, 2895, 1715. ¹H-NMR (500 MHz, pyridine-*d*₅+D₂O) δ : 0.99 (3H, t, $J=7.3$ Hz, ω -CH₃), 1.12 (3H, d, $J=6.7$ Hz), 1.15 (3H, d, $J=7.0$ Hz), 1.19 (3H, d, $J=7.0$ Hz), 1.21 (12H, d, $J=7.0$ Hz) [–CH(CH₃)₂ × 4], 1.40 (3H, d, $J=6.4$ Hz), 1.50 (3H, d, $J=6.4$ Hz), 1.57 (3H, d, $J=6.1$ Hz), 1.60 (3H, d, $J=6.1$ Hz) (6'-, 6''-, 6'''-, 6''''-H₃), 2.23 (1H, ddd, $J=3.0$, 6.9, 14.6 Hz, 2-H_a), 2.55, 2.64 (1H each, both m, –CH(CH₃)₂ × 2), 2.62 (1H, ddd, $J=3.0$, 6.9, 14.6 Hz, 2-H_b), 3.85 (1H, m, 11-H), 5.11 (1H, brs, 1'-H), 5.50 (1H, brs, 1'''-H), 5.54 (1H, dd, $J=3.0$, 9.8 Hz, 3''-H), 5.70 (1H, brs, 2''-H), 5.73 (1H, dd, $J=9.8$, 9.8 Hz, 4''''-H), 6.05 (1H, brs, 1'''-H), 6.30 (1H, brs, 1''-H). ¹³C-NMR (125 MHz, pyridine-*d*₅) δ : 100.0 (1''-C), 100.4 (1'-C), 102.2 (1'''-C), 103.5 (1''''-C), 174.5, 176.2, 176.6 (>C=O × 3). SIMS m/z : 1001 ($M+Na$)⁺, 1017 ($M+K$)⁺, 433 (xi), 217 (vi). Negative FAB-MS m/z : 977 ($M-H$)⁻, 907 (xii), 761 (xiii), 545 (ix), 417 ($x+H$). Anal. Calcd for C₄₈H₈₂O₂₀·H₂O: C, 57.82; H, 8.49. Found: C, 57.43; H, 8.47.

Merremoside c (3): Colorless fine crystals from EtOH, mp 126–127°C, [α]_D²⁰ –63° ($c=0.9$, in MeOH at 25°C). IR (KBr) cm⁻¹: 3370, 2880, 1717. ¹H-NMR (500 MHz, pyridine-*d*₅+D₂O) δ : 0.86 (3H, t, $J=7.3$ Hz, ω -CH₃), 0.92 (3H, t, $J=7.3$ Hz, –CH(CH₃)CH₂CH₃), 1.12 (3H, d, $J=7.0$ Hz, –CH(CH₃)CH₂CH₃), 1.18 (3H, d, $J=6.1$ Hz, –CH(CH₃)₂), 1.19 (3H, d, $J=6.7$ Hz, –CH(CH₃)₂), 1.38 (3H, d, $J=6.1$ Hz), 1.50 (3H, d, $J=6.4$ Hz), 1.57 (3H, d, $J=6.1$ Hz), 1.60 (3H, d, $J=6.1$ Hz) (6'-, 6''-, 6'''-, 6''''-H₃), 2.14 (1H, ddd, $J=3.0$, 6.9, 14.6 Hz, 2-H_a), 2.27 (1H, ddd, $J=3.0$, 6.9, 14.6 Hz, 2-H_b), 2.44, 2.62 (1H each, both m, –CH(CH₃)₂ and –CH(CH₃)CH₂CH₃), 3.79 (1H, m, 5'-H), 3.90 (1H, brs, 2'-H), 3.91

(1H, m, 11-H), 4.14 (1H, dd, $J=3.2, 9.5$ Hz, 3'-H), 4.26 (1H, m, 5'''-H), 4.36 (1H, dd, $J=3.4, 9.8$ Hz, 3'''-H), 4.41 (1H, brs, 2'''-H), 4.49 (1H, dd, $J=9.5, 9.5$ Hz, 4'-H), 4.52 (1H, dd, $J=9.6, 9.6$ Hz, 4'''-H), 4.64 (1H, brs, 2''-H), 4.68 (1H, dd, $J=10.1, 10.1$ Hz, 4''-H), 5.03 (1H, m, 5''-H), 5.20 (1H, brs, 2''-H), 5.33 (1H, brs, 1'-H), 5.63 (1H, dd, $J=2.8, 10.1$ Hz, 3''-H), 5.64 (1H, brs, 1'''-H), 5.66 (1H, dd, $J=2.8, 9.6$ Hz, 3'''-H), 5.77 (1H, dd, $J=9.8, 9.8$ Hz, 4'''-H), 5.83 (1H, brs, 1'''-H), 6.32 (1H, brs, 1''-H). $^{13}\text{C-NMR}$ (125 MHz, pyridine- d_5) δ : 99.9 (1'-C), 102.1 (1'-C), 102.3 (1'''-C), 102.9 (1'''-C), 174.2, 175.2, 176.5 ($>\text{C}=\text{O} \times 3$). SIMS m/z : 1015 ($\text{M}+\text{Na}$) $^+$, 993 ($\text{M}+\text{H}$) $^+$, 447 (xvii), 217 (vi). Negative FAB-MS m/z : 991 ($\text{M}-\text{H}$) $^-$, 921 (xviii), 775 (xix), 545 (ix), 417 ($\text{x}+\text{H}$). Anal. Calcd for $\text{C}_{49}\text{H}_{84}\text{O}_{20} \cdot \text{H}_2\text{O}$: C, 58.21; H, 8.57. Found: C, 58.42; H, 8.48.

Merremoside d (4): Colorless fine crystals from EtOH, mp 138–139 °C, $[\alpha]_{\text{D}} -77^\circ$ ($c=1.1$, in MeOH at 26 °C). IR (KBr) cm^{-1} : 3420, 2902, 1718. $^1\text{H-NMR}$ (500 MHz, pyridine- $d_5 + \text{D}_2\text{O}$) δ : 0.97 (3H, t, $J=7.3$ Hz, $\omega\text{-CH}_3$), 1.18, 1.19, 1.20, 1.23 (3H each, all d, $J=7.0$ Hz, $-\text{CH}(\text{CH}_3)_2 \times 4$), 1.32 (3H, d, $J=6.1$ Hz), 1.50 (3H, d, $J=6.4$ Hz), 1.56 (3H, d, $J=6.1$ Hz), 1.57 (3H, d, $J=6.1$ Hz) (6'-, 6'', 6''', 6'''-H₃), 2.16 (1H, ddd, $J=3.0, 6.9, 14.6$ Hz, 2-H_a), 2.24 (1H, ddd, $J=3.0, 6.9, 14.6$ Hz, 2-H_b), 2.66, 2.67 (1H each, both m, $-\text{CH}(\text{CH}_3)_2 \times 2$), 3.87 (1H, m, 11-H), 5.33 (1H, brs, 1'-H), 5.60 (1H, brs, 1'''-H), 5.61 (1H, dd, $J=3.0, 9.5$ Hz, 3''-H), 5.65 (1H, dd, $J=3.0, 9.5$ Hz, 3'''-H), 5.67 (1H, dd, $J=9.5, 9.5$ Hz, 4'''-H), 5.80 (1H, brs, 1''-H), 6.29 (1H, brs, 1''-H). $^{13}\text{C-NMR}$ (125 MHz, pyridine- d_5) δ : 99.8 (1'-C), 102.1 (1'-C), 102.3 (1'''-C), 103.0 (1'''-C), 174.1, 175.7, 176.5 ($>\text{C}=\text{O} \times 3$). SIMS m/z : 1001 ($\text{M}+\text{Na}$) $^+$, 1017 ($\text{M}+\text{K}$) $^+$, 433 (v), 217 (vi). Negative FAB-MS m/z : 977 ($\text{M}-\text{H}$) $^-$, 907 (vii), 761 (viii), 545 (ix), 417 ($\text{x}+\text{H}$). Anal. Calcd for $\text{C}_{48}\text{H}_{82}\text{O}_{20} \cdot 2\text{H}_2\text{O}$: C, 57.82; H, 8.49. Found: C, 57.99; H, 8.68.

Merremoside e (5): Colorless fine crystals from EtOH, mp 128–129 °C, $[\alpha]_{\text{D}} -68^\circ$ ($c=0.9$, in MeOH at 25 °C). IR (KBr) cm^{-1} : 3498, 2908, 1715. $^1\text{H-NMR}$ (500 MHz, pyridine- $d_5 + \text{D}_2\text{O}$) δ : 0.88 (3H, t, $J=7.3$ Hz, $\omega\text{-CH}_3$), 1.16, 1.16, 1.18, 1.19 (3H each, all d, $J=7.0$, $-\text{CH}(\text{CH}_3)_2 \times 4$), 1.25 (3H, d, $J=6.1$ Hz), 1.28 (3H, d, $J=6.4$ Hz), 1.31 (3H, d, $J=6.1$ Hz), 1.36 (3H, d, $J=6.1$ Hz) (6'-, 6'', 6''', 6'''-H₃), 2.13 (1H, ddd, $J=3.0, 7.0, 15.0$ Hz, 2-H_a), 2.25 (1H, ddd, $J=3.0, 7.0, 15.0$ Hz, 2-H_b), 2.61, 2.62 (1H each, both m, $-\text{CH}(\text{CH}_3)_2 \times 2$), 3.62 (1H, m, 11-H), 4.90 (1H, dd, $J=3.1, 9.8$ Hz), 5.00 (1H, dd, $J=2.9, 9.3$ Hz), 5.08 (1H, dd, $J=2.9, 9.3$ Hz) (3'-, 3'''-H), 4.75, 4.98, 5.13, 5.37 (1H each, all brs, 1'-, 1'', 1''', 1'''-H). $^{13}\text{C-NMR}$ (125 MHz, pyridine- d_5) δ : 100.2 (1'-C), 102.3 (1'-C), 102.5 (1'''-C), 102.8 (1'''-C), 174.3, 175.8, 176.6 ($>\text{C}=\text{O} \times 3$). SIMS m/z : 1001 ($\text{M}+\text{Na}$) $^+$, 979 ($\text{M}+\text{H}$) $^+$, 433 (xxiv), 217 (xxv). Negative FAB-MS m/z : 977 ($\text{M}-\text{H}$) $^-$, 907 (vii), 761 (viii), 545 (ix), 417 ($\text{x}+\text{H}$). Anal. Calcd for $\text{C}_{48}\text{H}_{82}\text{O}_{20} \cdot 2\text{H}_2\text{O}$: C, 57.82; H, 8.49. Found: C, 57.98; H, 8.31.

Treatment of Merremoside d (4) with 5% Aqueous KOH I) A solution of merremoside d (4, 5 mg) in acetone (1.0 ml) was treated with 5% aqueous KOH (1.0 ml) and the mixture was heated under reflux for 30 min. After cooling, the reaction mixture was acidified with 5% aqueous HCl and then extracted with ether. The ether extract was subjected to GLC analysis to determine isobutyric acid by comparison with an authentic sample. GLC conditions: column, 15% FFAP on Chromosorb GAW DMSC (100/120), i.d. 3 mm $\times$ 1 m glass column; column temperature, 140 °C; carrier gas, N_2 ; flow rate, 30 ml/min; injection temperature, 170 °C; detector, FID; t_{R} , 8 min 46 s. II) A solution of merremoside d (4, 40 mg) in acetone (1.0 ml) was mixed with 10% aqueous KOH (1.0 ml) and the whole was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Dowex 50W $\times$ 8 (H^+ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product, which was purified by column chromatography [SiO_2 10 g, CHCl_3 :MeOH: $\text{H}_2\text{O}=7:3:1$ (lower phase)] to give merremoside i (6, 31 mg).

Merremoside i (6): Colorless fine crystals from EtOH, mp 138–140 °C, $[\alpha]_{\text{D}} -89^\circ$ ($c=1.2$ in MeOH at 24 °C). IR (KBr) cm^{-1} : 3401, 2928, 1710. $^1\text{H-NMR}$ (500 MHz, pyridine- $d_5 + \text{D}_2\text{O}$) δ : 0.91 (3H, t, $J=7.3$ Hz, $\omega\text{-CH}_3$), 1.51, 1.58, 1.58 (3H each, all d, $J=6.0$ Hz, 6'-, 6'', 6'''-H₃), 2.31 (2H, t, $J=7.5$ Hz, 2-H₂), 5.32, 6.15, 6.21, 6.21 (1H each, all brs, 1'-, 1'', 1'''-H). Anal. Calcd for $\text{C}_{40}\text{H}_{72}\text{O}_{19} \cdot 2\text{H}_2\text{O}$: C, 53.80; H, 8.58. Found: C, 53.98; H, 8.49.

Treatment of Merremoside d (4) with 5% NaOMe in MeOH Merremoside d (4, 40 mg) was treated with 5% NaOMe–MeOH (1.0 ml) and the whole was heated under reflux for 30 min. After cooling, the reaction mixture was neutralized with Dowex 50W $\times$ 8 (H^+ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product, which was purified by column chromatography

(SiO_2 10 g, CHCl_3 :MeOH=3:1) to afford merremoside i methyl ester (6a, 32 mg).

6a: Colorless fine crystals from EtOH, mp 112–113 °C, $[\alpha]_{\text{D}} -81^\circ$ ($c=2.4$, in MeOH at 25 °C). IR (KBr) cm^{-1} : 3369, 2918, 1732. $^1\text{H-NMR}$ (500 MHz, pyridine- $d_5 + \text{D}_2\text{O}$) δ : 0.92 (3H, t, $J=7.3$ Hz, $\omega\text{-CH}_3$), 1.50, 1.57, 1.58, 1.58 (3H each, all d, $J=6.0$ Hz, 6'-, 6'', 6'''-H₃), 2.31 (2H, t, $J=7.5$ Hz, 2-H₂), 3.62 (3H, s, $-\text{COOCH}_3$), 5.33, 6.15, 6.19, 6.23 (1H each, all brs, 1'-, 1'', 1'''-H). $^{13}\text{C-NMR}$ (125 MHz, pyridine- d_5) δ : 101.4, 102.8, 102.8, 102.9 (1'-, 1'', 1'''-C, $J_{\text{C-H}}$: 169.9, 171.0, 171.5, 171.6 Hz), 174.0 ($-\text{COOH}$). SIMS m/z : 909 ($\text{M}+\text{K}$) $^+$, 893 ($\text{M}+\text{Na}$) $^+$, 585 (i), 439 (ii), 293 (iii), 147 (vi). Anal. Calcd. for $\text{C}_{41}\text{H}_{74}\text{O}_{19} \cdot 3\text{H}_2\text{O}$: C, 53.23; H, 8.71. Found: C, 53.54; H, 8.50.

Methanolysis of Merremoside i Methyl Ester (6a) A solution of merremoside i methyl ester (6a, 60 mg) in 9% HCl–MeOH (3.0 ml) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with an AgCO_3 powder and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (43 mg). Repeated column chromatography (SiO_2 20 g, CHCl_3 :MeOH=30:1 $\rightarrow$ 5:1 and n -hexane:EtOAc=7:1) of the product afforded methyl (11S)-(+)-jalapinolol (7, 6.2 mg) and methyl L-rhamnoside (18 mg).

7: Colorless needles from CHCl_3 , mp 45–46 °C, $[\alpha]_{\text{D}} +0.5^\circ$ ($c=2.6$, in CHCl_3 at 24 °C). IR (KBr) cm^{-1} : 3309, 2908, 1742. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ : 0.89 (3H, t, $J=6.7$ Hz, $\omega\text{-CH}_3$), 2.31 (2H, t, $J=7.5$ Hz, 2-H₂), 3.67 (3H, s, $-\text{COOCH}_3$). $^{13}\text{C-NMR}$ (22.5 MHz, CDCl_3) δ : 14.1 ($\omega\text{-CH}_3$), 51.5 ($-\text{COOCH}_3$), 72.1 (11-C), 174.3 ($-\text{COOCH}_3$). EI-MS m/z (%): 286 (M^+ , 20), 215 (100). High-resolution EI-MS m/z : Calcd for $\text{C}_{17}\text{H}_{34}\text{O}_3$: 286.4538. Found: 286.4548 (M^+).

A solution of methyl L-rhamnoside (1.0 mg) in pyridine (0.3 ml) was treated with N,O -bis(trimethylsilyl)trifluoroacetamide (0.5 ml) at room temperature for 1 h. The reaction mixture was directly subjected to GLC analysis to determine methyl 2,3,4- O -tri(trimethylsilyl)-L-rhamnopyranoside by comparison with an authentic sample. GLC conditions-1: column, 15% silicone OV-1 on Chromosorb WAW DMSC (80/100), i.d. 3 mm $\times$ 1 m glass column; column temperature, 150 °C; carrier gas, N_2 ; flow rate, 30 ml/min; injection temperature, 170 °C; detector: FID; t_{R} , 4 min 01 s. GLC conditions-2: column, 15% silicone SE-30 on Chromosorb WAW DMSC (80/100), i.d. 3 mm $\times$ 1 m glass column; column temperature, 150 °C; carrier gas, N_2 ; flow rate, 30 ml/min; injection temperature, 170 °C; detector: FID; t_{R} , 3 min 42 s.

A solution of methyl L-rhamnoside (15 mg) in 1 N aqueous HCl was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with AgCO_3 powder and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product, which was purified by column chromatography (SiO_2 7 g, CHCl_3 :MeOH=3:1) to afford L-rhamnose [8 mg, $[\alpha]_{\text{D}} +9.0^\circ$ ($c=0.9$, in H_2O at 25 °C)].

Alkaline Treatment of Methyl (11S)-(+)-Jalapinolol (7b) Giving (11S)-(+)-Jalapinolic Acid (7a) A solution of methyl (11S)-(+)-jalapinolol (7, 10 mg) in acetone (0.5 ml) was treated with 5% aqueous KOH (1.0 ml) and the mixture was stirred at room temperature for 1 h, then poured into ice-water and extracted with EtOAc. After usual work-up of the EtOAc extract, the solvent was evaporated off under reduced pressure to yield a product (9.5 mg), which was purified by column chromatography (SiO_2 5 g, n -hexane:EtOAc=5:1) to afford 7a, (8 mg).

7a: Colorless needles from petroleum ether; mp 65–67 °C, $[\alpha]_{\text{D}} +0.9^\circ$ ($c=0.7$ in CHCl_3 at 24 °C). IR (film) cm^{-1} : 1713. $^1\text{H-NMR}$ (90 MHz, CDCl_3) δ : 0.90 (3H, t-like, $\omega\text{-CH}_3$), 2.30 (2H, t, $J=8.0$ Hz, 2-H₂), 3.5–3.7 (1H, m, 11-H). EI-MS m/z (%): 257 ($\text{M}^+ - \text{CH}_3$, 0.6), 255 (8.2), 91 (100). High-resolution EI-MS m/z : Calcd for $\text{C}_{15}\text{H}_{29}\text{O}_3$ ($\text{M}^+ - \text{CH}_3$): 257.3761. Found: 257.3769.

Conversion of Cyclododecanone (8) to 10 via 9 A solution of 8 (25 g, 0.14 mol) in CH_2Cl_2 (200 ml) was treated with 70% m -chloroperbenzoic acid (48 g, 0.20 mmol) and the whole was stirred at 40 °C for 3 d. The reaction mixture was treated with aqueous saturated $\text{Na}_2\text{S}_2\text{O}_3$ and extracted with CH_2Cl_2 . The CH_2Cl_2 extract was washed with aqueous saturated Na_2CO_3 and brine, and then dried over MgSO_4 . Removal of the solvent under reduced pressure gave a product (50 g), which was purified by column chromatography (SiO_2 600 g, n -hexane:EtOAc=15:1) to afford a lactonic derivative (9, 24 g, 0.12 mol). A solution of 9 (15 g, 75 mmol) in MeOH (30 ml) was treated with 28% NaOMe–MeOH (20 ml) and the whole was stirred at room temperature for 30 min. The reaction mixture was neutralized with Dowex 50W $\times$ 8

(H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (18 g). A solution of this product in CH₂Cl₂ (150 ml) was treated with ethyl vinyl ether (11 ml) and *p*-toluenesulfonic acid (10 mg) and the whole was stirred at 0 °C for 15 min. The reaction was quenched with aqueous saturated NaHCO₃, the mixture was extracted with CH₂Cl₂. The CH₂Cl₂ extract was washed with aqueous saturated NaHCO₃ and brine, and then dried over MgSO₄. Removal of the solvent under reduced pressure gave a product (25 g), which was purified by column chromatography (SiO₂ 400 g, *n*-hexane:EtOAc=2:1) to afford **10** (21.2 g, 70 mmol).

10: A colorless oil. IR (film) cm⁻¹: 1732. ¹H-NMR (90 MHz, CDCl₃) δ: 1.21 (3H, t, *J*=7.0 Hz, -OCH(CH₃)OCH₂CH₃), 1.31 (3H, d, *J*=5.0 Hz, -OCH(CH₃)OCH₂CH₃), 2.31 (2H, t, *J*=7.0 Hz, -CH₂-COOCH₃), 3.67 (3H, s, -COOCH₃), 4.68 (1H, q, *J*=5.0 Hz, -OCH(CH₃)OCH₂CH₃). EI-MS *m/z* (%): 287 (M⁺-CH₃, 16), 173 (100). High-resolution EI-MS *m/z*: Calcd for C₁₆H₃₁O₄ (M⁺-CH₃): 287.2212. Found: 287.2210.

α,β-Unsaturated Ester Derivative (11) from 10 A solution of **10** (5.0 g, 16.6 mmol) in tetrahydrofuran (THF, 20 ml) was added dropwise to a solution of lithium diisopropylamide (LDA, 33.2 mmol) in THF (8.0 ml) at -78 °C and the mixture was stirred at -78 °C for 10 min. Then a solution of phenylselenenyl chloride (4.1 g, 21.6 mmol) in THF (8.0 ml) was added slowly at -78 °C and the whole was further stirred at -78 °C for 15 min. The reaction was quenched with 5% aqueous NH₄Cl, and the mixture was extracted with EtOAc. The EtOAc extract was washed with brine, then dried over MgSO₄. Removal of the solvent under reduced pressure gave a product (50 g), which was purified by column chromatography (SiO₂ 100 g, benzene:EtOAc=60:1) to afford a phenylselenenyl derivative (5.5 g). A solution of the phenylselenenyl derivative (5.5 g) in THF (160 ml) was treated with 30% H₂O₂ (8.2 ml) at 0 °C and the whole was stirred at room temperature for 2 h. Then 5% aqueous Na₂S₂O₃ was added at 0 °C and the whole was extracted with EtOAc. The EtOAc extract was washed successively with aqueous saturated NaHCO₃ and brine, then dried over MgSO₄. Removal of the solvent under reduced pressure gave a product (5 g), which was purified by column chromatography (SiO₂ 100 g, toluene:EtOAc=40:1) to afford **11** (3.8 g, 12.3 mmol).

11: A colorless oil. IR (film) cm⁻¹: 1725. ¹H-NMR (90 MHz, CDCl₃) δ: 1.21 (3H, t, *J*=6.0 Hz, -OCH(CH₃)OCH₂CH₃), 1.31 (3H, d, *J*=5.0 Hz, -OCH(CH₃)OCH₂CH₃), 3.73 (3H, s, -COOCH₃), 4.69 (1H, q, *J*=5.0 Hz, -OCH(CH₃)OCH₂CH₃), 5.82 (1H, dt, *J*=16.0, 1.0 Hz, olefinic proton), 6.98 (1H, dt, *J*=16.0, 7.0 Hz, olefinic proton). EI-MS *m/z* (%): 300 (M⁺, 0.7), 285 (M⁺-CH₃, 2), 73 (100). High-resolution MS *m/z*: Calcd for C₁₇H₃₂O₄: 300.2305. Found: 300.2300 (M⁺).

Reduction of 11 Giving 12 A solution of **11** (3.1 g, 10.3 mmol) in toluene (40 ml) was treated with diisobutylaluminum hydride (DIBAL, 20.7 mmol) at -78 °C and the whole was stirred at -78 °C for 30 min. The reaction was quenched with aqueous saturated ether and 4 N aqueous KOH, and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (4.0 g). Column chromatography (SiO₂ 70 g, *n*-hexane:EtOAc=2:1) of the product afforded an allylic alcohol (**12**, 2.25 g, 8.3 mmol).

12: A colorless oil. IR (film) cm⁻¹: 2980, 2940, 2860. ¹H-NMR (90 MHz, CDCl₃) δ: 1.21 (3H, t, *J*=7.0 Hz, -OCH(CH₃)OCH₂CH₃), 1.32 (3H, d, *J*=5.0 Hz, -OCH(CH₃)OCH₂CH₃), 4.0-4.2 (2H, m, -CH₂O), 4.69 (1H, q, *J*=5.0 Hz, -OCH(CH₃)OCH₂CH₃). EI-MS *m/z* (%): 257 (M⁺-CH₃, 0.7), 73 (100). High-resolution EI-MS *m/z*: Calcd for C₁₅H₂₉O₃ (M⁺-CH₃): 257.2114. Found: 257.2114.

Asymmetric Epoxidation of 12 Using Diethyl D-(+)-Tartrate [(+)-DET] Giving 13a A solution of **12** (950 mg, 3.5 mmol) in CH₂Cl₂ (30 ml) was added dropwise to a solution of Ti(O-iso-Pr)₄ (1.03 ml, 3.5 mmol) and (+)-DET (0.60 ml, 3.5 mmol) in CH₂Cl₂ (35 ml) during 15 min at -30 °C and the whole was stirred at -30 °C for 30 min. To this solution, *tert*-BuOOH-CH₂Cl₂ (2.9 M, 2.45 ml, 7.0 mmol) was added dropwise during 10 min at -30 °C. The resulting solution was further stirred at -30 °C for 30 min. Then 10% aqueous tartaric acid (10 ml) was added, and the whole was stirred at -30 °C for 30 min and at room temperature for 1 h. The reaction mixture was extracted with CH₂Cl₂. The CH₂Cl₂ extract was washed with brine, and dried over MgSO₄. Removal of the solvent under reduced pressure gave a product (1.08 g), which was purified by column chromatography (SiO₂ 150 g, *n*-hexane:EtOAc=40:1) to furnish the epoxy alcohol **13a** (837 mg, 2.91 mmol).

13a: A colorless oil, [α]_D²⁰ -18° (*c*=3.1 in CHCl₃ at 27 °C). IR

(film) cm⁻¹: 3395, 2907. ¹H-NMR (90 MHz, CDCl₃) δ: 1.21 (3H, t, *J*=7.0 Hz, -OCH(CH₃)OCH₂CH₃), 1.31 (3H, d, *J*=5.0 Hz, -OCH(CH₃)OCH₂CH₃), 2.9-3.0 (2H, m), 4.69 (1H, q, *J*=5.0 Hz, -OCH(CH₃)OCH₂CH₃). EI-MS *m/z* (%): 273 (M⁺-CH₃, 0.6), 73 (100). High-resolution EI-MS *m/z*: Calcd for C₁₅H₂₉O₄ (M⁺-CH₃): 273.2071. Found: 273.2066.

Asymmetric Epoxidation of 12 Using Diethyl L-(-)-Tartrate [(-)-DET] Giving 13b A solution of **12** (543 mg, 2.0 mmol) in CH₂Cl₂ (17 ml) was added dropwise to a solution of Ti(O-iso-Pr)₄ (0.59 ml, 2.0 mmol) and (-)-DET (0.34 ml, 2.0 mmol) in CH₂Cl₂ (20 ml) during 10 min at -30 °C, and the whole was stirred at -30 °C for 30 min. To this solution, *tert*-BuOOH-CH₂Cl₂ (2.9 M, 1.4 ml, 4.0 mmol) was added dropwise during 5 min at -30 °C. The resulting solution was stirred at -30 °C for 30 min. Then, 10% aqueous tartaric acid (5.0 ml) was added, and the whole was stirred at -30 °C for 30 min and at room temperature for 1 h. The reaction mixture was extracted with CH₂Cl₂. The CH₂Cl₂ extract was washed with brine, and dried over MgSO₄. Removal of the solvent under reduced pressure gave a product (610 mg), which was purified by column chromatography (SiO₂ 70 g, *n*-hexane:EtOAc=40:1) to furnish the epoxy alcohol **13b** (473 mg, 1.64 mmol).

13b: A colorless oil, [α]_D²⁰ +17° (*c*=2.1 in CHCl₃ at 27 °C).

Determination of Enantiomeric Excess of 13a and 13b Ice-cooled solutions of **13a** (20 mg) and **13b** (20 mg), respectively, in acetic anhydride (0.5 ml) and pyridine (1 ml) were left standing at room temperature for 6 h. Each reaction mixture was poured into ice-water and extracted with EtOAc. After usual work-up of the EtOAc extracts, the solvent was evaporated off under reduced pressure to yield products. Purification of the products by column chromatography (SiO₂ 5 g, *n*-hexane:EtOAc=3:1) afforded the corresponding acetate derivatives, **13c** (19.2 mg) and **13d** (18.7 mg).

13c and 13d: ¹H-NMR (500 MHz, CDCl₃) δ: 1.21 (3H, t, *J*=7.2 Hz), 2.10 (3H, s, -OCOCH₃), 2.85, 2.97 (1H each, both ddd-like), 3.42, 3.49, 3.57, 3.66 (1H each, all ddd, *J*=7.0, 9.5, 14.0 Hz, -OCH₂CH₂O-), 3.93 (2H, dd, *J*=6.4, 12.2 Hz), 4.36 (2H, dd *J*=3.4, 12.2 Hz), 4.68 (2H, q, *J*=7.2 Hz, -OCH₂CH₃).

Enantiomeric excess of **13c** and **13d** was determined from the ratio of the signal intensity of an acetoxy methyl moiety in the ¹H-NMR spectra in the presence of Tris[3-(heptafluoropropyl)hydroxymethylene]-(+)-camphorato]europium(III) (0.6 eq), and was 92% in both cases.

Conversion of 13a to 14 A solution of **13a** (150 mg, 0.52 mmol) in dry toluene (3.4 ml) was treated with 1.5 M DIBAL-toluene reagent (1.4 ml, 2.1 mmol), and the mixture was stirred at room temperature for 15 min. After usual work-up of the reaction mixture, the solvent was evaporated off under reduced pressure to yield a product (220 mg), which was purified by column chromatography (SiO₂ 30 g, *n*-hexane:EtOAc=2:1) to afford a product (140 mg). A solution of this product in pyridine (1.5 ml) was treated with *p*-toluenesulfonyl chloride (99 mg), and the whole was allowed to stand at 0 °C. The reaction mixture was poured into ice-water and the whole was extracted with EtOAc. The EtOAc extract was washed successively with aqueous 5% HCl, aqueous saturated NaHCO₃ and brine, then dried over MgSO₄. Removal of the solvent under reduced pressure gave a monotosylate derivative. A solution of this derivative in MeOH (0.5 ml) was treated with 28% NaOMe-MeOH (0.2 ml) and the whole was stirred for 10 min at 0 °C. After usual work-up of the reaction mixture, the solvent was evaporated under reduced pressure to yield a product. Column chromatography (SiO₂ 30 g, *n*-hexane:EtOAc=3:1) of the product afforded **14** (86 mg, 0.32 mmol).

14: A colorless oil, [α]_D²⁰ +3.7° (*c*=2.0 in CHCl₃ at 26 °C). IR (film) cm⁻¹: 2976, 2930, 2858. ¹H-NMR (90 MHz, CDCl₃) δ: 1.20 (3H, t, *J*=7.0 Hz, -OCH(CH₃)OCH₂CH₃), 1.30 (3H, d, *J*=5.0 Hz, -OCH(CH₃)OCH₂CH₃), 2.46 (1H, m), 2.8-3.0 (2H, m). EI-MS *m/z* (%): 257 (M⁺-CH₃, 0.8), 227 (0.4), 73 (100). High-resolution EI-MS *m/z*: Calcd for C₁₅H₂₉O₃ (M⁺-CH₃): 257.2112. Found: 257.2114.

Conversion of 14 to 15 A solution of **14** (86 mg, 0.32 mmol) in THF (7.0 ml) was treated with 2.0 M *n*-butylmagnesium chloride-THF reagent (1.6 ml, 3.2 mmol) and the mixture was stirred at room temperature for 5 h. The reaction was quenched with 5% aqueous NH₄Cl and the whole was extracted with EtOAc. The EtOAc extract was washed with brine and then dried over MgSO₄. Removal of the solvent under reduced pressure gave a product (106 mg), which was purified by column chromatography (SiO₂ 10 g, *n*-hexane:EtOAc=20:1) and HPLC (Cosmosil 5SL, *n*-hexane:EtOAc=10:1) to furnish an alcoholic derivative (46 mg). A solution of this derivative (46 mg) in benzoyl chloride (1.5 ml) and pyridine (2.0 ml) was stirred at 0 °C for 30 min. The

reaction mixture was poured into ice-water and extracted with EtOAc. After usual work-up of the EtOAc extract, the solvent was evaporated under reduced pressure to yield a benzoyl derivative (174 mg). A solution of this product (174 mg) in 95% EtOH (1.5 ml) was treated with *p*-toluenesulfonic acid (10 mg) and the whole was stirred at room temperature for 1 h. The reaction mixture was poured into ice-water and extracted with EtOAc. After usual work-up of the EtOAc extract, the solvent was evaporated under reduced pressure to yield a product, which was purified by column chromatography (SiO₂ 10 g, *n*-hexane:EtOAc=6:1) to afford **15** (44.3 mg, 0.12 mmol).

15: A colorless oil, $[\alpha]_D^{+1.4}$ ($c=2.5$ in CHCl₃ at 27°C). IR (film) cm⁻¹: 1707. ¹H-NMR (90 MHz, CDCl₃, δ): 0.88 (3H, t-like, ω -CH₃), 3.64 (2H, t, $J=6.0$ Hz, -CH₂OH), 5.11 (1H, m, -CH-OBz), 7.3–7.6, 7.9–8.1 (totally 5H, m, aromatic protons). EI-MS m/z (%): 362 (M^+ , 0.4), 123 (100). High-resolution EI-MS m/z : Calcd for C₂₃H₃₈O₃; 362.2839. Found: 362.2821 (M^+).

Methyl (11S)-(+)-Jalapinate (16a) from 15 A solution of **15** (44 mg, 0.12 mmol) in acetone (1.0 ml) was treated with the Jones reagent (CrO₃-H₂SO₄, 2 ml)⁹ and the mixture was stirred at 0°C for 1 h. Then 2-propanol (0.5 ml) was added and the mixture was extracted with ether. The ether extract was washed with brine, and then dried over MgSO₄. Removal of the solvent under reduced pressure gave a product (50 mg). A solution of this product (50 mg) in ether (2.0 ml) was treated with a CH₂N₂ ether solution and the whole was left standing at 0°C for 1 h. The solvent was evaporated under reduced pressure to yield a product (44 mg). A solution of the product in MeOH (1.0 ml) was treated with 28% NaOMe-MeOH (0.2 ml) and the reaction mixture was stirred at room temperature for 2 h, poured into ice-water and extracted with EtOAc. After usual work-up of the EtOAc extract, the solvent was concentrated under reduced pressure to yield a product. Column chromatography (SiO₂ 5 g, *n*-hexane:EtOAc=7:1) of the product afforded **16a** (19 mg, 0.065 mmol).

The physical data for **16a** $\{[\alpha]_D^{+0.9}$ ($c=1.8$, in CHCl₃ at 25°C) $\}$ were identical with those for **7** prepared from merremoside d (**4**).

Alkaline Hydrolysis of 16a Giving (11S)-(+)-Jalapinic Acid (16b) Methyl (11S)-(+)-jalapinate (**16a**, 10 mg) was converted into **16b** (7 mg) through a similar procedure to that used to obtain **7a** from **7**. The physical data for **16b** $\{[\alpha]_D^{+0.7}$ ($c=0.7$, in CHCl₃ at 25°C) $\}$ were identical with those for **7a**.

Methyl (11R)-(-)-Jalapinic Acid (18a) and (11R)-(-)-Jalapinic Acid (18b) from 13b Through a similar procedure to that used to convert **13a** to **16a** and **16b**, **13b** (150 mg) was converted to **18a** (17 mg) and **18b** (8 mg).

18a: Colorless needles from petroleum ether; $[\alpha]_D^{-0.9}$ ($c=1.7$ in CHCl₃ at 24°C).

18b: Colorless needles from petroleum ether; mp 65–67°C, $[\alpha]_D^{-0.8}$ ($c=0.8$ in CHCl₃ at 24°C).

Application of Horeau's Method to 7, 16a, and 18a A solution of **7** (20 mg) in pyridine (3 ml) was treated with ($\pm$)-2-phenylbutyric anhydride (80 mg), and the mixture was stirred at room temperature for 24 h. Ice-water and ether were added, followed by 5% aqueous NaHCO₃. The NaHCO₃ phase was acidified with 3N HCl, and extracted with ether. The extract was washed with brine, and dried over MgSO₄. The solvent was evaporated under reduced pressure to give a product, which was purified by silica gel column chromatography (SiO₂ 10 g, *n*-hexane-EtOAc=2:1) to afford 2-phenylbutyric acid [56 mg, $[\alpha]_D^{+0.18}$ ($c=5.1$ in benzene at 25°C)].

By means of the same procedure as described above for **7**, 2-phenylbutyric acid $\{[\alpha]_D^{+0.13}$ ($c=3.1$ in benzene at 25°C) $\}$ was recovered from **16a** and also $\{[\alpha]_D^{-0.19}$ ($c=3.3$ in benzene at 25°C) $\}$ from **18a**.

Complete Methylation of Merremoside i Methyl Ester (6a) Followed by Methanolysis A solution of merremoside i methyl ester (**6a**, 41 mg) in dimethylsulfoxide (DMSO, 2.0 ml) was treated with the dimethyl sodium reagent [1.0 ml, prepared from 60% NaH (1.0 g) and DMSO (10 ml)],¹⁶ and the whole was stirred at room temperature for 2 h. Methyl iodide (4.0 ml) was added and stirring was continued at room temperature for 7.5 h. The reaction mixture was poured into ice-water and extracted with EtOAc. The EtOAc extract was washed with H₂O and the solvent was concentrated under reduced pressure to give a product (26 mg). A solution of this product (26 mg) in 9% HCl-MeOH (3.0 ml) was heated under reflux for 2 h. After cooling, the reaction mixture was neutralized with AgCO₃ powder and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (43 mg). The

product was subjected to GLC analysis to identify methyl 2,3-di-*O*-methyl-L-rhamnopyranoside and methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside in a ratio of 3:1. GLC conditions-1: column, 15% NPGS on Chromosorb WAW (80/100), i.d. 3 mm $\times$ 2 m glass column; column temperature, 170°C; carrier gas, N₂; flow rate, 35 ml/min; injection temperature, 190°C; detector: FID; t_R , 6 min 38 s for methyl 2,3-di-*O*-methyl-L-rhamnopyranoside, 2 min 41 s for methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside. GLC conditions-2: column, SE-52, 25 m capillary column; column temperature, 125°C; carrier gas, N₂; flow rate, 50 ml/min; injection temperature, 150°C; detector: FID; t_R , 4 min 22 s for methyl 2,3-di-*O*-methyl-L-rhamnopyranoside, 3 min 44 s for methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside.

Glycosidation of Methyl (11S)-(+)-Jalapinate (7) Giving Monoglycoside (20) A solution of **7** (450 mg, 1.57 mmol) and 2,3,4-tri-*O*-acetyl-L-rhamnopyranosyl-1-*O*-trichloroacetimidate (**19**, 1.03 g, 2.36 mmol) in CH₂Cl₂ (30 ml) was treated with BF₃-Et₂O (14 μ l, 0.05 eq) and molecular sieves 4 Å (10 g). The mixture was stirred at -40°C for 3 h, then poured into ice-water and extracted with CH₂Cl₂. After usual work-up of the CH₂Cl₂ extract, the solvent was evaporated under reduced pressure to yield a product (1.36 g). Purification of the product by column chromatography (SiO₂ 50 g, *n*-hexane:EtOAc=4:1) afforded a glycoside (840 mg). A solution of this product (840 mg) in MeOH (5 ml) was treated with 2% NaOMe-MeOH (5 ml) and the whole was stirred at room temperature for 30 min. The reaction mixture was neutralized with Dowex 50W $\times$ 8 (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (800 mg) which was purified by column chromatography (SiO₂ 20 g, *n*-hexane:EtOAc=1:4) to afford **20** (578 mg, 1.34 mmol).

20: A white powder, $[\alpha]_D^{-45}$ ($c=2.1$, in CHCl₃ at 24°C). IR (CHCl₃) cm⁻¹: 3590, 2985, 1730. ¹H-NMR (500 MHz, CDCl₃) δ : 0.90 (3H, t, $J=7.0$ Hz, ω -CH₃), 1.31 (3H, d, $J=6.1$ Hz, 6'-H₃), 2.31 (2H, t, $J=7.7$ Hz, 2-H), 3.46 (1H, m, 11-H), 3.60 (1H, dd, $J=9.2$, 9.2 Hz, 4'-H), 3.67 (3H, s, -COOCH₃), 3.75 (1H, m, 5'-H), 3.77 (1H, dd, $J=3.1$, 9.2 Hz, 3'-H), 3.89 (1H, brs, 2'-H), 4.86 (1H, brs, 1'-H). Anal. Calcd for C₂₃H₄₄O₇·H₂O: C, 61.31; H, 10.29. Found: C, 61.11; H, 10.39.

Conversion of 20 to 21 A solution of **20** (200 mg, 0.46 mmol) in *N,N*-dimethylformamide (3.0 ml) was treated with 2,2-dimethoxypropane (230 μ l, 2.5 mmol) and (1*R*)-(-)-10-camphorsulfonic acid (5 mg) and the whole was stirred at room temperature for 3 h. It was then poured into ice-water and extracted with EtOAc. After usual work-up of the EtOAc extract, the solvent was evaporated off under reduced pressure to yield a product (410 mg). Purification of the product by column chromatography (SiO₂ 20 g, *n*-hexane:EtOAc=2:1) afforded **21** (214 mg, 0.45 mmol).

21: A white powder, $[\alpha]_D^{-24}$ ($c=2.5$, in CHCl₃ at 26°C). IR (CHCl₃) cm⁻¹: 3595, 2985, 1728. ¹H-NMR (500 MHz, CDCl₃) δ : 0.88 (3H, t, $J=7.0$ Hz, ω -CH₃), 1.38, 1.42 (3H each, both s), 1.49 (3H, d, $J=6.4$ Hz, 6'-H₃), 2.31 (2H, t, $J=7.1$ Hz, 2-H₂), 3.57 (1H, m, 11-H), 3.67 (3H, s, -COOCH₃), 3.79 (1H, dd, $J=4.0$, 6.8 Hz, 4'-H), 4.05 (1H, m, 5'-H), 4.59 (1H, brd, $J=7.0$ Hz, 2'-H), 4.86 (1H, dd, $J=4.0$, 7.0 Hz, 3'-H), 5.12 (1H, brs, 1'-H). EI-MS m/z (%): 457 (M^+ -CH₃, 24), 315 (87), 269 (100), 99 (91). High-resolution EI-MS m/z : Calcd for C₂₅H₄₅O₇ (M^+ -CH₃): 457.3162. Found: 457.3161.

Conversion of 21 to 22 A solution of **21** (200 mg, 0.42 mmol) in CH₂Cl₂ (15 ml) was treated with **19** (400 mg, 0.92 mmol), BF₃-Et₂O (6 μ l, 0.05 eq), and molecular sieves 4 Å (7 g). The mixture was stirred at -40°C for 4 h, then poured into ice-water and extracted with CH₂Cl₂. After usual work-up of the CH₂Cl₂ extract, the solvent was concentrated under reduced pressure to yield a product (620 mg). A solution of the product (620 mg) in MeOH (2.5 ml) was treated with 10% NaOMe-MeOH (2.5 ml) and the mixture was stirred at room temperature for 30 min. It was then neutralized with Dowex 50W $\times$ 8 (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (500 mg), which was purified by column chromatography (SiO₂ 15 g, *n*-hexane:EtOAc=2:7) to afford **22** (152 mg, 0.24 mmol).

22: A colorless oil, $[\alpha]_D^{-56}$ ($c=1.9$, in CHCl₃ at 25°C). IR (CHCl₃) cm⁻¹: 3610, 2970, 1730. ¹H-NMR (500 MHz, CDCl₃) δ : 0.90 (3H, t, $J=7.7$ Hz, ω -CH₃), 1.24–1.34 (3H $\times$ 4), 2.31 (2H, t, $J=7.7$ Hz, 2-H₂), 3.53 (1H, dd, $J=7.3$, 10.1 Hz, 4'-H), 3.63 (1H, dd, $J=5.8$, 7.3 Hz, 3'-H), 3.67 (3H, s, -COOCH₃), 3.70–3.78 (2H, m, 5'-H, 5''-H), 3.72 (1H dd, $J=7.3$, 11.1 Hz, 4'-H), 3.98 (1H, brs, 2'-H), 4.06 (1H, brd, $J=5.6$ Hz, 2'-H), 4.17 (1H, dd, $J=5.6$, 7.3 Hz, 3'-H), 5.04 (1H, brs, 1'-H), 5.37 (1H, brs, 1''-H). Anal. Calcd for C₃₂H₅₈O₁₁·H₂O: C, 60.36; H, 9.50.

Found: C, 60.56; H, 9.29.

Conversion of 22 to 23 A solution of **22** (152 mg, 0.24 mmol) in *N,N*-dimethylformamide (2.0 ml) was treated with 2,2-dimethoxypropane (90 μ l, 0.76 mmol) and (1*R*)-(–)-10-camphorsulfonic acid (5 mg), and the mixture was stirred at room temperature for 2 h, then poured into ice-water and extracted with EtOAc. Usual work-up of the EtOAc solution followed by evaporation under reduced pressure afforded a product (148 mg). Purification of the product by column chromatography (SiO₂ 15 g, *n*-hexane:EtOAc=3:1) afforded a diisopropylidene derivative (148 mg, 0.21 mmol). A solution of the diisopropylidene derivative (148 mg, 0.21 mmol) in CH₂Cl₂ (10 ml) was treated with **19** (140 mg, 0.32 mmol), BF₃·Et₂O (3 ml, 0.05 eq) and molecular sieves 4 Å (5 g). The mixture was stirred at –40 °C for 2 h, then poured into ice-water and extracted with CH₂Cl₂. After usual work-up of the CH₂Cl₂ extract, the solvent was evaporated under reduced pressure to yield a product (210 mg). A solution of this product in MeOH (2.5 ml) was treated with 10% NaOMe–MeOH (2.5 ml), and the mixture was stirred at room temperature for 30 min. It was then neutralized with Dowex 50W × 8 (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (330 mg), which was purified by column chromatography (SiO₂ 15 g, *n*-hexane:EtOAc=2:3) to afford a triglycoside (108 mg). A solution of the triglycoside (50 mg, 0.087 mmol) in *N,N*-dimethylformamide (1 ml) was treated with 2,2-dimethoxypropane (50 μ l, 0.42 mmol) and (1*R*)-(–)-10-camphorsulfonic acid (5 mg), and the whole was stirred at room temperature for 2 h. The reaction mixture was poured into ice-water and extracted with EtOAc. After usual work-up of the EtOAc extract, the solvent was evaporated off under reduced pressure to yield a product (148 mg). Purification of the product by column chromatography (SiO₂ 10 g, *n*-hexane:EtOAc=3:1) afforded **23** (72 mg, 0.085 mmol).

23: A colorless oil, $[\alpha]_D^{25} -41^\circ$ ($c=1.3$, in CHCl₃ at 25 °C). IR (CHCl₃) cm^{–1}: 3510, 2993, 1725. ¹H-NMR (500 MHz, CDCl₃) δ : 0.90 (3H, t, $J=7.5$ Hz, ω -CH₃), 1.28–1.64 (totally 3H × 9), 2.31 (2H, t, $J=7.6$ Hz, 2-H₂), 3.67 (3H, s, –COOCH₃), 5.05 (1H, brs, 1'-H), 5.61 (2H, brs, 1''-H, 1'''-H). Anal. Calcd for C₄₄H₇₆O₁₅·2H₂O: C, 59.99; H, 9.15. Found: C, 60.13; H, 9.02.

Conversion of 23 to Merremoside i Methyl Ester (6a) A solution of **23** (30 mg, 0.036 mmol) and **19** (30 mg, 0.069 mmol) in CH₂Cl₂ (2.0 ml) was treated with BF₃·Et₂O (1.5 μ l, 0.05 eq) in the presence of molecular sieves 4 Å (2 g), and stirred at –40 °C for 2 h. The reaction mixture was poured into ice-water and then extracted with CH₂Cl₂. After usual work-up of the CH₂Cl₂ extract, the solvent was evaporated off under reduced pressure to yield a product (85 mg). A solution of the product in MeOH (1.0 ml) was treated with 2% NaOMe–MeOH (1.0 ml) and the reaction mixture was stirred at room temperature for 20 min, poured into ice-water and extracted with CHCl₃. After usual work-up of the EtOAc extract, the solvent was concentrated under reduced pressure to yield a product (33.1 mg), which was purified by column chromatography (SiO₂ 10 g, *n*-hexane:EtOAc=1:4) to afford a product (72 mg). This product (10 mg) was treated with 1% HCl–MeOH (1.0 ml) with stirring at room temperature for 2 h. The reaction mixture was neutralized with AgCO₃ powder and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (23 mg). Purification of this product by column chromatography (SiO₂ 7 g, CHCl₃:MeOH=3:1) afforded the product (7.0 mg, 0.008 mmol), which was identified as merremoside i methyl ester (**6a**), prepared from merremoside d (**4**).

Preparation of 25 from Merremoside d (4) via 24 A solution of merremoside d (**4**, 200 mg) in *N,N*-dimethylformamide (2.0 ml) was treated with 2,2-dimethoxypropane (1.0 ml) in the presence of (1*R*)-(–)-10-camphorsulfonic acid (5 mg) with stirring at room temperature for 4 h. The reaction mixture was poured into ice-water and extracted with EtOAc. After usual work-up of the EtOAc extract, the solvent was evaporated off under reduced pressure to yield a product (**24**, 324 mg). A solution of **24** in MeOH (2.0 ml) was treated with 10% NaOMe–MeOH (1.0 ml), and the whole was stirred at room temperature for 1 h. The reaction mixture was neutralized with Dowex 50W × 8 (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (225 mg). Purification of the product by column chromatography (SiO₂ 50 g, CHCl₃:MeOH=10:1) afforded **25** (84.2 mg).

25: Colorless fine crystals from EtOH, mp 115–116 °C, $[\alpha]_D^{25} -80^\circ$ ($c=1.1$, in MeOH at 20 °C). IR (CHCl₃) cm^{–1}: 3400, 2920, 1720. ¹H-NMR (90 MHz, pyridine-*d*₅ + D₂O) δ : 0.96 (3H, t, $J=6.7$ Hz,

ω -CH₃), 1.37–1.62 (3H × 4, 6'-, 6''-, 6'''-, 6''''-H₃), 1.70–1.74 (totally 3H × 4), 2.30 (2H, t, $J=7.0$ Hz, 2-H₂), 3.69 (3H, s, –COOCH₃), 5.33, 5.96, 6.30, 6.45 (1H each, all brs, 1'-, 1''-, 1'''-, 1''''-H). Anal. Calcd. for C₄₇H₈₂O₁₉·2H₂O: C, 58.25; H, 8.74. Found: C, 57.78; H, 8.67.

Conversion of 25 to 27 via 26 A solution of **25** (68 mg) in MeOH (2.0 ml) was treated with 1% aqueous sodium periodate (1.0 ml) and the mixture was stirred at room temperature for 2 h, then poured into ice-water and extracted with *n*-BuOH. Removal of the solvent under reduced pressure gave a product (104 mg). A solution of this product in MeOH (4.0 ml) was treated with 10% KOH–MeOH (1 ml) and the whole was stirred at room temperature for 1 h. The reaction mixture was neutralized with Dowex 50W × 8 (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (42 mg), which was purified by column chromatography [SiO₂ 20 g, CHCl₃:MeOH:H₂O=10:3:1 (lower phase)] to afford **26** (18 mg). A solution of **26** (6 mg) in pyridine (0.2 ml) was treated with acetic anhydride (0.2 ml) and the whole was left standing at room temperature for 10 h, then poured into ice-water and extracted with EtOAc. After usual work-up of the EtOAc extract, the solvent was evaporated under reduced pressure to yield a product (15 mg). Purification of the product by column chromatography (SiO₂ 5 g, *n*-hexane:EtOAc=4:1) afforded **27** (6 mg).

27: A colorless oil, $[\alpha]_D^{25} +20^\circ$ ($c=0.5$, in CHCl₃ at 26 °C). IR (KBr) cm^{–1}: 2936, 1731. ¹H-NMR (90 MHz, CDCl₃) δ : 0.88 (3H, t-like, ω -CH₃), 1.26, 1.34 (3H each, both s), 1.50 (3H, d, $J=6.4$ Hz, 6-H₃), 2.06 (3H, s, –OCOCH₃), 2.30 (2H, t-like, 2-H₂), 3.67 (3H, s, –COOCH₃), 4.92 (1H, dd, $J=8.0$, 8.0 Hz, 4'-H), 5.12 (1H, brs, 1'-H). ¹³C-NMR (22.5 MHz, CDCl₃) δ_C : 14.2 (C-16), 21.1 (–OCOCH₃), 51.5 (–COOCH₃), 101.5 (C-1'), 110.2, 169.6 (–OCOCH₃), 174.4 (–COOCH₃). EI-MS m/z (%): 499 (M⁺–CH₃, 3), 269 (47), 115 (100). High-resolution EI-MS m/z : Calcd for C₂₇H₄₇O₈ (M⁺–CH₃): 499.3269. Found: 499.3254.

Treatment of Merremoside b (2) with 5% Aqueous KOH I) A solution of merremoside b (**2**, 5.0 mg) in acetone (1.0 ml) was treated with 5% aqueous KOH (1.0 ml) and the whole mixture was heated under reflux for 30 min. After cooling, the reaction mixture was neutralized with 5% aqueous HCl and extracted with ether. The extract was directly subjected to GLC analysis to determine isobutyric acid. GLC conditions: column, 15% FFAP on Chromosorb GAW DMSC (100/120), i.d. 3 mm × 1 m glass column; column temperature, 140 °C; carrier gas, N₂; flow rate, 30 ml/min; injection temperature, 170 °C; detector: FID; *t*_R, 8 min 46 s (isobutyric acid). II) A solution of merremoside b (**2**, 40 mg) in acetone (1.0 ml) was treated with 10% aqueous KOH (1.0 ml) and the mixture was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Dowex 50W × 8 (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product, which was purified by column chromatography [SiO₂ 10 g, CHCl₃:MeOH:H₂O=7:3:1 (lower phase)] to afford merremoside i (**6**, 32 mg).

Treatment of Merremoside b (2) with 5% NaOMe in MeOH Followed by Acidic Hydrolysis Merremoside b (**2**, 40 mg) was treated with 5% NaOMe–MeOH (1.0 ml) and the mixture was heated under reflux for 30 min. After cooling, the reaction mixture was neutralized with Dowex 50W × 8 (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product, which was purified by column chromatography (SiO₂ 10 g, CHCl₃:MeOH=3:1) to afford merremoside i methyl ester (**6a**, 31 mg). Then, a solution of **6a** (30 mg) in 9% HCl–MeOH (1.5 ml) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with AgCO₃ powder and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (21 mg). Repeated column chromatography (SiO₂ 20 g, CHCl₃:MeOH=30:1→5:1 and *n*-hexane:EtOAc=7:1) of the product afforded methyl (11*S*)-(+)-jalapinate (**7**, 3.0 mg) and methyl L-rhamnoside (9 mg).

Partial Hydrolysis of Merremoside b (2) I) Merremoside b (**2**, 70 mg) was treated with 2% NaOMe–MeOH (2.0 ml) and the whole was stirred at –15 °C for 10 min. The reaction mixture was neutralized with Dowex 50W × 8 (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (76 mg), which was purified by column chromatography (SiO₂ 50 g, CHCl₃:MeOH=15:1→12:1) to afford merremoside d (**6**, 32 mg), **28** (11 mg) and **29** (9 mg).

28: Colorless fine crystals from EtOH, mp 118–120 °C, $[\alpha]_D^{25} -48^\circ$ ($c=0.7$, in MeOH at 25 °C). IR (KBr) cm^{–1}: 3380, 2910, 1717. ¹H-NMR (500 MHz, pyridine-*d*₅ + H₂O) δ : 0.95 (3H, t, $J=7.5$ Hz, ω -CH₃), 1.14,

1.16, (3H each, both d, $J=7.0$ Hz, $-\text{CH}(\text{CH}_3)_2 \times 2$), 1.49 (3H, d, $J=6.5$ Hz), 1.55 (3H, d, $J=6.0$ Hz), 1.62 (3H, d, $J=6.0$ Hz), 1.66 (3H, d, $J=6.0$ Hz) (6'-, 6''-, 6'''-, 6''''-H₃), 2.24 (1H, ddd, $J=3.0, 6.9, 14.6$ Hz, 2-H_a), 2.62 (1H, ddd, $J=3.0, 6.9, 14.6$ Hz, 2-H_b), 3.88 (1H, m, 11-H), 5.54 (1H, dd, $J=3.0, 10.0$ Hz, 3''-H), 5.71 (1H, brs, 2''-H), 5.12, 5.50, 6.11, 6.29 (1H each, all brs, 1'-, 1''-, 1'''-, 1''''-H). ¹³C-NMR (125 MHz, pyridine-*d*₅) δ_c : 100.1, 101.5, 102.1, 103.5, 174.6, 175.8. Negative FAB-MS m/z : 907 (M-H)⁻, 761 (xiii), 545 (ix). *Anal.* Calcd for C₄₄H₇₆O₁₉·2H₂O: C, 55.92; H, 8.53. Found: C, 56.20; H, 8.71.

29: Colorless fine crystals from EtOH, mp 110–111 °C, $[\alpha]_D -45^\circ$ ($c=0.7$, in MeOH at 25 °C). IR (KBr) cm^{-1} : 3380, 2905, 1717. ¹H-NMR (500 MHz, pyridine-*d*₅ + H₂O) δ : 0.95 (3H, t, $J=7.5$ Hz, $\omega\text{-CH}_3$), 1.18, 1.24 (3H each, both d, $J=7.0$ Hz, $-\text{CH}(\text{CH}_3)_2 \times 2$), 1.50 (3H, d, $J=6.5$ Hz), 1.54 (3H, d, $J=6.0$ Hz), 1.55 (3H, d, $J=6.0$ Hz), 1.57 (3H, d, $J=6.0$ Hz) (6'-, 6''-, 6'''-, 6''''-H₃), 2.14 (1H, ddd, $J=3.0, 7.0, 14.8$ Hz, 2-H_a), 2.28 (1H, ddd, $J=3.0, 7.0, 14.8$ Hz, 2-H_b), 3.85 (1H, m, 11-H), 5.62 (1H, dd, $J=3.0, 10.0$ Hz, 3''-H), 5.66 (1H, dd, $J=3.0, 10.0$ Hz, 3'''-H), 5.14, 5.65, 5.82, 6.31 (1H each, all brs, 1'-, 1''-, 1'''-, 1''''-H). ¹³C-NMR (125 MHz, pyridine-*d*₅) δ_c : 99.8, 101.4, 102.1, 103.2, 174.1, 175.8. Negative FAB-MS m/z : 907 (M-H)⁻, 761 (viii), 545 (ix). *Anal.* Calcd for C₄₄H₇₆O₁₉·3H₂O: C, 54.87; H, 8.58. Found: C, 54.59; H, 8.81.

II) Merremoside b (2, 80 mg) was treated with 4% NaOMe–MeOH (2.0 ml) and the whole was stirred at 0 °C for 30 min. The reaction mixture was neutralized with Dowex 50W $\times 8$ (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (76 mg). Purification of the product by column chromatography (SiO₂ 50 g, CHCl₃:MeOH=5:1) afforded merremoside i methyl ester (**6a**, 31 mg), **30** (16 mg), and **31** (3 mg).

30: Colorless fine crystals from EtOH, mp 144–146 °C, $[\alpha]_D -75^\circ$ ($c=1.0$, in MeOH at 25 °C). IR (KBr) cm^{-1} : 3384, 2920, 1718. ¹H-NMR (500 MHz, pyridine-*d*₅ + H₂O) δ : 0.95 (3H, t, $J=7.5$ Hz, $\omega\text{-CH}_3$), 1.49 (3H, d, $J=6.5$ Hz), 1.56 (3H, d, $J=6.0$ Hz), 1.57 (3H, d, $J=6.0$ Hz), 1.57 (3H, d, $J=6.0$ Hz) (6'-, 6''-, 6'''-, 6''''-H₃), 2.24 (1H, ddd, $J=3.0, 7.0, 15.0$ Hz, 2-H_a), 2.28 (1H, ddd, $J=3.0, 7.0, 15.0$ Hz, 2-H_b), 3.82 (1H, m, 11-H), 5.55 (1H, dd, $J=3.0, 10.0$ Hz, 3''-H), 5.11, 5.76, 6.20, 6.31 (1H each, all brs, 1'-, 1''-, 1'''-, 1''''-H). ¹³C-NMR (125 MHz, pyridine-*d*₅) δ_c : 100.0, 102.3, 102.9, 103.1, 174.4. Negative FAB-MS m/z : 837 (M-H)⁻, 691 (xiv), 545 (ix). *Anal.* Calcd for C₄₀H₇₈O₁₈·3H₂O: C, 54.31; H, 8.71. Found: C, 54.24; H, 8.59.

31: Colorless fine crystals from EtOH, mp 103–104 °C, $[\alpha]_D -74^\circ$ ($c=0.3$, in MeOH at 25 °C). IR (KBr) cm^{-1} : 3380, 2917, 1715. ¹H-NMR (500 MHz, pyridine-*d*₅ + H₂O) δ : 0.93 (3H, t, $J=7.5$ Hz, $\omega\text{-CH}_3$), 1.18, 1.32 (3H each, both d, $J=7.0$ Hz, $-\text{CH}(\text{CH}_3)_2 \times 2$), 1.50 (3H, d, $J=6.8$ Hz), 1.58 (3H, d, $J=7.0$ Hz), 1.58 (3H, d, $J=6.4$ Hz), 1.59 (3H, d, $J=6.4$ Hz) (6'-, 6''-, 6'''-, 6''''-H₃), 2.31 (2H, t, $J=7.4$ Hz, 2-H₂), 3.63 (3H, s, $-\text{COOCH}_3$), 3.97 (1H, m, 11-H), 5.73 (1H, dd, $J=3.0, 10.0$ Hz, 3''-H), 5.11, 5.74, 6.15, 6.20 (1H each, all brs, 1'-, 1''-, 1'''-, 1''''-H). ¹³C-NMR (125 MHz, pyridine-*d*₅) δ_c : 101.3, 102.2, 102.9, 103.0, 174.1, 175.8. Negative FAB-MS m/z : 939 (M-H)⁻, 793 (xv), 577 (xvi). *Anal.* Calcd for C₄₅H₈₀O₂₀·3H₂O: C, 53.80; H, 8.58. Found: C, 54.01; H, 8.52.

Treatment of Merremoside c (3) with 5% Aqueous KOH **I)** A solution of merremoside c (**3**, 5.0 mg) in acetone (1.0 ml) was treated with 5% aqueous KOH (1.0 ml) and the mixture was heated under reflux for 30 min. After cooling, the reaction mixture was neutralized with 5% aqueous HCl, and then extracted with ether. The extract was directly subjected to GLC analysis to determine isobutyric acid and methylbutyric acid. GLC conditions: column, 15% FFAP on Chromosorb GAW DMSC (100/120), i.d. 3 mm $\times$ 1 m glass column; column temperature, 140 °C; carrier gas, N₂; flow rate, 30 ml/min; injection temperature, 170 °C; detector: FID; t_R , 8 min 46 s (isobutyric acid), 12 min 46 s (methylbutyric acid). **II)** A solution of merremoside c (**3**, 40 mg) in acetone (1.0 ml) was treated with 10% aqueous KOH (1.0 ml) and the whole was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Dowex 50W $\times 8$ (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product, which was purified by column chromatography [SiO₂ 10 g, CHCl₃:MeOH:H₂O=7:3:1 (lower phase)] to afford merremoside i (**6**, 28 mg).

Absolute Configuration of Methylbutyric Acid A solution of merremoside c (**3**, 1.0 g) in CHCl₃–acetone (1:1, 5.0 ml) was treated with 5% aqueous KOH (5.0 ml) and stirred under reflux for 4 h. After the removal of acetone under reduced pressure, the reaction mixture was neutralized with 5% aqueous HCl, and extracted with EtOAc. After

usual work-up of the EtOAc extract, the solvent was evaporated off under reduced pressure to yield a product (720 mg). A solution of the product in *N,N*-dimethylformamide (3 ml) was treated with potassium fluoride (300 mg) and α -bromoacetophenone (400 mg) with stirring at room temperature for 1 h. The reaction mixture was poured into ice-water and extracted with ether. After usual work-up of the ether extract, the solvent was concentrated under reduced pressure to give a product (1.32 g). Purification of this product by column chromatography (SiO₂ 10 g, *n*-hexane:EtOAc=15:1) and HPLC (Zorbax SIL, 0.25 m $\times$ 4.6 mm, *n*-hexane:EtOAc=7:1) afforded isobutyric acid phenacyl ester (92.1 mg) and (2*S*)-(+)-methylbutyric acid phenacyl ester [50.0 mg, $[\alpha]_D +15^\circ$ ($c=4.6$, in CHCl₃ at 25 °C)].

Treatment of Merremoside c (3) with 5% NaOMe in MeOH Merremoside c (**3**, 40 mg) was treated with 5% NaOMe–MeOH (1.0 ml) and the mixture was heated under reflux for 30 min. After cooling, the reaction mixture was neutralized with Dowex 50W $\times 8$ (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product, which was purified by column chromatography (SiO₂ 10 g, CHCl₃:MeOH=3:1) to afford merremoside i methyl ester (**6a**, 30 mg).

Methanolysis of Merremoside c (3) A solution of merremoside c (**3**, 60 mg) in 9% HCl–MeOH (2.0 ml) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with AgCO₃ powder and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (43 mg). Repeated column chromatography (SiO₂ 20 g, CHCl₃:MeOH=30:1 $\rightarrow$ 5:1, *n*-hexane:EtOAc=7:1) of the product afforded methyl (1*S*)-(+)-jalapinololate (**7**, 5.9 mg) and methyl L-rhamnoside (15 mg). A solution of methyl L-rhamnoside (1 mg) in pyridine (0.3 ml) was treated with *N,O*-bis(trimethylsilyl)trifluoroacetamide (0.5 ml) at room temperature for 1 h. The reaction mixture was subjected to GLC analysis to identify methyl 2,3,4-*O*-tri(trimethylsilyl)-L-rhamnopyranoside. GLC conditions-1: column, 15% silicone OV-1 on Chromosorb WAW DMSC (80/100), i.d. 3 mm $\times$ 1 m glass column; column temperature, 150 °C; carrier gas, N₂; flow rate, 30 ml/min; injection temperature, 170 °C; detector: FID; t_R , 4 min 01 s. GLC conditions-2: column, 15% silicone SE-30 on Chromosorb WAW DMSC (80/100), i.d. 3 mm $\times$ 1 m glass column; column temperature, 150 °C; carrier gas, N₂; flow rate, 30 ml/min; injection temperature, 170 °C; detector: FID; t_R , 3 min 42 s.

A solution of methyl L-rhamnoside (15 mg) in 1*N* HCl was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with AgCO₃ powder and the precipitate was removed by filtrate. The filtrate was concentrated under reduced pressure to give a product, which was purified by column chromatography (SiO₂ 7 g, CHCl₃:MeOH=3:1) to afford L-rhamnose [10 mg, $[\alpha]_D +9.0^\circ$ ($c=0.9$, in H₂O at 25 °C)].

Treatment of Merremoside a (1) with 5% Aqueous KOH **I)** A solution of merremoside a (**1**, 5.0 mg) in acetone (1.0 ml) was treated with 5% aqueous KOH (1.0 ml) and the mixture was heated under reflux for 30 min. After cooling, the reaction mixture was neutralized with 5% aqueous HCl and extracted with ether. The extract was subjected to GLC analysis to determine methylbutyric acid. GLC conditions: column, 15% FFAP on Chromosorb GAW DMSC (100/120), i.d. 3 mm $\times$ 1 m glass column; column temperature, 140 °C; carrier gas, N₂; flow rate, 30 ml/min; injection temperature, 170 °C; detector: FID; t_R , 12 min 46 s (methylbutyric acid). **II)** A solution of merremoside a (**1**, 40 mg) in acetone (1.0 ml) was treated with 10% aqueous KOH (1.0 ml) and the mixture was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Dowex 50W $\times 8$ (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product, which was purified by column chromatography [SiO₂ 10 g, CHCl₃:MeOH:H₂O=7:3:1 (lower phase)] to afford merremoside i (**6**, 28 mg).

Methanolysis of Merremoside a (1) A solution of merremoside a (**1**, 50 mg) in 9% HCl–MeOH was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with AgCO₃ powder and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (43 mg), which was purified by column chromatography (SiO₂ 20 g, CHCl₃:MeOH=30:1 $\rightarrow$ 5:1, *n*-hexane:EtOAc=7:1) to afford methyl (1*S*)-(+)-jalapinololate (**6a**, 6.0 mg) and methyl L-rhamnoside (15 mg). A solution of methyl L-rhamnoside (1.0 mg) in pyridine (0.3 ml) was treated with *N,O*-bis(trimethylsilyl)trifluoroacetamide (0.5 ml) at room temperature for 1 h. The reaction mixture was subjected to GLC analysis to identify methyl 2,3,4-*O*-tri(trimethylsilyl)-L-rhamnopyranoside. GLC conditions-1: column, 15%

silicone OV-1 on Chromosorb WAW DMSC (80/100), i.d. 3 mm $\times$ 1 m glass column; column temperature, 150 °C; carrier gas, N₂; flow rate, 30 ml/min; injection temperature, 170 °C; detector: FID; t_R , 4 min 01 s. GLC conditions-2: column, 15% silicone SE-30 on Chromosorb WAW DMSC (80/100), i.d. 3 mm $\times$ 1 m glass column; column temperature, 150 °C; carrier gas, N₂; flow rate, 30 ml/min; injection temperature, 170 °C; detector: FID; t_R , 3 min 42 s.

A solution of methyl L-rhamnoside (15 mg) in 1 N HCl was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with AgCO₃ powder and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product. Purification of this product by column chromatography (SiO₂ 7 g, CHCl₃:MeOH=3:1) afforded L-rhamnose [11 mg, $[\alpha]_D^{+9.0}$ ($c=0.9$, H₂O, after 1 h, at 25 °C)].

Treatment of Merremoside e (5) with 5% Aqueous KOH A solution of merremoside e (5, 50 mg) in acetone (2.0 ml) was treated with 5% aqueous KOH (1.0 ml) and the mixture was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Dowex 50W $\times$ 8 (H⁺ form) and the resin was removed by filtration. The filtrate was concentrated under reduced pressure to give a product. Purification of this product by column chromatography [SiO₂ 10 g, CHCl₃:MeOH:H₂O=7:3:1 (lower phase)] afforded merremoside i (6, 28 mg) and isobutyric acid, which was detected by GLC analysis. GLC conditions: column, 15% FFAP on Chromosorb GAW DMSC (100/120), i.d. 3 mm $\times$ 1 m glass column; column temperature, 140 °C; carrier gas, N₂; flow rate, 30 ml/min; injection temperature, 170 °C; detector: FID; t_R , 8 min 46 s (isobutyric acid).

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