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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)

Isao KITAGAWA,[a] Nam In BAEK,[a] Keiko KAWASHIMA,[a] Yoshihiro YOKOKAWA,[a] Masayuki YOSHIKAWA,[b] Kazuyoshi OHASHI,[c] and Hirotaka SHIBUYA*,[c]

Faculty of Pharmaceutical Sciences, Osaka University,[a] 1–6 Yamada-oka, Suita, Osaka 565, Japan, Kyoto Pharmaceutical University,[b] 5 Nakauchi-cho, Misasagi, Yamashina-ku, Kyoto 607, Japan, and Faculty of Pharmacy and Pharmaceutical Sciences, Fukuyama University,[c] Sanzo, 1 Gakuen-cho, Fukuyama, Hiroshima 729–02, Japan.

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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 (11*S*)-(+)- and (11*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 constituents[2] of convolvulaceous plants (*e.g.*, *Pharbitis mil* 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]

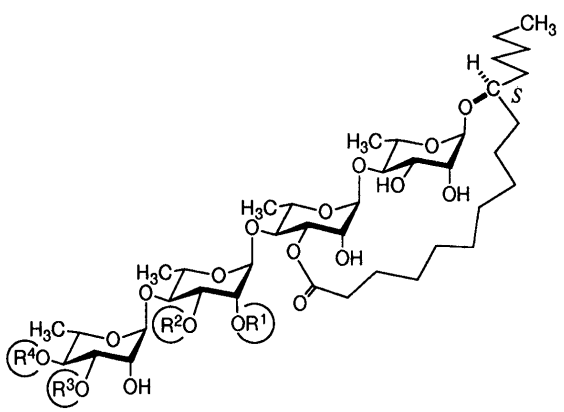
The tuber of *Merremia mammosa* (LOUR.) HALLIER f. (Convolvulaceae, Javanese name "Bidara upas") is one of the so-called jamu raw materials[5] and is said to be useful for treating diabetes and illnesses involving the throat and respiratory system.[5] As a part of our chemical characterization of naturally 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, h_1 and h_2, and mammosides A, B, H_1 and H_2, 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%), h_1 (0.033%), h_2 (0.039%), and mammosides A (0.010%), B (0.072%), H_1 (0.097%), and H_2 (0.109%).[4b–d]

Merremoside d (4) Merremoside d (**4**), colorless fine crystals, $C_{48}H_{82}O_{20}$, 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**, $[\alpha]_D$ +0.5° ($CHCl_3$)}, which was hydrolyzed with aqueous KOH to give jalapinolic acid {**7a**, $[\alpha]_D$ +0.9° ($CHCl_3$)}.

In order to determine the absolute configuration of jalapinolic acid (**7a**), syntheses of (11*S*)- and (11*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**): $R^1=R^4=$ COCH(S)$(CH_3)C_2H_5$; $R^2=R^3=H$

merremoside b (**2**): $R^1=R^4=$ $COCH(CH_3)_2$; $R^2=R^3=H$

merremoside c (**3**): $R^1=R^3=H$; $R^2=$ COCH(S)$(CH_3)C_2H_5$; $R^4=$ $COCH(CH_3)_2$

merremoside d (**4**): $R^1=R^3=H$; $R^2=R^4=$ $COCH(CH_3)_2$

merremoside e (**5**): $R^1=R^4=H$; $R^2=R^3=$ $COCH(CH_3)_2$

Fig. 1

* To whom correspondence should be addressed.

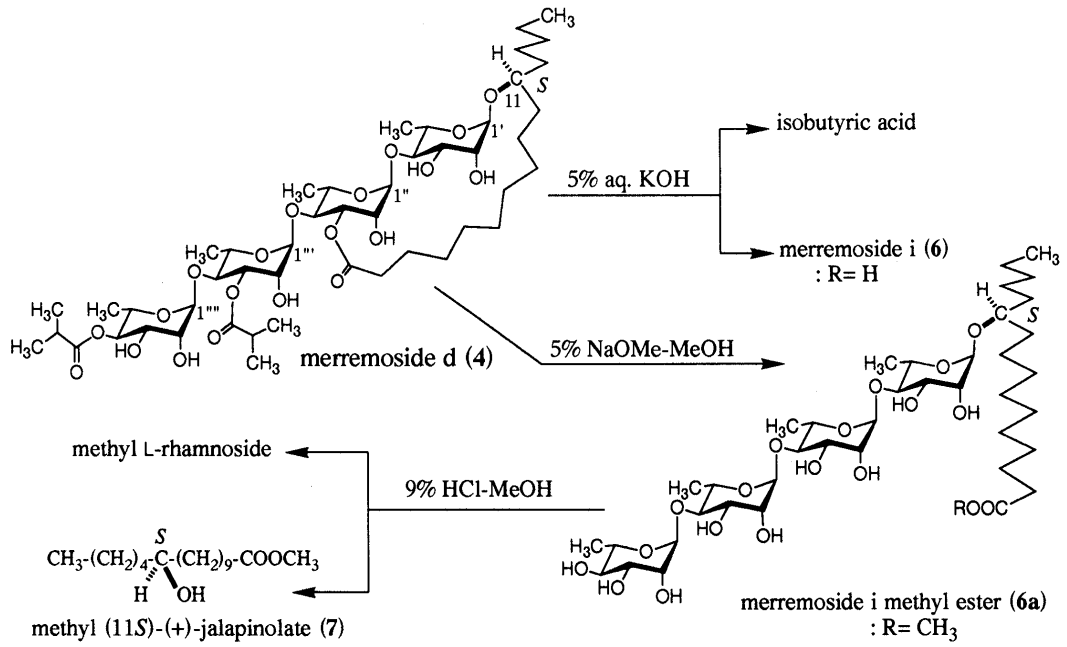


Chart 1

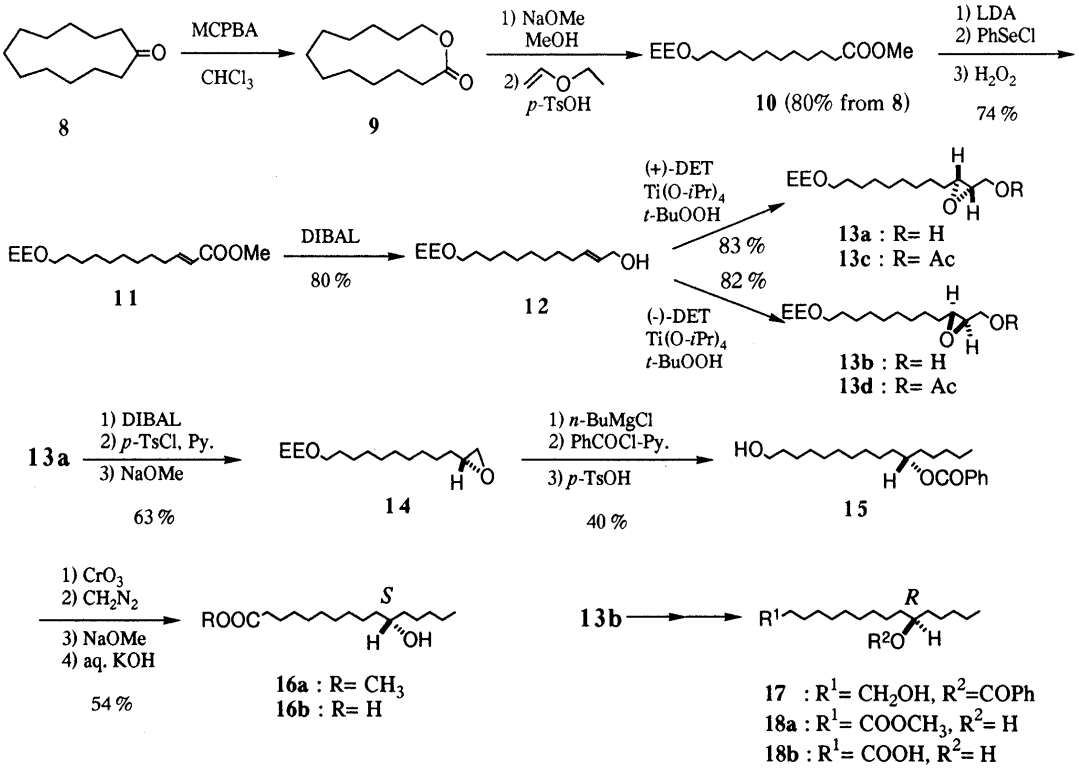


Chart 2

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 epoxidation[7] 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 enantiomeric excess (ee) was determined by the proton nuclear magnetic resonance (^{1}H-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°} in 40% yield. Finally, the Jones oxidation[9] of **15**, followed by diazomethane treatment and methanolysis, afforded methyl (11*S*)-(+)-jalapinolate [**16a**, $[\alpha]_D$ +0.9° ($CHCl_3$)], which was further converted by treatment with aqueous KOH into (11*S*)-(+)-jalapinolic acid {**16b**, $[\alpha]_D$ +0.7° ($CHCl_3$)} 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*)-(−)-jalapinolic acid {**18b**, $[\alpha]_D$ −0.8° ($CHCl_3$)} *via* the (11*R*)-diol 11-monobenzoate {**17**, $[\alpha]_D$ −1.4° ($CHCl_3$)} and methyl (11*R*)-(−)-jalapinolate {**18a**, $[\alpha]_D$ −0.9° ($CHCl_3$)} in a fairly good yield.

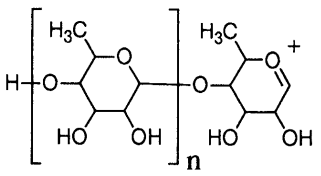
Synthetic (11*S*)-(+)-jalapinolic acid (**16b**) and methyl (11*S*)-(+)-jalapinolate (**16a**) were respectively identical with **7a** and **7b** derived from merremoside d (**4**), based on comparisons of their physicochemical properties including the specific rotation. Thus, the absolute configuration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

Next, we applied Horeau's method[10] to two synthetic methyl esters (**16a** and **18a**) and natural methyl jalapinolate (**7**). In the cases of **16a** and **7**, the resulting 2-phenylbutanoic acid exhibited a positive specific rotation: $[\alpha]_D$ +0.13° (benzene) for **16a** and $[\alpha]_D$ +0.18° (benzene) for **7**. In contrast, when **18a** was submitted to the method, the specific rotation was negative: $[\alpha]_D$ −0.19° (benzene). These findings would suggest an opposite assignment[10] 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 $(M+K)^+$ and *m/z* 893 $(M+Na)^+$. The ^{1}H-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 br s]. The carbon-13 (^{13}C)-NMR spectrum showed four anomeric carbon signals [δ_C 101.4, 102.8 (2C), 102.9] with ^{13}C–^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*)-(+)-jalapinolate (**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*)-(+)-jalapinolate (**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 $(M+K)^+$ and at *m/z* 1001 $(M+Na)^+$, and the negative ion fast atom bombardment (negative FAB)-MS gave an ion peak at *m/z* 977 $(M-H)^-$. 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 jalapinolic acid is attached to a hydroxyl group of the oligosaccharide moiety.



n = 0 : *m/z* 147 (**iv**)
n = 1 : *m/z* 293 (**iii**)
n = 2 : *m/z* 439 (**ii**)
n = 3 : *m/z* 585 (**i**)

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

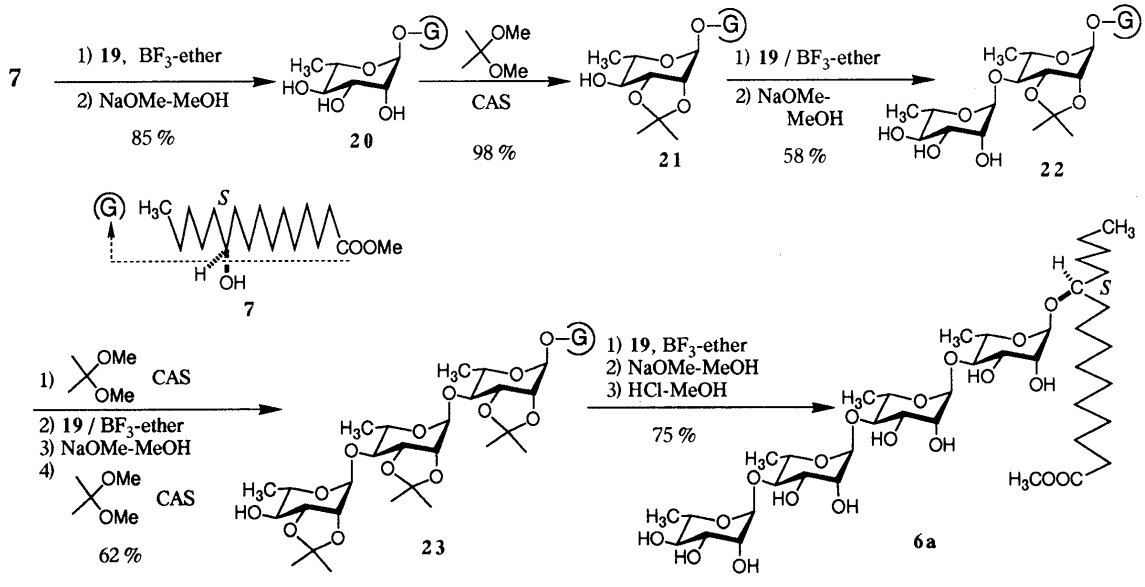


Chart 3

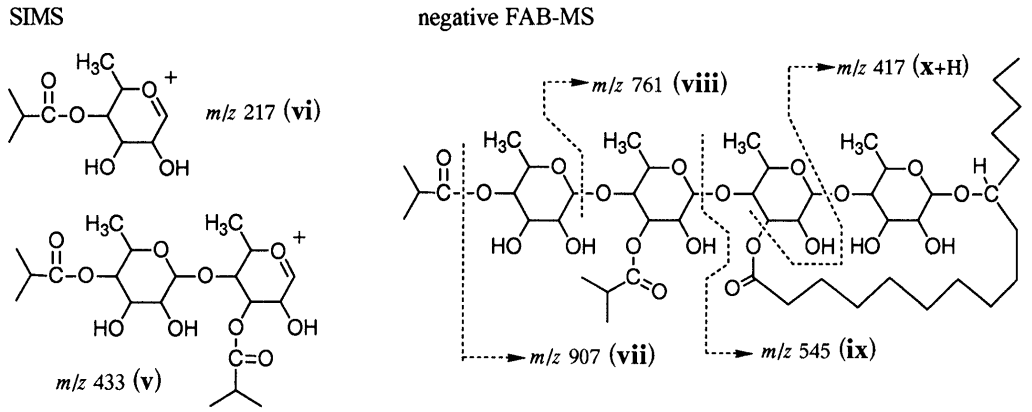


Fig. 3. SIMS and Negative FAB-MS of Merremoside d (**4**)

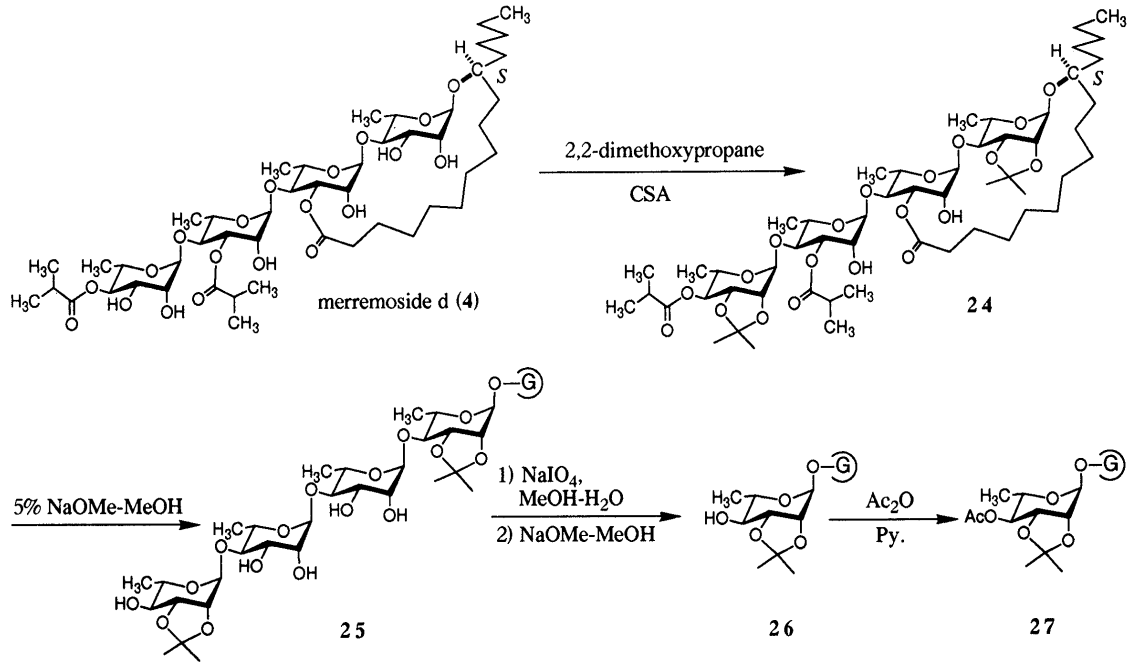


Chart 4

The ^{1}H-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 isobutyroxyl 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 ^{1}H-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, $C_{48}H_{82}O_{20}$, 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*)-(+)-jalapinolate (**7**) on treatment with 9% HCl–MeOH.

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

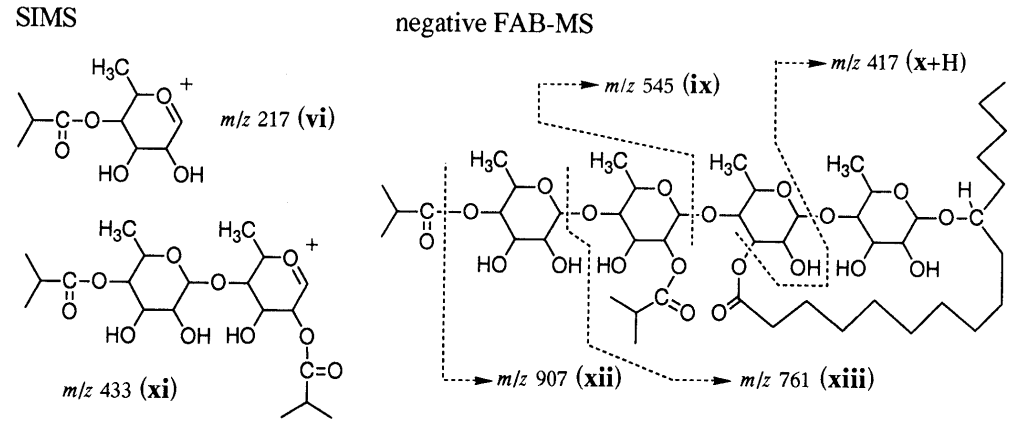


Fig. 4. SIMS and Negative FAB-MS of Merremoside b (**2**)

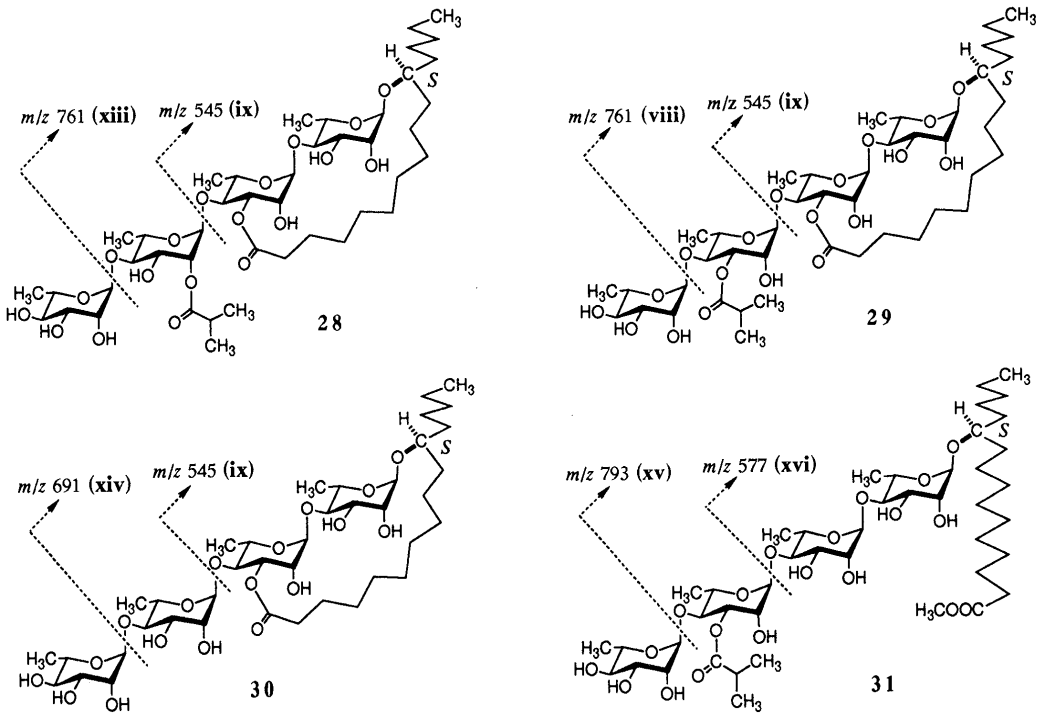


Fig. 5. Negative FAB-MS of **28**, **29**, **30**, and **31**

(**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 ^{1}H-NMR spectrum showed signals of three methine protons on carbons bearing three ester functions; two isobutyroxyl groups [δ 5.70, br s (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 monoisobutyroxyl derivative (**31**, 5%). Detailed analysis of the negative FAB-MS and ^{1}H-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, $C_{49}H_{84}O_{20}$, 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 analysis[14]) 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 (11*S*)-(+)-jalapinolate (**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 ^{1}H-NMR spectrum showed signals of three methine protons attached to one

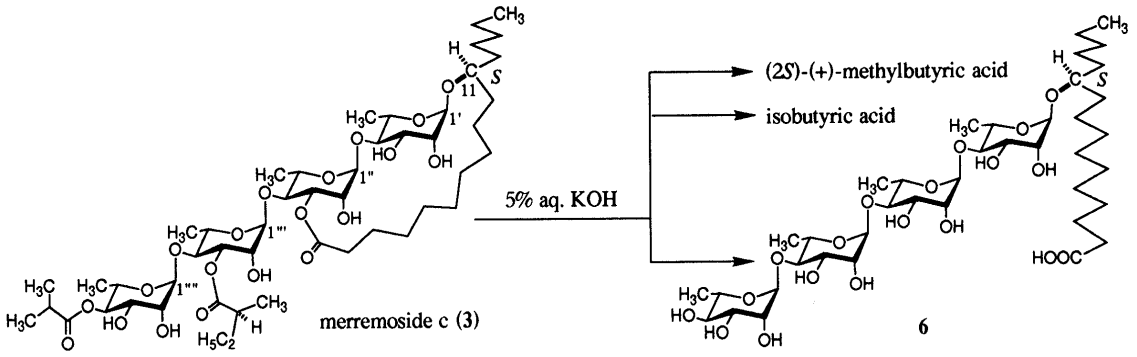


Chart 5

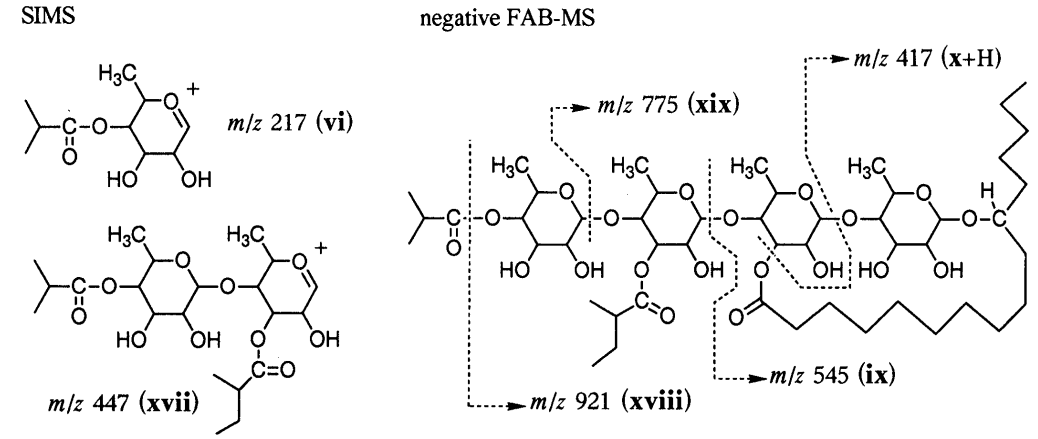


Fig. 6. SIMS and Negative FAB-MS of Merremoside c (3)

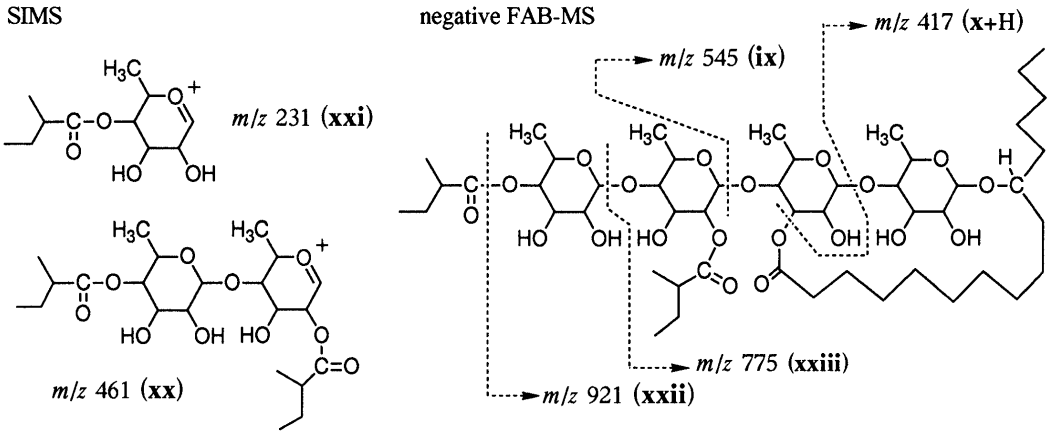


Fig. 7. SIMS and Negative FAB-MS of Merremoside a (1)

isobutyroxyl [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 (2*S*)-(+)-methylbutyric acid. In addition, on methanolysis with 9% HCl–MeOH, **1** gave methyl L-rhamnoside and methyl (11*S*)-(+)-jalapinolate (**7**).

The ^{1}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 $(M+Na)^+$ 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 $(M-H)^-$, *m/z* 921 (**xix**), *m/z* 775 (**xxii**), *m/z* 545 (**ix**), and *m/z* 417 (**x**+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}H-NMR

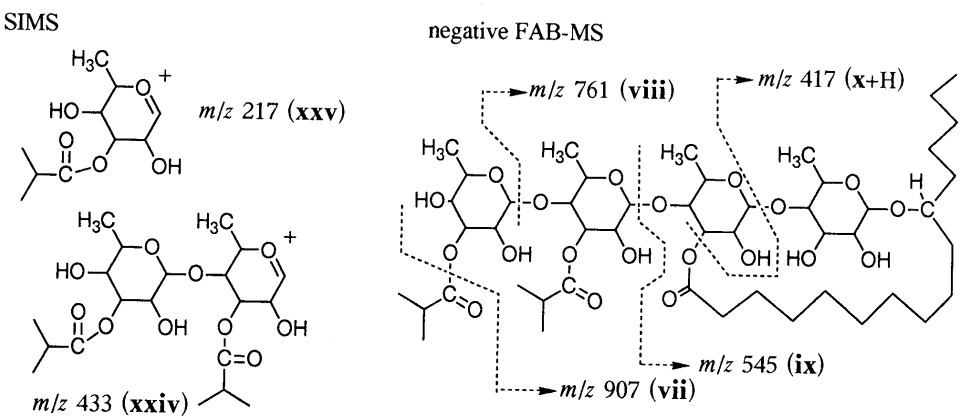


Fig. 8. SIMS and Negative FAB-MS of Merremoside e (**5**)

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 [ED_{80} (mice): 10 μg/ml for 2 and 2 μg/ml for **4**], and merremosides a (**1**), b (**2**), c (**3**), and d (**4**) show ionophoretic activities against Na^+, K^+, and Ca^{2+} 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. ^{1}H- and ^{13}C-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 F_{254} 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 $CHCl_3$ extract (412 g, 1.03%). The $CHCl_3$ extract (100 g) was purified by silica gel column chromatography [SiO_2 2 kg, with $CHCl_3$:MeOH=15:1→10:1→7:1→6:1 and $CHCl_3$:MeOH:H_2O=7:3:1 (lower phase)] and reversed-phase HPLC (Shimpak Prep-ODS, 0.25 m×20 mm, CH_3OH:H_2O=5:1 and CH_3OH:H_2O=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%), h_1 (3.19 g, 0.033%), h_2 (3.77 g, 0.0039%), and mammosides A (982 mg, 0.010%), B (6.99 g, 0.072%), H_1 (9.40 g, 0.097%), and H_2 (10.5 g, 0.109%).

Merremoside a (**1**): Colorless fine crystals from EtOH, mp 125—126 °C, $[\alpha]_D$ −108° ($c=1.1$, in MeOH at 25 °C). IR (KBr) cm^{-1}: 3360, 2938, 1717. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O, 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-CH_3, –$CH(CH_3)CH_2C\underline{H}_3\times2$], 1.16 (3H, d, $J=7.0$ Hz), 1.21 (3H, d, $J=6.7$ Hz) [–$CH(C\underline{H}_3)CH_2CH_3\times2$], 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⁗-H_3), 2.27 (1H, ddd, $J=3.0$, 6.9, 14.6 Hz, 2-H_a), 2.43, 2.52 (1H each, both m, –$C\underline{H}(CH_3)CH_2CH_3$), 2.62 (1H, ddd, $J=3.0$, 6.9, 14.6 Hz, 2-H_b), 3.83 (1H, m, 11-H), 5.12 (1H, br s, 1′-H), 5.53 (1H, br s, 1‴-H), 5.54 (1H, dd, $J=2.8$, 10.1 Hz, 3″-H), 5.72 (1H, br s, 2‴-H), 5.74 (1H, dd, $J=9.5$, 9.5 Hz, 4⁗-H), 6.04 (1H, br s, 1⁗-H), 6.31 (1H, br s, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: 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 $C_{50}H_{86}O_{20}\cdot2H_2O$: 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, $[\alpha]_D$ −90° ($c=2.0$, in MeOH at 25 °C). IR (KBr) cm^{-1}: 3350, 2895, 1715. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 0.99 (3H, t, $J=7.3$ Hz, ω-CH_3), 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) [–$CH(C\underline{H}_3)_2\times4$], 1.40 (3H, d, $J=6.4$ Hz), 1.50 (3H, d, $J=6.4$ Hz), 1.57 (3H, d, $J=6.4$ Hz), 1.63 (3H, d, $J=6.1$ Hz) (6′-, 6″-, 6‴-, 6⁗-H_3), 2.23 (1H, ddd, $J=3.0$, 6.9, 14.6 Hz, 2-H_a), 2.55, 2.64 (1H each, both m, –$C\underline{H}(CH_3)_2\times2$), 2.62 (1H, ddd, $J=3.0$, 6.9, 14.6 Hz, 2-H_b), 3.85 (1H, m, 11-H), 5.11 (1H, br s, 1′-H), 5.50 (1H, br s, 1‴-H), 5.54 (1H, dd, $J=3.0$, 9.8 Hz, 3″-H), 5.70 (1H, br s, 2‴-H), 5.73 (1H, dd, $J=9.8$, 9.8 Hz, 4⁗-H), 6.05 (1H, br s, 1⁗-H), 6.30 (1H, br s, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: 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 $C_{48}H_{82}O_{20}\cdot H_2O$: 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, $[\alpha]_D$ −63° ($c=0.9$, in MeOH at 25 °C). IR (KBr) cm^{-1}: 3370, 2880, 1717. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 0.86 (3H, t, $J=7.3$ Hz, ω-CH_3), 0.92 (3H, t, $J=7.3$ Hz, –$CH(CH_3)CH_2C\underline{H}_3$), 1.12 (3H, d, $J=7.0$ Hz, –$CH(C\underline{H}_3)CH_2CH_3$), 1.18 (3H, d, $J=6.1$ Hz, –$CH(C\underline{H}_3)_2$), 1.19 (3H, d, $J=6.7$ Hz, –$CH(C\underline{H}_3)_2$), 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⁗-H_3), 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, –$C\underline{H}(CH_3)_2$ and –$C\underline{H}(CH_3)CH_2CH_3$), 3.79 (1H, m, 5′-H), 3.90 (1H, br s, 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, br s, 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, br s, 2'''-H), 4.68 (1H, dd, J=10.1, 10.1 Hz, 4''-H), 5.03 (1H, m, 5''-H), 5.20 (1H, br s, 2''-H), 5.33 (1H, br s, 1'-H), 5.63 (1H, dd, J=2.8, 10.1 Hz, 3''-H), 5.64 (1H, br s, 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, br s, 1'''-H), 6.32 (1H, br s, 1''-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: 99.9 (1''-C), 102.1 (1'-C), 102.3 (1'''-C), 102.9 (1''''-C), 174.2, 175.2, 176.5 (>C=O×3). SIMS m/z: 1015 $(M+Na)^+$, 993 $(M+H)^+$, 447 (**xvii**), 217 (**vi**). Negative FAB-MS m/z: 991 $(M-H)^-$, 921 (**xviii**), 775 (**xix**), 545 (**ix**), 417 (**x**+H). *Anal.* Calcd for $C_{49}H_{84}O_{20}\cdot H_2O$: 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, $[\alpha]_D$ −77° (c=1.1, in MeOH at 26 °C). IR (KBr) cm^{-1}: 3420, 2902, 1718. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 0.97 (3H, t, J=7.3 Hz, ω-CH_3), 1.18, 1.19, 1.20, 1.23 (3H each, all d, J=7.0 Hz, –CH(CH_3)$_2$×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''''-H_3), 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, –CH(CH_3)$_2$×2), 3.87 (1H, m, 11-H), 5.33 (1H, br s, 1'-H), 5.60 (1H, br s, 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, br s, 1'''-H), 6.29 (1H, br s, 1''-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: 99.8 (1''-C), 102.1 (1'-C), 102.3 (1'''-C), 103.0 (1''''-C), 174.1, 175.7, 176.5 (>C=O×3). SIMS m/z: 1001 $(M+Na)^+$, 1017 $(M+K)^+$, 433 (**v**), 217 (**vi**). Negative FAB-MS m/z: 977 $(M-H)^-$, 907 (**vii**), 761 (**viii**), 545 (**ix**), 417 (**x**+H). *Anal.* Calcd for $C_{48}H_{82}O_{20}\cdot 2H_2O$: 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, $[\alpha]_D$ −68° (c=0.9, in MeOH at 25 °C). IR (KBr) cm^{-1}: 3498, 2908, 1715. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 0.88 (3H, t, J=7.3 Hz, ω-CH_3), 1.16, 1.16, 1.18, 1.19 (3H each, all d, J=7.0, –CH(CH_3)$_2$×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''''-H_3), 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, –CH(CH_3)$_2$×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'''-, 3''''-H), 4.75, 4.98, 5.13, 5.37 (1H each, all br s, 1'-, 1''-, 1'''-, 1''''-H). ^{13}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 (>C=O×3). SIMS m/z: 1001 $(M+Na)^+$, 979 $(M+H)^+$, 433 (**xxiv**), 217 (**xxv**). Negative FAB-MS m/z: 977 $(M-H)^-$, 907 (**vii**), 761 (**viii**), 545 (**ix**), 417 (**x**+H). *Anal.* Calcd for $C_{48}H_{82}O_{20}\cdot 2H_2O$: 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 × 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×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 : H_2O = 7 : 3 : 1 (lower phase)] to give merremoside i (**6**, 31 mg).

Merremoside i (**6**): Colorless fine crystals from EtOH, mp 138—140 °C, $[\alpha]_D$ −89° (c=1.2 in MeOH at 24 °C). IR (KBr) cm^{-1}: 3401, 2928, 1710. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 0.91 (3H, t, J=7.3 Hz, ω-CH_3), 1.51, 1.58, 1.58 1.58 (3H each, all d, J=6.0 Hz, 6'-, 6''-, 6'''-, 6''''-H_3), 2.31 (2H, t, J=7.5 Hz, 2-H_2), 5.32, 6.15, 6.21, 6.21 (1H each, all br s, 1'-, 1''-, 1'''-, 1''''-H). *Anal.* Calcd for $C_{40}H_{72}O_{19}\cdot 2H_2O$: 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×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, $[\alpha]_D$ −81° (c=2.4, in MeOH at 25 °C). IR (KBr) cm^{-1}: 3369, 2918, 1732. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 0.92 (3H, t, J=7.3 Hz, ω-CH_3), 1.50, 1.57, 1.58, 1.58 (3H each, all d, J=6.0 Hz, 6'-, 6''-, 6'''-, 6''''-H_3), 2.31 (2H, t, J=7.5 Hz, 2-H_2), 3.62 (3H, s, –$COOCH_3$), 5.33, 6.15, 6.19, 6.23 (1H each, all br s, 1'-, 1''-, 1'''-, 1''''-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: 101.4, 102.8, 102.8, 102.9 (1'-, 1''-, 1'''-, 1''''-C, J_{C-H}: 169.9, 171.0, 171.5, 171.6 Hz), 174.0 (–COOH). SIMS m/z: 909 $(M+K)^+$, 893 $(M+Na)^+$, 585 (**i**), 439 (**ii**), 293 (**iii**), 147 (**vi**). *Anal.* Calcd. for $C_{41}H_{74}O_{19}\cdot 3H_2O$: 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 → 5 : 1 and n-hexane : EtOAc = 7 : 1) of the product afforded methyl (11*S*)-(+)-jalapinolate (**7**, 6.2 mg) and methyl L-rhamnoside (18 mg).

7: Colorless needles from $CHCl_3$, mp 45—46 °C, $[\alpha]_D$ +0.5° (c=2.6, in $CHCl_3$ at 24 °C). IR (KBr) cm^{-1}: 3309, 2908, 1742. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.89 (3H, t, J=6.7 Hz, ω-CH_3), 2.31 (2H, t, J=7.5 Hz, 2-H_2), 3.67 (3H, s, –$COOCH_3$). ^{13}C-NMR (22.5 MHz, $CDCl_3$) δ_C: 14.1 (ω-CH_3), 51.5 (–$COOCH_3$), 72.1 (11-C), 174.3 (–$COOCH_3$). EI-MS m/z (%): 286 (M^+, 20), 215 (100). High-resolution EI-MS m/z: Calcd for $C_{17}H_{34}O_3$: 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)trifluoroacetoamide (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 × 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 × 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, $[\alpha]_D$ +9.0° (c=0.9, in H_2O at 25 °C)].

Alkaline Treatment of Methyl (11*S*)-(+)-Jalapinolate (7b) Giving (11*S*)-(+)-Jalapinolic Acid (7a) A solution of methyl (11*S*)-(+)-jalapinolate (**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, $[\alpha]_D$ +0.9° (c=0.7 in $CHCl_3$ at 24 °C). IR (film) cm^{-1}: 1713. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.90 (3H, t-like, ω-CH_3), 2.30 (2H, t, J=8.0 Hz, 2-H_2), 3.5—3.7 (1H, m, 11-H). EI-MS m/z (%): 257 (M^+-CH_3, 0.6), 255 (8.2), 91 (100). High-resolution EI-MS m/z: Calcd for $C_{15}H_{29}O_3$ (M^+-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 $Na_2S_2O_3$ 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×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 CH_2Cl_2 (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 $NaHCO_3$, the mixture was extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed with aqueous saturated $NaHCO_3$ and brine, and then dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product (25 g), which was purified by column chromatography (SiO_2 400 g, *n*-hexane : EtOAc = 2 : 1) to afford **10** (21.2 g, 70 mmol).

10: A colorless oil. IR (film) cm^{-1}: 1732. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.21 (3H, t, J=7.0 Hz, –OCH(CH_3)OCH$_2$C$\underline{H}_3$), 1.31 (3H, d, J=5.0 Hz, –OCH(C$\underline{H}_3$)OCH$_2$CH$_3$), 2.31 (2H, t, J=7.0 Hz, –C$\underline{H}_2$–COOCH$_3$), 3.67 (3H, s, –COOCH$_3$), 4.68 (1H, q, J=5.0 Hz, –OC$\underline{H}$(CH$_3$)OCH$_2$CH$_3$). EI-MS m/z (%): 287 ($M^+ - CH_3$, 16), 173 (100). High-resolution EI-MS m/z: Calcd for $C_{16}H_{31}O_4$ ($M^+ - CH_3$): 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 phenylselenyl 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 NH_4Cl, and the mixture was extracted with EtOAc. The EtOAc extract was washed with brine, then dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product (50 g), which was purified by column chromatography (SiO_2 100 g, benzene : EtOAc = 60 : 1) to afford a phenylselenyl derivative (5.5 g). A solution of the phenylselenyl derivative (5.5 g) in THF (160 ml) was treated with 30% H_2O_2 (8.2 ml) at 0 °C and the whole was stirred at room temperature for 2 h. Then 5% aqueous $Na_2S_2O_3$ was added at 0 °C and the whole was extracted with EtOAc. The EtOAc extract was washed successively with aqueous saturated $NaHCO_3$ and brine, then dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product (5 g), which was purified by column chromatography (SiO_2 100 g, toluene : EtOAc = 40 : 1) to afford **11** (3.8 g, 12.3 mmol).

11: A colorless oil. IR (film) cm^{-1}: 1725. ^{1}H-NMR (90 MHz, $CDCl_3$, δ): 1.21 (3H, t, J=6.0 Hz, –OCH(CH_3)OCH$_2$C$\underline{H}_3$), 1.31 (3H, d, J=5.0 Hz, –OCH(C$\underline{H}_3$)OCH$_2$CH$_3$), 3.73 (3H, s, –COOCH$_3$), 4.69 (1H, q, J=5.0 Hz, –OC$\underline{H}$(CH$_3$)OCH$_2$CH$_3$), 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 ($M^+ - CH_3$, 2), 73 (100). High-resolution MS m/z: Calcd for $C_{17}H_{32}O_4$: 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 (SiO_2 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. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.21 (3H, t, J=7.0 Hz, –OCH(CH_3)OCH$_2$C$\underline{H}_3$), 1.32 (3H, d, J=5.0 Hz, –OCH(C$\underline{H}_3$)OCH$_2$CH$_3$), 4.0—4.2 (2H, m, –C$\underline{H}_2$OH), 4.69 (1H, q, J=5.0 Hz, –OC$\underline{H}$(CH$_3$)CH$_2$CH$_3$). EI-MS m/z (%): 257 ($M^+ - CH_3$, 0.7), 73 (100). High-resolution EI-MS m/z: Calcd for $C_{15}H_{29}O_3$ ($M^+ - CH_3$): 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 CH_2Cl_2 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 CH_2Cl_2 (35 ml) during 15 min at −30 °C and the whole was stirred at −30 °C for 30 min. To this solution, *tert*-BuOOH–CH_2Cl_2 (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 tartric 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 CH_2Cl_2. The CH_2Cl_2 extract was washed with brine, and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product (1.08 g), which was purified by column chromatography (SiO_2 150 g, *n*-hexane : EtOAc = 40 : 1) to furnish the epoxy alcohol **13a** (837 mg, 2.91 mmol).

13a: A colorless oil, $[\alpha]_D$ −18° (c=3.1 in $CHCl_3$ at 27 °C). IR (film) cm^{-1}: 3395, 2907. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.21 (3H, t, J=7.0 Hz, –OCH(CH_3)OCH$_2$C$\underline{H}_3$), 1.31 (3H, d, J=5.0 Hz, –OCH(C$\underline{H}_3$)OCH$_2$CH$_3$), 2.9—3.0 (2H, m), 4.69 (1H, q, J=5.0 Hz, –OC$\underline{H}$(CH$_3$)OCH$_2$CH$_3$). EI-MS m/z (%): 273 ($M^+ - CH_3$, 0.6), 73 (100). High-resolution EI-MS m/z: Calcd for $C_{15}H_{29}O_4$ ($M^+ - CH_3$): 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 CH_2Cl_2 (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 CH_2Cl_2 (20 ml) during 10 min at −30 °C, and the whole was stirred at −30 °C for 30 min. To this solution, *tert*-BuOOH–CH_2Cl_2 (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 tartric 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 CH_2Cl_2. The CH_2Cl_2 extract was washed with brine, and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product (610 mg), which was purified by column chromatography (SiO_2 70 g, *n*-hexane : EtOAc = 40 : 1) to furnish the epoxy alcohol **13b** (473 mg, 1.64 mmol).

13b: A colorless oil, $[\alpha]_D$ +17° (c=2.1 in $CHCl_3$ 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 (SiO_2 5 g, *n*-hexane : EtOAc = 3 : 1) afforded the corresponding acetate derivatives, **13c** (19.2 mg) and **13d** (18.7 mg).

13c and **13d**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.21 (3H, t, J=7.2 Hz), 2.10 (3H, s, –OCOCH$_3$), 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, –OCH$_2$CH$_2$O–), 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, –OC$\underline{H}_2$CH$_3$).

Enantiomeric excess of **13c** and **13d** was determined from the ratio of the signal intensity of an acetoxy methyl moiety in the ^{1}H-NMR spectra in the presence of Tris[3-(heptafluoropropylhydroxymethylene)-(+)-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 (SiO_2 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 $NaHCO_3$ and brine, then dried over $MgSO_4$. 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 (SiO_2 30 g, *n*-hexane : EtOAc = 3 : 1) of the product afforded **14** (86 mg, 0.32 mmol).

14: A colorless oil, $[\alpha]_D$ +3.7° (c=2.0 in $CHCl_3$ at 26 °C). IR (film) cm^{-1}: 2976, 2930, 2858. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 1.20 (3H, t, J=7.0 Hz, –OCH(CH_3)OCH$_2$C$\underline{H}_3$), 1.30 (3H, d, J=5.0 Hz, –OCH(C$\underline{H}_3$)OCH$_2$C$\underline{H}_3$), 2.46 (1H, m), 2.8—3.0 (2H, m). EI-MS m/z (%): 257 ($M^+ - CH_3$, 0.8), 227 (0.4), 73 (100). High-resolution EI-MS m/z: Calcd for $C_{15}H_{29}O_3$ ($M^+ - CH_3$): 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 NH_4Cl and the whole was extracted with EtOAc. The EtOAc extract was washed with brine and then dried over $MgSO_4$. Removal of the solvent under reduced pressure gave a product (106 mg), which was purified by column chromatography (SiO_2 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 (SiO_2 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 $CHCl_3$ at 27 °C). IR (film) cm^{-1}: 1707. ^{1}H-NMR (90 MHz, $CDCl_3$, δ): 0.88 (3H, t-like, ω-CH_3), 3.64 (2H, t, J = 6.0 Hz, -C<u>H</u>$_2$OH), 5.11 (1H, m, -C<u>H</u>-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 $C_{23}H_{38}O_3$: 362.2839. Found: 362.2821 (M^+).

Methyl (11*S*)-(+)-Jalapinolate (16a) from 15 A solution of **15** (44 mg, 0.12 mmol) in acetone (1.0 ml) was treated with the Jones reagent (CrO_3–H_2SO_4, 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 $MgSO_4$. 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 CH_2N_2 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 (SiO_2 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 $CHCl_3$ at 25 °C)} were identical with those for **7** prepared from merremoside d (**4**).

Alkaline Hydrolysis of 16a Giving (11*S*)-(+)-Jalapinolic Acid (16b) Methyl (11*S*)-(+)-jalapinolate (**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 $CHCl_3$ at 25 °C)} were identical with those for **7a**.

Methyl (11*R*)-(−)-Jalapinolic Acid (18a) and (11*R*)-(−)-Jalapinolic 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 $CHCl_3$ at 24 °C).

18b: Colorless needles from petroleum ether; mp 65—67 °C, $[\alpha]_D$ −0.8° (c = 0.8 in $CHCl_3$ 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 (±)-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 $NaHCO_3$. The $NaHCO_3$ phase was acidified with 3 N HCl, and extracted with ether. The extract was washed with brine, and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give a product, which was purified by silica gel column chromatography (SiO_2 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 dimsyl 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 H_2O 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 $AgCO_3$ 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 × 2 m glass column; column temperature, 170 °C; carrier gas, N_2; 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, N_2; 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 (11*S*)-(+)-Jalapinolate (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 CH_2Cl_2 (30 ml) was treated with BF_3–Et_2O (14 μl, 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 CH_2Cl_2. After usual work-up of the CH_2Cl_2 extract, the solvent was evaporated under reduced pressure to yield a product (1.36 g). Purification of the product by column chromatography (SiO_2 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 × 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 (SiO_2 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 $CHCl_3$ at 24 °C). IR ($CHCl_3$) cm^{-1}: 3590, 2985, 1730. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.90 (3H, t, J = 7.0 Hz, ω-CH_3), 1.31 (3H, d, J = 6.1 Hz, 6′-H_3), 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, -$COOCH_3$), 3.75 (1H, m, 5′-H), 3.77 (1H, dd, J = 3.1, 9.2 Hz, 3′-H), 3.89 (1H, br s, 2′-H), 4.86 (1H, br s, 1′-H). *Anal.* Calcd for $C_{23}H_{44}O_7 \cdot H_2O$: 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 μl, 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 (SiO_2 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 $CHCl_3$ at 26 °C). IR ($CHCl_3$) cm^{-1}: 3595, 2985, 1728. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.88 (3H, t, J = 7.0 Hz, ω-CH_3), 1.38, 1.42 (3H each, both s), 1.49 (3H, d, J = 6.4 Hz, 6′-H_3), 2.31 (2H, t, J = 7.1 Hz, 2-H_2), 3.57 (1H, m, 11-H), 3.67 (3H, s, -$COOCH_3$), 3.79 (1H, dd, J = 4.0, 6.8 Hz, 4′-H), 4.05 (1H, m, 5′-H), 4.59 (1H, br d, J = 7.0 Hz, 2′-H), 4.86 (1H, dd, J = 4.0, 7.0 Hz, 3′-H), 5.12 (1H, br s, 1′-H). EI-MS m/z (%): 457 ($M^+ - CH_3$, 24), 315 (87), 269 (100), 99 (91). High-resolution EI-MS m/z: Calcd for $C_{25}H_{45}O_7$ ($M^+ - CH_3$): 457.3162. Found: 457.3161.

Conversion of 21 to 22 A solution of **21** (200 mg, 0.42 mmol) in CH_2Cl_2 (15 ml) was treated with **19** (400 mg, 0.92 mmol), BF_3–Et_2O (6 μl, 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 CH_2Cl_2. After usual work-up of the CH_2Cl_2 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 × 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 (SiO_2 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 $CHCl_3$ at 25 °C). IR ($CHCl_3$) cm^{-1}: 3610, 2970, 1730. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.90 (3H, t, J = 7.7 Hz, ω-CH_3), 1.24—1.34 (3H × 4), 2.31 (2H, t, J = 7.7 Hz, 2-H_2), 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, -$COOCH_3$), 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, br s, 2″-H), 4.06 (1H, br d, J = 5.6 Hz, 2′-H), 4.17 (1H, dd, J = 5.6, 7.3 Hz, 3′-H), 5.04 (1H, br s, 1′-H), 5.37 (1H, br s, 1″-H). *Anal.* Calcd for $C_{32}H_{58}O_{11} \cdot H_2O$: 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 μl, 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 (SiO_2 15 g, *n*-hexane : EtOAc = 3 : 1) afforded a diisopropyridene derivative (148 mg, 0.21 mmol). A solution of the diisopropyridene derivative (148 mg, 0.21 mmol) in CH_2Cl_2 (10 ml) was treated with **19** (140 mg, 0.32 mmol), BF_3–Et_2O (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 CH_2Cl_2. After usual work-up of the CH_2Cl_2 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 (SiO_2 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 μl, 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 (SiO_2 10 g, *n*-hexane : EtOAc = 3 : 1) afforded **23** (72 mg, 0.085 mmol).

23: A colorless oil, $[\alpha]_D$ −41° (*c* = 1.3, in $CHCl_3$ at 25 °C). IR ($CHCl_3$) cm^{-1}: 3510, 2993, 1725. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.90 (3H, t, *J* = 7.5 Hz, ω-CH_3), 1.28—1.64 (totally 3H × 9), 2.31 (2H, t, *J* = 7.6 Hz, 2-H_2), 3.67 (3H, s, –$COOCH_3$), 5.05 (1H, br s, 1′-H), 5.61 (2H, br s, 1″-H, 1‴-H). *Anal.* Calcd for $C_{44}H_{76}O_{15}\cdot 2H_2O$: 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 CH_2Cl_2 (2.0 ml) was treated with BF_3–Et_2O (1.5 μl, 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 CH_2Cl_2. After usual work-up of the CH_2Cl_2 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 $CHCl_3$. 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 (SiO_2 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 $AgCO_3$ 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 (SiO_2 7 g, $CHCl_3$: 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 (SiO_2 50 g, $CHCl_3$: MeOH = 10 : 1) afforded **25** (84.2 mg).

25: Colorless fine crystals from EtOH, mp 115—116 °C, $[\alpha]_D$ −80° (*c* = 1.1, in MeOH at 20 °C). IR ($CHCl_3$) cm^{-1}: 3400, 2920, 1720. ^{1}H-NMR (90 MHz, pyridine-d_5 + D_2O) δ: 0.96 (3H, t, *J* = 6.7 Hz, ω-CH_3), 1.37—1.62 (3H × 4, 6′-, 6″-, 6‴-, 6⁗-H_3), 1.70—1.74 (totally 3H × 4), 2.30 (2H, t, *J* = 7.0 Hz, 2-H_2), 3.69 (3H, s, –$COOCH_3$), 5.33, 5.96, 6.30, 6.45 (1H each, all br s, 1′-, 1″-, 1‴-, 1⁗-H) *Anal.* Calcd. for $C_{47}H_{82}O_{19}\cdot 2H_2O$: 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 [SiO_2 20 g, $CHCl_3$: MeOH : H_2O = 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 (SiO_2 5 g, *n*-hexane : EtOAc = 4 : 1) afforded **27** (6 mg).

27: A colorless oil, $[\alpha]_D$ +20° (*c* = 0.5, in $CHCl_3$ at 26 °C). IR (KBr) cm^{-1}: 2936, 1731. ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.88 (3H, t-like, ω-CH_3), 1.26, 1.34 (3H each, both s), 1.50 (3H, d, *J* = 6.4 Hz, 6-H_3), 2.06 (3H, s, –$OCOCH_3$), 2.30 (2H, t-like, 2-H_2), 3.67 (3H, s, –$COOCH_3$), 4.92 (1H, dd, *J* = 8.0, 8.0 Hz, 4′-H), 5.12 (1H, br s, 1′-H). ^{13}C-NMR (22.5 MHz, $CDCl_3$) δ_C: 14.2 (C-16), 21.1 (–$OCO\underline{C}H_3$), 51.5 (–$COO\underline{C}H_3$), 101.5 (C-1′), 110.2, 169.6 (–$\underline{C}OCH_3$), 174.4 (–$\underline{C}OOCH_3$). EI-MS *m*/*z* (%): 499 ($M^+ - CH_3$, 3), 269 (47), 115 (100). High-resolution EI-MS *m*/*z*: Calcd for $C_{27}H_{47}O_8$ ($M^+ - CH_3$): 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, N_2; 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 [SiO_2 10 g, $CHCl_3$: MeOH : H_2O = 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 (SiO_2 10 g, $CHCl_3$: 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 $AgCO_3$ powder and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product (21 mg). Repeated column chromatography (SiO_2 20 g, $CHCl_3$: MeOH = 30 : 1 → 5 : 1 and *n*-hexane : EtOAc = 7 : 1) of the product afforded methyl (11*S*)-(+)-jalapinolate (**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 (SiO_2 50 g, $CHCl_3$: 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, $[\alpha]_D$ −48° (*c* = 0.7, in MeOH at 25 °C). IR (KBr) cm^{-1}: 3380, 2910, 1717. ^{1}H-NMR (500 MHz, pyridine-d_5 + H_2O) δ: 0.95 (3H, t, *J* = 7.5 Hz, ω-CH_3), 1.14,

1.16, (3H each, both d, J=7.0 Hz, –CH(C$\underline{H}_3$)$_2$ × 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⁗-H_3), 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, br s, 2‴-H), 5.12, 5.50, 6.11, 6.29 (1H each, all br s, 1′-, 1″-, 1‴-, 1⁗-H). ^{13}C-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 $C_{44}H_{76}O_{19}\cdot 2H_2O$: 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° (c=0.7, in MeOH at 25 °C). IR (KBr) cm^{-1}: 3380, 2905, 1717. ^{1}H-NMR (500 MHz, pyridine-d_5+H_2O) δ: 0.95 (3H, t, J=7.5 Hz, ω-CH_3), 1.18, 1.24 (3H each, both d, J=7.0 Hz, –CH(C$\underline{H}_3$)$_2$ × 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⁗-H_3), 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 br s, 1′-, 1″-, 1‴-, 1⁗-H). ^{13}C-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 $C_{44}H_{76}O_{19}\cdot 3H_2O$: 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 × 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 (SiO_2 50 g, $CHCl_3$: 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° (c=1.0, in MeOH at 25 °C). IR (KBr) cm^{-1}: 3384, 2920,1718. ^{1}H-NMR (500 MHz, pyridine-d_5+H_2O) δ: 0.95 (3H, t, J=7.5 Hz, ω-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⁗-H_3), 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 br s, 1′-, 1″-, 1‴-, 1⁗-H). ^{13}C-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 $C_{40}H_{78}O_{18}\cdot 3H_2O$: 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° (c=0.3, in MeOH at 25 °C). IR (KBr) cm^{-1}: 3380, 2917, 1715. ^{1}H-NMR (500 MHz, pyridine-d_5+H_2O) δ: 0.93 (3H, t, J=7.5 Hz, ω-CH_3), 1.18, 1.32 (3H each, both d, J=7.0 Hz, –CH(C$\underline{H}_3$)$_2$ × 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⁗-H_3), 2.31 (2H, t, J=7.4 Hz, 2-H_2), 3.63 (3H, s, –$COOCH_3$), 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 br s, 1′-, 1″-, 1‴-, 1⁗-H). ^{13}C-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 $C_{45}H_{80}O_{20}\cdot 3H_2O$: 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 × 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 (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 × 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 : H_2O = 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 $CHCl_3$–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 (SiO_2 10 g, *n*-hexane : EtOAc = 15 : 1) and HPLC (Zorbax SIL, 0.25 m × 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° (c=4.6, in $CHCl_3$ 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 × 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**, 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 $AgCO_3$ 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 → 5 : 1, *n*-hexane : EtOAc = 7 : 1) of the product afforded methyl (11*S*)-(+)-jalapinolate (**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 × 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 × 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 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 filtrate. 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 [10 mg, $[\alpha]_D$ +9.0° (c=0.9, in H_2O 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 × 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, 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 × 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 : H_2O = 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 $AgCO_3$ 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 (SiO_2 20 g, $CHCl_3$: MeOH = 30 : 1 → 5 : 1, *n*-hexane : EtOAc = 7 : 1) to afford methyl (11*S*)-(+)-jalapinolate (**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 × 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 × 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 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. Purification of this product by column chromatography (SiO_2 7 g, $CHCl_3$: MeOH = 3 : 1) afforded L-rhamnose [11 mg, $[\alpha]_D$ +9.0° (c = 0.9, H_2O, 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 × 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 [SiO_2 10 g, $CHCl_3$: MeOH : H_2O = 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 × 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 (isobutyric acid).

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