Indonesian Medicinal Plants. XIX.[1] Chemical Structures of Four Additional Resin-Glycosides, Mammosides A, B, H_1, and H_2, from the Tuber of *Merremia mammosa* (Convolvulaceae)

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Four new resin-glycosides, named mammosides A (10), B (11), H_1 (12), and H_2 (13), were isolated from the tuber of *Merremia mammosa* (Convolvulaceae), a Jamu raw material. Their chemical structures have been elucidated on the bases of chemical and physicochemical evidence, including synthesis of a glycosidic acid designated as mammoside I.

Key words Indonesian medicinal plant; *Merremia mammosa*; Convolvulaceae; resin-glycoside; mammoside

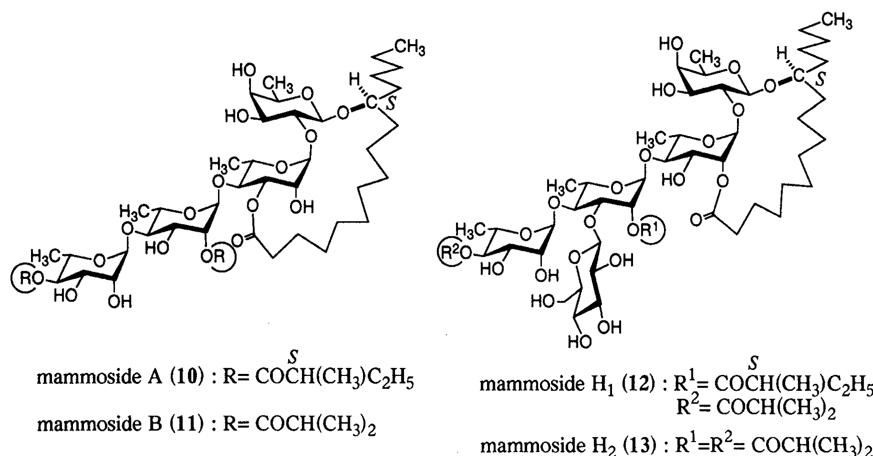
In our previous paper,[2] we reported the chemical characterization of nine resin-glycosides, merremosides a (**1**), b (**2**), c (**3**), d (**4**), e (**5**), f (**6**), g (**7**), h_1 (**8**), and h_2 (**9**), isolated from the chloroform-soluble portion of the fresh tuber of *Merremia mammosa* (LOUR.) HALL. f., one of the Jamu raw materials.[3] In a continuing study of the fresh tuber, we have investigated the chemical constituents of the tuber and isolated four additional resin-glycosides, mammosides A (**10**), B (**11**), H_1 (**12**), and H_2 (**13**). This paper describes in detail the elucidation of the chemical

merremoside a (**1**): $R^1=R^4=\overset{S}{CO}CH(CH_3)C_2H_5$; $R^2=R^3=H$
merremoside b (**2**): $R^1=R^4=COCH(CH_3)_2$; $R^2=R^3=H$
merremoside c (**3**): $R^1=R^3=H$; $R^2=\overset{S}{CO}CH(CH_3)C_2H_5$; $R^4=COCH(CH_3)_2$
merremoside d (**4**): $R^1=R^3=H$; $R^2=R^4=COCH(CH_3)_2$
merremoside e (**5**): $R^1=R^4=H$; $R^2=R^3=COCH(CH_3)_2$

merremoside f (**6**): $R^1=\overset{S}{CO}CH(CH_3)C_2H_5$; $R^4=COCH(CH_3)_2$; R^2= β-D-glucopyranosyl; $R^3=H$
merremoside g (**7**): $R^1=R^4=COCH(CH_3)_2$; $R^3=H$; R^2= β-D-glucopyranosyl

merremoside h_1 (**8**): $R=\overset{S}{CO}CH(CH_3)C_2H_5$
merremoside h_2 (**9**): $R=COCH(CH_3)_2$

Fig. 1



mammoside A (**10**) : $R=\overset{S}{CO}CH(CH_3)C_2H_5$
mammoside B (**11**) : $R=COCH(CH_3)_2$

mammoside H_1 (**12**) : $R^1=\overset{S}{CO}CH(CH_3)C_2H_5$, $R^2=COCH(CH_3)_2$
mammoside H_2 (**13**) : $R^1=R^2=COCH(CH_3)_2$

Fig. 2

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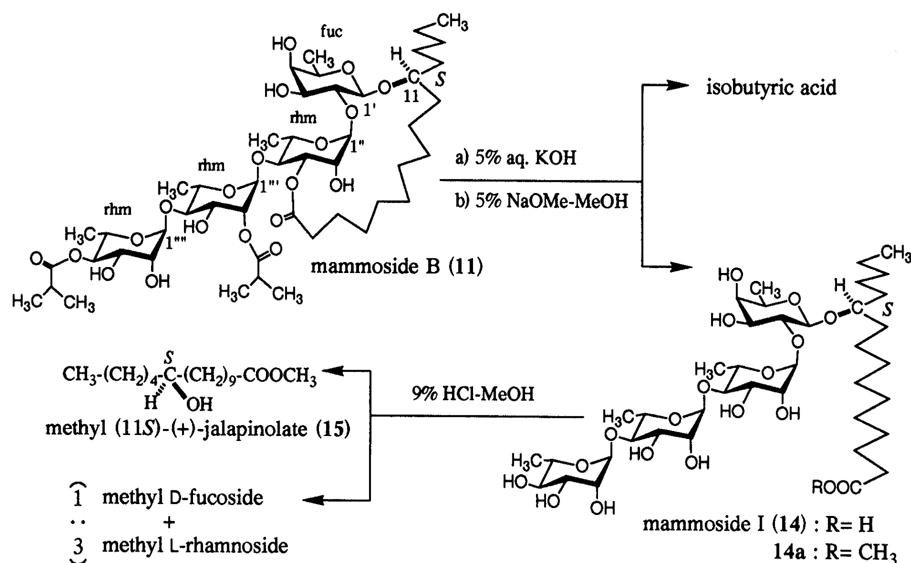

Chart 1

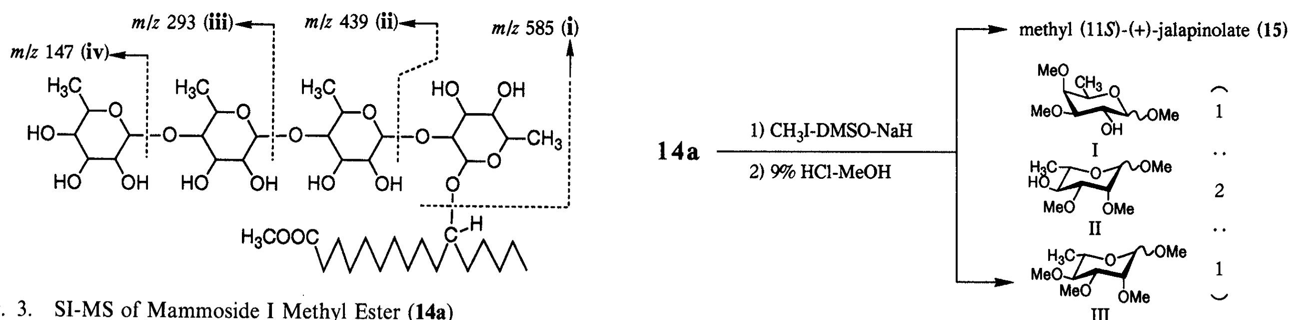

Fig. 3. SI-MS of Mammoside I Methyl Ester (**14a**)

Chart 2

structures of **10**, **11**, **12**, and **13**.

Mammoside B (11) Mammoside B (**11**), obtained as colorless fine crystals, $C_{48}H_{82}O_{20}$, showed absorption bands due to a hydroxyl ($3348\,cm^{-1}$) group and an ester group ($1724\,cm^{-1}$) in the infrared (IR) spectrum.

Hydrolysis with 5% aqueous KOH of **11** yielded a glycosidic acid designated as mammoside I (**14**) and isobutyric acid. On treatment with 5% NaOMe–MeOH, **11** gave mammoside I methyl ester (**14a**). Furthermore, methanolysis of **14a** with 9% HCl–MeOH furnished methyl (11*S*)-(+)-jalapinolate (**15**)[2a] and two methyl glycosides; methyl D-fucoside and methyl L-rhamnoside in 1:3 ratio.

The secondary ion mass spectroscopy (SI-MS) of mammoside I methyl ester (**14a**) showed characteristic fragment ions, *m/z* 585 (**i**), *m/z* 439 (**ii**), *m/z* 293 (**iii**), and *m/z* 147 (**iv**), together with two quasi-molecular ions at *m/z* 909 $(M+K)^+$ and *m/z* 893 $(M+Na)^+$.

The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **14a** showed signals assignable to one primary methyl, one carbomethoxyl, four secondary methyls, and four anomeric protons [δ 4.75, d, $J=7.9$ Hz (fucose) indicating a β-glycosyl linkage, and δ 5.50, 6.05, 6.30, all br s (rhamnose × 3)]. Furthermore, the nuclear Overhauser effect (NOE) was observed between 11-H and 1′-H of D-fucose, implying that the D-fucose is located at 11-OH of methyl jalapinolate (**15**). The carbon-13 (^{13}C)-NMR spectrum of **14a** showed four anomeric carbon signals [δ_C 100.0, 100.4, 101.4, 103.5] with ^{13}C–^{1}H coupling constants[4] of 159.9 (for fucose), 169.9, 171.0 and 171.6 Hz (for rhamnoses), respectively. The J_{C-H} values of the rhamnoses indicated that all glycosyl linkages must be α-oriented.

Complete methylation of **14a** with CH_3I–DMSO–NaH followed by methanolysis provided methyl (11*S*)-(+)-jalapinolate (**15**) and three methyl glycosides; methyl 3,4-di-*O*-methyl-D-fucopyranoside (I), methyl 2,3-di-*O*-methyl-L-rhamnopyranoside (II), and methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside (III) in a ratio of 1:2:1. From the above evidence, the chemical structures of mammoside I (**14**) and mammoside I methyl ester (**14a**) have been presumed to be as shown.

Glycosidation of (11*S*)-(+)-jalapinolate (**15**) with 2,3,4-tri-*O*-benzyl-D-fucopyranosyl-1-*O*-trichloroacetimidate (**16**)[5] in CH_2Cl_2 at $-30\,°C$ in the presence of boron trifluoride etherate and molecular sieves 4 Å followed by alkaline hydrolysis afforded the β-glycoside (**17**). Treatment of **17** with 2,2-dimethoxypropane and camphor-10-sulfonic acid gave an acetonide (**18**). By repeated glycosidation with 2,3,4-tri-*O*-acetyl-L-rhamnopyranosyl-1-*O*-trichloroacetoimidate (**19**)[5] and subsequent acetonization, the acetonide (**18**) was converted into mammoside I methyl ester (**14a**), which was identical with that prepared from mammoside B (**11**).

Mammoside B (**11**) showed characteristic fragment ions, *m/z* 977 $(M-H)^-$, *m/z* 761 (**vii**), *m/z* 545 (**viii**), and *m/z* 417 (**ix**+H), in the negative fast atom bombardment

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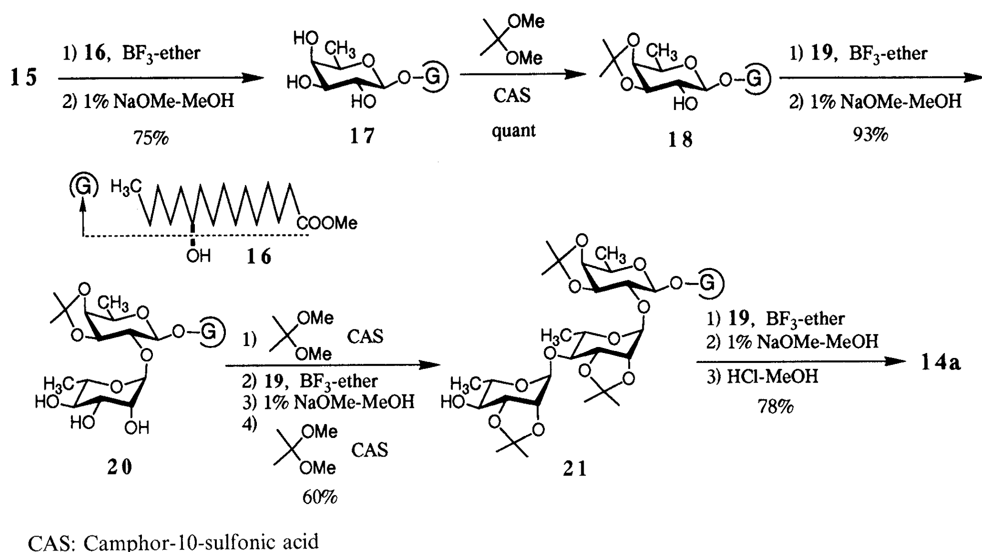

CAS: Camphor-10-sulfonic acid

Chart 3

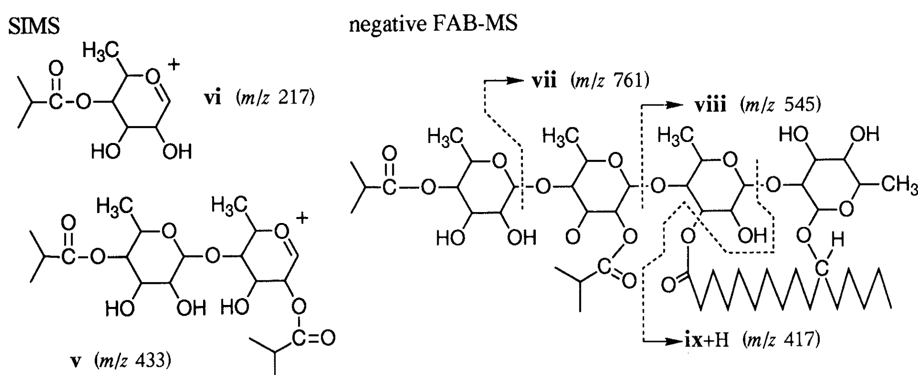

Fig. 4. SI-MS and Negative FAB-MS of Mammoside B (**11**)

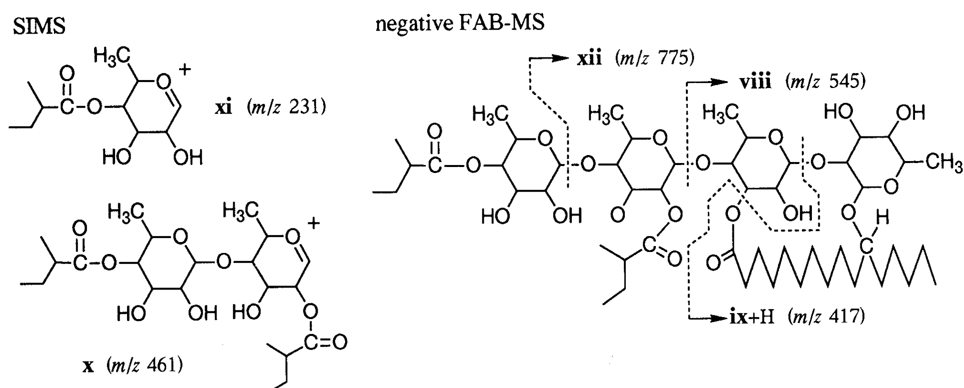

Fig. 5. SI-MS and Negative FAB-MS of Mammoside A (**10**)

(negative FAB)-MS. The ^{1}H-NMR spectrum of **11** exhibited signals due to one primary methyl, eight secondary methyls, four anomeric protons, and three methine protons on carbons bearing two isobutyroxyl groups [δ 5.70, br s, 2‴-H, δ 5.73, dd, J=9.8, 9.8 Hz, 4⁗-H] and another ester group [δ 5.54, dd, J=3.0, 9.8 Hz, 3″-H]. Furthermore, in the SI-MS, **11** showed two characteristic fragment ions at m/z 433 (**v**) and m/z 217 (**vi**). These findings indicated that the isobutyryl groups were located at 2‴-OH and 4⁗-OH. Consequently, the whole structure of mammoside B (**11**) has been elucidated to be as shown.

Mammoside A (10) Mammoside A (**10**), colorless fine crystals, $C_{50}H_{86}O_{20}$, showed absorption bands due to a hydroxyl (3355 cm^{-1}) group and an ester (1718 cm^{-1}) group in the IR spectrum.

Hydrolysis of mammoside A (**10**) with 5% aqueous KOH yielded mammoside I (**14**), and (2*S*)-(+)-methylbutyric acid, which was identified as the phenacyl ester derivative {$[\alpha]_D$ +15° ($CHCl_3$)}.[6] On the other hand, treatment of **10** with 5% NaOMe–MeOH gave mammoside I methyl ester (**14a**).

In the SI-MS, mammoside A (**10**) showed quasi-molecular ion peaks at m/z 1045 $(M+K)^+$ and m/z 1029 $(M+Na)^+$, together with fragment ion peaks m/z 461 (**x**)

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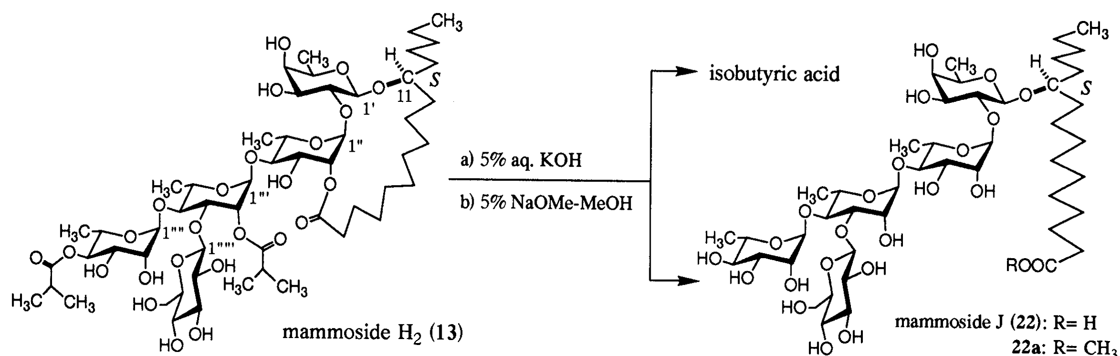

Chart 4

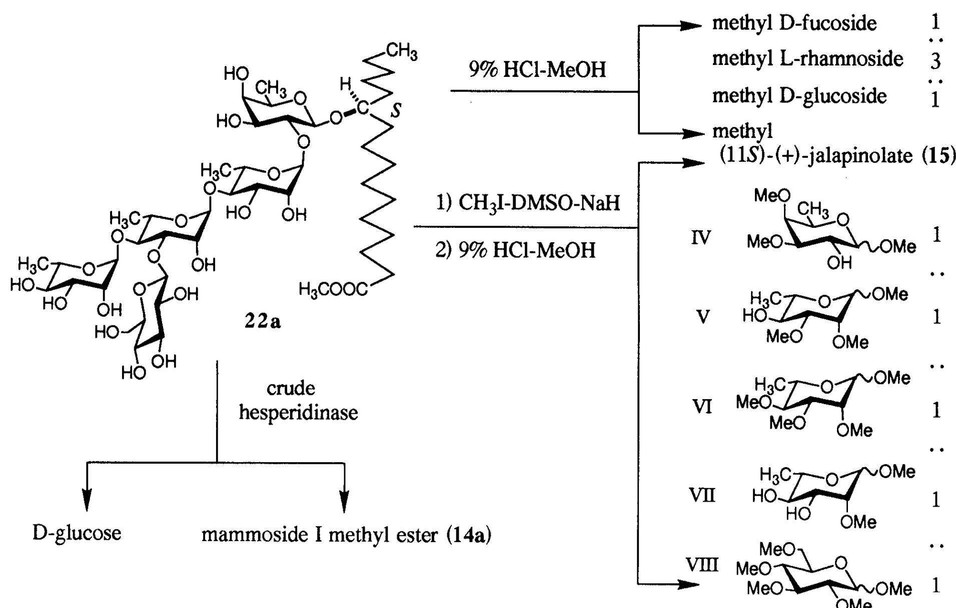

Chart 5

and m/z 231 (**xi**), and the negative FAB-MS showed ion peaks at m/z 1005 $(M-H)^-$, m/z 775 (**xii**), m/z 545 (**viii**), and m/z 417 (**ix**+H).

Furthermore, the ^{1}H-NMR spectrum of **10** showed signals assignable to three primary methyls, six secondary methyls, four anomeric protons, and three methine protons on carbons bearing two methylbutyroxyl groups [δ 5.73 (dd, J=9.8, 9.8 Hz, 4''''-H), δ 5.70 (br s, 2'''-H)] and another ester group [δ 5.54 (dd, J=3.0, 9.8 Hz, 3''-H)]. Based on the above findings, the chemical structure of mammoside A has been elucidated to be **10**.

Mammoside H$_2$ (13) Mammoside H$_2$ (**13**), colorless fine crystals, $C_{54}H_{92}O_{25}$, showed the presence of a hydroxyl (3356 cm^{-1}) group and an ester (1716 cm^{-1}) group in the IR spectrum. Hydrolysis of mammoside H$_2$ (**13**) with 5% aqueous KOH yielded a jalapinolic acid-glycoside (**22**) and isobutyric acid. On the other hand, treatment of **13** with 5% NaOMe–MeOH gave mammoside J methyl ester (**22a**).

Methanolysis of **22a** with 9% HCl–MeOH furnished methyl (11S)-(+)-jalapinolate (**15**) and three methyl glycosides, methyl D-fucoside, methyl L-rhamnoside, and methyl D-glucoside, in a ratio of 1 : 3 : 1. On enzymatic hydrolysis using crude hesperidinase, **22a** gave D-glucose, and mammoside I methyl ester (**14a**), which was identical

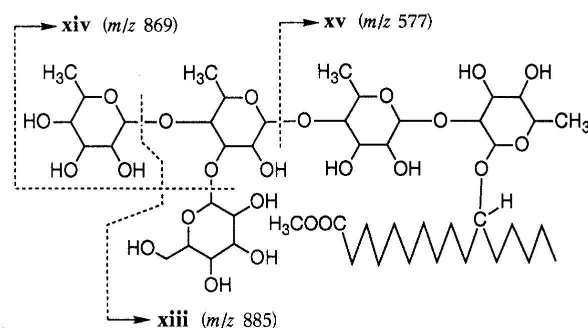

Fig. 6. Negative FAB-MS of Mammoside J Methyl Ester (**22a**)

with that prepared from mammoside B (**11**). Furthermore, treatment of **22a** with CH_3I–DMSO–NaH followed by methanolysis with 9% HCl–MeOH yielded methyl (11S)-(+)-jalapinolate (**15**) and five partially methylated methyl glycosides, methyl 3,4-di-O-methyl-D-fucopyranoside (IV), methyl 2,3-di-O-methyl-L-rhamnopyranoside (V), methyl 2,3,4-tri-O-methyl-L-rhamnopyranoside (VI), methyl 2-O-methyl-L-rhamnopyranoside (VII), and methyl 2,3,4,6-tetra-O-methyl-D-glucopyranoside (VIII), in a 1 : 1 : 1 : 1 : 1 ratio.

The negative FAB-MS of mammoside J methyl ester (**22a**) showed ion peaks at m/z 1031 $(M-H)^-$, m/z 885

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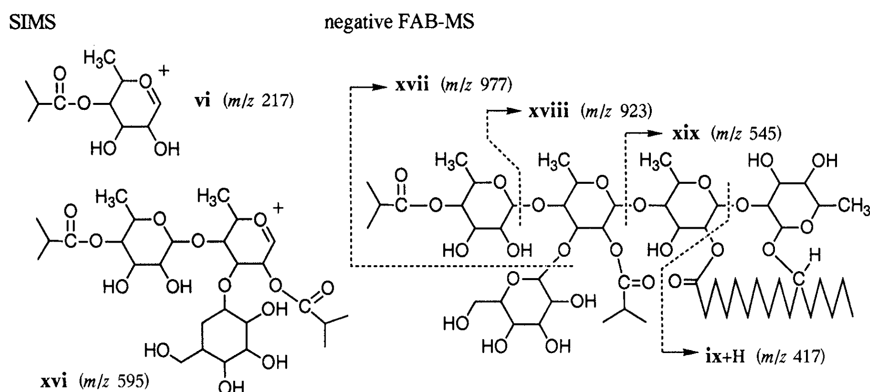

Fig. 7. SI-MS and Negative FAB-MS of Mammoside H_2 (**13**)

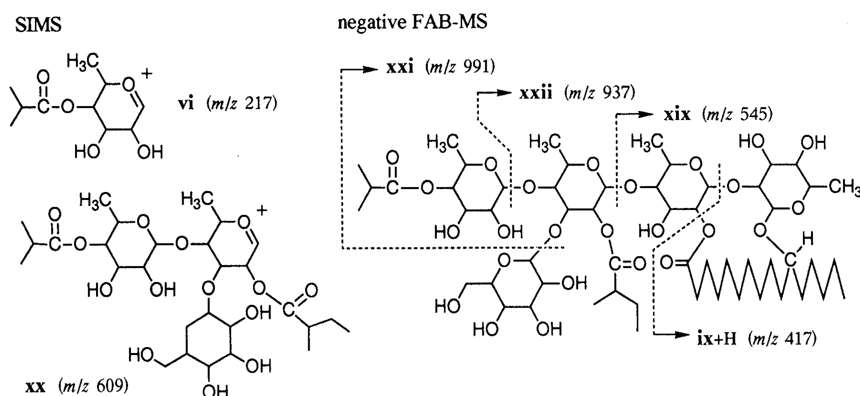

Fig. 8. SI-MS and Negative FAB-MS of Mammoside H_1 (**12**)

(**xiii**), *m/z* 869 (**xiv**), and *m/z* 577 (**xv**), which indicated that a D-glucose must be attached to the second L-rhamnose.

The ^{1}H-NMR spectrum of **22a** showed signals due to one primary methyl, one ester methyl, four secondary methyls, five anomeric protons [δ 4.81, d, $J=7.5$ Hz (D-fucose); δ 5.82, 6.13, 6.15, all br s (L-rhamnose × 3); δ 5.17, d, $J=7.5$ Hz (D-glucose) indicating a β-orientation]. From the above evidence, the chemical structure of **22a** has been presumed to be as shown.

In SI-MS, mammoside H_2 (**13**) showed two major fragment ions, *m/z* 595 (**xvi**) and *m/z* 217 (**vi**). These imply that one isobutyryl group is attached to the second L-rhamnose and another isobutyryl group is attached to the terminal L-rhamnose.

The ^{1}H-NMR spectrum of mammoside H_2 (**13**) showed signals due to one primary methyl, eight secondary methyls, five anomeric protons, and three methine protons on carbons bearing two isobutyroxyl groups [δ 5.70, dd, $J=9.5$, 9.5 Hz, 4''''-H, δ 5.87, br s, 2'''-H] and another ester group [δ 6.23, br s, 2''-H]. These results were supported by the negative FAB-MS (Fig. 7). Consequently, the chemical structure of mammoside H_2 (**13**) has been determined to be as shown.

Mammoside H_1 (12) Mammoside H_1 (**12**), colorless fine crystals, $C_{55}H_{94}O_{25}$, showed the presence of a hydroxyl (3360 cm^{-1}) group and an ester (1718 cm^{-1}) group in the IR spectrum.

Alkaline hydrolysis of **12** with 5% aqueous KOH gave mammoside J (**22**), isobutyric acid, and (2*S*)-(+)-methylbutyric acid. Treatment of **12** with 5% NaOMe–MeOH gave mammoside J methyl ester (**22a**).

The SI-MS of mammoside H_1 (**12**) showed ion peaks at *m/z* 1177 $(M+Na)^+$, *m/z* 609 (**xx**) and *m/z* 217 (**vi**), and the negative FAB-MS showed ion peaks at *m/z* 1153 $(M-H)^-$, *m/z* 991 (**xxi**), *m/z* 937 (**xxii**), *m/z* 545 (**xix**) and *m/z* 417 (**ix**+H).

The ^{1}H-NMR spectrum of **12** showed signals due to one primary methyl, eight secondary methyls, five anomeric protons, and three methine protons on carbons bearing two isobutyroyl groups [δ 5.76, dd, $J=9.5$, 9.5 Hz, 4''''-H; δ 5.92, br s, 2'''-H] and another ester group [δ 6.31, br s, 2''-H]. From the above-mentioned evidence, the chemical structure of mammoside H_1 was concluded to be **12**.

Finally, it should be mentioned here that mammosides A (**10**), B (**11**), H_1 (**12**), and H_2 (**13**) exhibit ionophoretic activity against transport of Na^+, K^+, and Ca^{2+} ions across human erythrocyte membrane.[7]

Experimental

The instruments used to obtain physical data and the experimental conditions for chromatography were the same as in our previous paper.[2]

Mammoside A (**10**): Colorless fine crystals from EtOH, mp 122—123 °C, $[\alpha]_D$ −101° ($c=1.0$, in MeOH at 24 °C). IR (KBr) cm^{-1}: 3355, 2930, 1718. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 1.42 (3H, d, $J=6.4$ Hz, 6''''-H_3), 1.50 (3H, d, $J=6.4$ Hz, 6'-H_3), 1.57 (3H, d, $J=6.1$ Hz, 6''-H_3), 1.64 (3H, d, $J=6.1$ Hz, 6'''-H_3), 2.22 (1H, ddd, $J=2.4$, 7.0, 14.0 Hz, 2-H_a), 2.61 (1H, ddd, $J=3.4$, 7.0, 14.0 Hz, 2-H_b), 3.79 (1H, m, 5'-H), 3.83 (1H, m, 11-H), 3.89 (1H, d, $J=3.4$ Hz, 4'-H), 4.14 (1H, dd, $J=3.4$, 9.5 Hz, 3'-H), 4.16 (1H, dd, $J=9.2$, 9.2 Hz, 4'''-H), 4.32 (1H, m, 5'''-H), 4.37 (1H, m, 5''''-H), 4.43 (1H, dd, $J=3.4$, 9.5 Hz, 3''''-H), 4.47 (dd, $J=7.9$, 9.5 Hz, 2'-H), 4.54 (1H, d-like, 3'''-H), 4.58 (1H, dd, $J=9.8$, 9.8 Hz, 4''-H), 4.72 (1H, br s, 2''''-H), 4.74 (1H, d, $J=7.9$ Hz,

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1′-H), 4.96 (1H, m, 5″-H), 5.24 (1H, br s, 2″-H), 5.53 (1H, br s, 1‴-H), 5.54 (1H, dd, J=2.8, 9.8 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, 100.0, 100.9, 103.1, 174.3, 175.6, 176.0. SI-MS m/z: 1045 $(M+K)^+$, 1029 $(M+Na)^+$, 461 (**x**), 231 (**xi**). Negative FAB-MS m/z: 1005 $(M-H)^-$, 775 (**xii**), 545 (**viii**), 417 (**ix**+H). *Anal.* Calcd for $C_{50}H_{86}O_{20}\cdot 2H_2O$: C, 57.56; H, 8.69. Found: C, 57.47; H, 8.79.

Mammoside B (**11**): Colorless fine crystals from EtOH, mp 125—126 °C, $[\alpha]_D$ −89° (c=1.2, in MeOH at 25 °C). IR (KBr) cm^{-1}: 3348, 2890, 1724. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 1.40 (3H, d, J=6.4 Hz, 6⁗-H$_3$), 1.50 (3H, d, J=6.4 Hz, 6′-H$_3$), 1.57 (3H, d, J=6.4 Hz, 6″-H$_3$), 1.63 (3H, d, J=6.1 Hz, 6‴-H$_3$), 2.22 (1H, ddd, J=3.1, 7.0, 14.4 Hz, 2-H$_a$), 2.61 (1H, ddd, J=3.1, 7.0 Hz, 14.4 Hz, 2-H$_b$), 3.79 (1H, m, 5′-H), 3.85 (1H, m, 11-H), 3.89 (1H, d, J=3.4 Hz, 4′-H), 4.13 (1H, dd, J=3.4, 9.3 Hz, 3′-H), 4.16 (1H, dd, J=9.5, 9.5 Hz, 4‴-H), 4.31 (1H, m, 5‴-H), 4.36 (1H, m, 5⁗-H), 4.44 (1H, dd, J=3.4, 9.8 Hz, 3⁗-H), 4.45 (1H, dd, J=3.4, 9.5 Hz, 3‴-H), 4.47 (1H, dd, J=7.9, 9.3 Hz, 2′-H), 4.56 (1H, dd, J=9.8, 9.8 Hz, 4″-H), 4.73 (1H, br s, 2⁗-H), 4.75 (1H, d, J=7.9 Hz, 1′-H), 4.96 (1H, m, 5″-H), 5.23 (1H, br s, 2″-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, 100.4, 101.4, 103.5, 174.5, 176.2, 176.6. SI-MS m/z: 1017 $(M+K)^+$, 1001 $(M+Na)^+$, 433 (**v**), 217 (**vi**). Negative FAB-MS m/z: 977 $(M-H)^-$, 761 (**vii**), 545 (**viii**), 417 (**ix**+H). *Anal.* Calcd for $C_{48}H_{82}O_{20}\cdot H_2O$: C, 57.82; H, 8.49. Found: C, 57.43; H, 8.42.

Mammoside H$_1$ (**12**): Colorless fine crystals from EtOH, mp 145—146 °C, $[\alpha]_D$ −18° (c=1.2, in MeOH at 26 °C). IR (KBr) cm^{-1}: 3360, 2915, 1718. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 0.87 (3H, t, J=7.3 Hz, ω-H$_3$), 0.88 (3H, t, J=6.9 Hz, –CH(CH$_3$)CH$_2$C$\underline{H}_3$), 1.03 (3H, d, J=7.1 Hz), 1.19 (3H, d, J=6.7 Hz), 1.21 (3H, d, J=6.7 Hz) [–CH(C$\underline{H}_3$)$_2$×2, –CH(C$\underline{H}_3$)CH$_2$CH$_3$], 1.40 (3H, d, J=6.4 Hz), 1.50 (3H, d, J=6.4 Hz), 1.64 (3H, d, J=6.1 Hz), 1.66 (3H, d, J=6.1 Hz) (6′-, 6″-, 6‴, 6⁗-H$_3$), 2.27 (1H, ddd, J=3.0, 7.0, 14.5 Hz, 2-H$_a$), 2.42 (1H, ddd, J=3.0, 7.0, 14.5 Hz, 2-H$_b$), 3.82 (1H, m, 11-H), 4.70 (1H, d, J=7.6 Hz, 1′-H), 5.04 (1H, d, J=7.6 Hz, 1′′′′′-H), 5.50, 5.84, 6.20 (1H each, all br s, 1″-, 1‴-, 1⁗-H), 5.76 (1H, dd, J=9.5, 9.5 Hz, 4⁗-H), 5.92, 6.31 (1H each, both br s, 2″-, 2‴-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: 98.4, 100.0, 103.2, 104.2, 105.3, 173.0, 176.2, 176.6. SI-MS m/z 1177 $(M+Na)^+$, 609 (**xx**), 217 (**vi**). Negative FAB-MS m/z: 1153 $(M-H)^-$, 991 (**xxi**), 937 (**xxii**), 545 (**xix**), 417 (**ix**+H). *Anal.* Calcd for $C_{55}H_{94}O_{25}\cdot 2H_2O$: C, 55.49; H, 8.29. Found: C, 55.40; H, 8.33.

Mammoside H$_2$ (**13**): Colorless fine crystals from EtOH, mp 146—147 °C, $[\alpha]_D$ −21° (c=1.6, in MeOH at 25 °C). IR (KBr) cm^{-1}: 3356, 2915, 1716. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 0.88 (3H, t, J=6.7 Hz, ω-H$_3$), 1.04, 1.07 (3H each, both d, J=6.7 Hz, –CH(C$\underline{H}_3$)$_2$×2), 1.19, 1.21 (3H each, both d, J=7.0 Hz, –CH(C$\underline{H}_3$)$_2$×2), 1.40 (3H, d, J=6.1 Hz), 1.50 (3H, d, J=6.1 Hz), 1.64 (3H, d, J=6.4 Hz), 1.65 (3H, d, J=6.4 Hz) (6′-, 6″-, 6‴-, 6‴-H$_3$), 2.26 (1H, ddd, J=3.0, 7.0, 14.5 Hz, 2-H$_a$), 2.45 (1H, ddd, J=3.0, 6.9, 14.5 Hz, 2-H$_b$), 2.53, 2.65 (1H each, both m, –C$\underline{H}$(CH$_3$)$_2$), 3.81 (1H, m, 11-H), 4.70 (1H, d, J=7.6 Hz, 1′-H), 5.02 (1H, d, J=7.6 Hz, 1′′′′′-H), 5.74 (1H, dd, J=9.5, 9.5 Hz, 4⁗-H), 5.49, 5.82, 6.18 (1H each, all br s, 1″-, 1‴-, 1⁗-H), 5.90, 6.25 (1H each, both br s, 2″-, 2‴-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: 98.4, 100.0, 103.2, 104.2, 105.3, 173.0, 176.2, 176.6. SI-MS m/z: 1163 $(M+Na)^+$, 595 (**xvi**), 217 (**vi**). Negative FAB-MS m/z: 1139 $(M-H)^-$, 977 (**xvii**), 923 (**xviii**), 545 (**xix**), 417 (**ix**+H). *Anal.* Calcd for $C_{54}H_{92}O_{25}\cdot 2H_2O$: C, 55.09; H, 8.22. Found: C, 55.29; H, 8.16.

Treatment of Mammoside B (11) with 5% Aqueous KOH A solution of mammoside B (**11**, 500 mg) in acetone (10 ml) was treated with 5% aqueous KOH (10 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 (480 mg). Column chromatography [SiO_2 100 g, $CHCl_3$: MeOH : H_2O=7 : 3 : 1 (lower phase)] of the product (400 mg) afforded mammoside I (**14**, 347 mg). Furthermore, the product (10 mg) was subjected to GLC analysis to identify isobutyric acid by comparison with an authentic sample. GLC conditions: column, 15% free fatly acid phase (FFAP) on Chromosorb GAW dimethyldichlorosilane (DMCS) (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 (hydrogen flame ionization detector (FID)); t_R, 8 min 46 s (isobutyric acid).

Mammoside I (**14**): Colorless fine crystals from EtOH, mp 131—132 °C, $[\alpha]_D$ −87° (c=2.0, in MeOH at 24 °C). IR (KBr) cm^{-1}: 3420, 2930, 1710. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 0.92 (3H, t, J=7.3 Hz, ω-H$_3$), 1.50, 1.56, 1.58, 1.58 (3H each, all d-like, 6′-, 6″-, 6‴-, 6⁗-H$_3$), 2.30 (2H, t, J=7.5 Hz, 2-H$_2$), 3.92 (1H, m, 11-H), 4.73 (1H, d, J=7.0 Hz, 1′-H), 6.15, 6.23, 6.25 (1H each, all br s, 1″-, 1‴-, 1⁗-H). *Anal.* Calcd for $C_{40}H_{72}O_{19}\cdot H_2O$: C, 54.91; H, 8.52. Found: C, 54.89; H, 8.53.

Treatment of Mammoside B (11) with 5% NaOMe–MeOH A solution of mammoside B (**11**, 500 mg) in MeOH (20 ml) was treated with 5% NaOMe–MeOH (20 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 (401 mg), which was purified by column chromatography (SiO_2 100 g, $CHCl_3$: MeOH=3 : 1) to afford mammoside I methyl ester (**14a**, 320 mg).

Mammoside I methyl ester (**14a**): Colorless fine crystals from EtOH, mp 115—116 °C, $[\alpha]_D$ −76° (c=1.8, in MeOH at 24 °C). IR (KBr) cm^{-1}: 3418, 2925, 1718. ^{1}H-NMR (500 MHz, pyridine-d_5+D_2O) δ: 0.92 (3H, t, J=7.3 Hz, ω-H$_3$), 1.50 (3H, J=6.2 Hz, 6′-H), 1.54, 1.55, 1.57 (3H each, all d-like, 6″-, 6‴-, 6⁗-H$_3$), 2.31 (2H, t, J=7.5 Hz, 2-H$_2$), 3.62 (3H, s, –COOCH$_3$), 3.75 (1H, m, 5′-H), 3.92 (1H, br s, 4′-H), 3.93 (1H, m, 11-H), 4.11 (1H, dd, J=3.4, 9.5 Hz, 3′-H), 4.25 (1H, dd, J=9.5, 9.5 Hz, 4⁗-H), 4.29 (1H, dd, J=10.2, 10.2 Hz, 4‴-H), 4.39 (1H, dd, J=9.2, 9.2 Hz, 4″-H), 4.43 (1H, dd, J=3.4, 9.5 Hz, 3⁗-H), 4.44 (1H, dd, J=8.5, 9.5 Hz, 2′-H), 4.52 (1H, dd, J=3.4, 9.2 Hz, 3″-H), 4.58 (1H, dd, J=3.4, 10.2 Hz, 3‴-H), 4.63 (1H, br s, 2‴-H), 4.73 (1H, d, J=7.9 Hz, 1′-H), 4.74 (1H, br s, 2″-H), 4.79 (1H, br s, 2⁗-H), 4.30, 4.31, 4.82 (1H each, all m, 5″-, 5‴-, 5⁗-H), 6.19, 6.21, 6.27 (1H each, all br s, 1″-, 1‴-, 1⁗-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: 101.4, 101.4, 102.8, 102.8 [1′-, 1″-, 1‴-, 1⁗-C, J_{C-H}: 159.9 Hz (fucopyranosyl moiety), 171.0, 171.5, 171.6 Hz (rhamnopyranosyl moieties)], 174.0. SI-MS m/z: 909 $(M+K)^+$, 893 $(M+Na)^+$, 585 (**i**), 439 (**ii**), 293 (**iii**), 147 (**iv**). *Anal.* Calcd for $C_{41}H_{74}O_{19}\cdot 2H_2O$: C, 54.29; H, 8.67. Found: C, 54.32; H, 8.65.

Methanolysis of Mammoside I Methyl Ester (14a) A solution of mammoside I methyl ester (**14a**, 30 mg) in 9% HCl–MeOH (2.0 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 (29 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 (11S)-(+)-jalapinolate[2a)] (**15**, 3.8 mg) and a methyl glycoside mixture (19 mg). A solution of the methyl glycoside mixture (3 mg) in pyridine (0.3 ml) was treated with N,O-bis(trimethylsilyl)-trifluoroacetoamide (0.6 ml) at room temperature for 1 h. The reaction mixture was directly subjected to GLC analysis to identify methyl 2,3,4-O-tri(trimethylsilyl)-D-fucopyranoside and methyl 2,3,4-O-tri(trimethylsilyl)-L-rhamnopyranoside in a 1 : 3 ratio by comparison with authentic samples. GLC conditions-1: column, 15% silicone OV-1 on Chromosorb WAW DMCS (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 [methyl 2,3,4-O-tri(trimethylsilyl)-L-rhamnopyranoside], 4 min 22 s [methyl 2,3,4-O-tri(trimethylsilyl)-D-fucopyranoside]. GLC conditions-2: column, 15% silicone SE-30 on Chromosorb WAW DMCS (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 [methyl 2,3,4-O-tri(trimethylsilyl)-L-rhamnopyranoside], 4 min 02 s [methyl 2,3,4-O-tri(trimethylsilyl)-D-fucopyranoside].

Complete Methylation of Mammoside I Methyl Ester (14a) Followed by Methanolysis A solution of mammoside I methyl ester (**14a**, 200 mg) in DMSO (3.0 ml) was treated with a dimsylsodium reagent [5 ml, prepared from 60% NaH (1.0 g) and DMSO (10 ml)][8)] and the whole was stirred at room temperature for 2 h. Methyl iodide (5.0 ml) was added at 0 °C and the reaction mixture was stirred at room temperature for 12 h, poured into ice-water and extracted with EtOAc. The EtOAc extract was washed with H_2O and dried over $MgSO_4$. The solvent was evaporated off under reduced pressure to give a product (180 mg). A solution of the product (100 mg) in 9% HCl–MeOH (10 ml) was heated under reflux for 2 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 (132 mg). Repeated column chromatography (SiO_2 20 g, $CHCl_3$: MeOH=30 : 1 and n-hexane : EtOAc=7 : 1) of the product

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(50 mg) afforded methyl (11*S*)-(+)-jalapinolate (**15**, 13 mg). Furthermore, the product (1 mg) was subjected to GLC analysis, which revealed methyl 3,4-di-*O*-methyl-D-fucopyranoside (I), methyl 2,3-di-*O*-methyl-L-rhamnopyranoside (II), and methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside (III) in a 1 : 2 : 1 ratio. GLC conditions-1: column, 15% neopenthylglycol succinate (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 49 s (I), 6 min 38 s (II), 2 min 41 s (III). 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 38 s (I), 4 min 22 s (II), 3 min 44 s (III).

Glycosidation of Methyl (11*S*)-(+)-Jalapinolate (15) Giving the Monoglycoside (17) A solution of methyl (11*S*)-(+)-jalapinolate (**15**, 450 mg, 1.57 mmol) and 2,3,4-tri-*O*-benzyl-D-fucopyranosyl-1-*O*-trichloroacetimidate (**16**, 1.49 g, 2.36 mmol) in CH_2Cl_2 (30 ml) was treated with boron trifluoride etherate (14 μl, 0.05 eq) and molecular sieves 4 Å (10 g). The mixture was stirred at −40 °C for 3 h. The reaction mixture was 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 give a product (1.83 g). Purification of the product by column chromatography (SiO_2 50 g, *n*-hexane : EtOAc = 4 : 1) afforded a glycoside (915 mg). A solution of the glycoside (915 mg) in MeOH (5 ml) was treated with 1% 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 (850 mg), which was purified by column chromatography (SiO_2 20 g, *n*-hexane : EtOAc = 1 : 4) to afford **17** (505 mg, 1.17 mmol).

17: A white powder, $[\alpha]_D$ −13° (c = 1.8, in $CHCl_3$ at 21 °C). IR ($CHCl_3$) cm^{-1}: 3590, 2985, 1730. ^1H-NMR (500 MHz, $CDCl_3$) δ: 0.89 (3H, t, J = 7.0 Hz, ω-H_3), 1.35 (3H, d, J = 6.4 Hz, 6′-H_3), 2.31 (2H, t, J = 7.5 Hz, 2-H_2), 3.47 (1H, m, 11-H), 3.67 (3H, s, –$COOCH_3$), 3.51—3.74 (4H, m, 2′-, 3′-, 4′-, 5′-H), 4.23 (1H, d, J = 7.4 Hz, 1′-H). *Anal.* Calcd for $C_{23}H_{44}O_7 \cdot H_2O$: C, 61.31; H, 10.29. Found: C, 61.21; H, 10.32.

Conversion of 17 to 18 A solution of **17** (175 mg, 0.41 mmol) in *N*,*N*-dimethylformamide (3.0 ml) was treated with 2,2-dimethoxypropane (200 μl, 2.1 mmol) and (1*R*)-(−)-10-camphorsulfonic acid (5 mg) and the whole was stirred at room temperature for 3 h. The reaction mixture 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 give a product (290 mg). Column chromatography (SiO_2 20 g, *n*-hexane : EtOAc = 2 : 1) of the product afforded **18** (195 mg, 0.41 mmol).

18: A white powder, $[\alpha]_D$ +9.8° (c = 1.2, in $CHCl_3$ at 26 °C). IR ($CHCl_3$) cm^{-1}: 3600, 2990, 1728. ^1H-NMR (500 MHz, $CDCl_3$) δ: 0.89 (3H, t, J = 7.2 Hz, ω-H_3), 1.40 (3H, d, J = 6.7 Hz, 6′-H_3), 1.54, 1.59 (3H each, both s), 2.31 (2H, t, J = 7.5 Hz, 2-H_2), 3.51 (1H, dd, J = 8.2, 7.3 Hz, 2′-H), 3.61 (1H, m, 11-H), 3.67 (3H, s, –$COOCH_3$), 3.84 (1H, dq, J = 2.1, 6.7 Hz, 5′-H), 4.00 (1H, dd, J = 5.5, 2.1 Hz, 4′-H), 4.04 (1H, dd, J = 5.5, 7.3 Hz, 3′-H), 4.16 (1H, d, J = 8.2 Hz, 1′-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: 51.5, 69.2, 73.8, 76.5, 78.9, 79.9, 101.5, 109.8, 174.4. EI-MS m/z (%): 457 ($M^+ - CH_3$, 21), 441 (12), 269 (100), 99 (90). *Anal.* Calcd for $C_{26}H_{48}O_7$: C, 66.07; H, 10.24. Found: C, 66.29; H, 10.18.

Conversion of 18 to 20 A solution of **18** (195 mg, 0.41 mmol) in CH_2Cl_2 (15 ml) was treated with **19** (400 mg, 0.92 mmol), boron trifluoride etherate (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 evaporated under reduced pressure to give a product (620 mg). A solution of the product (620 mg) in MeOH (2.5 ml) was treated with 1% NaOMe–MeOH (2.5 ml) and the mixture was stirred at room temperature for 30 min. The reaction mixture 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 **20** (218 mg, 0.38 mmol).

20: A colorless oil, $[\alpha]_D$ −26° (c = 1.4, in $CHCl_3$ at 25 °C). IR ($CHCl_3$) cm^{-1}: 3580, 2990, 1725. ^1H-NMR (500 MHz, $CDCl_3$) δ: 0.89 (3H, t, J = 7.2 Hz, ω-H_3), 1.26 (3H, d, J = 6.4 Hz), 1.34 (3H, s), 1.39 (3H, d, J = 6.4 Hz), 1.58 (3H, s), 2.31 (2H, t, J = 7.5 Hz, 2-H_2), 3.43 (1H, dd, J = 7.1, 8.2 Hz, 2′-H), 3.60 (1H, m, 11-H), 3.67 (3H, s, –$COOCH_3$), 3.80 (1H, dq, J = 2.1, 6.4 Hz, 5′-H), 3.96 (1H, dd, J = 2.1, 5.4 Hz, 4′-H), 4.10 (1H, m, 5″-H), 4.13 (1H, dd, J = 5.4, 7.1 Hz, 3′-H), 4.24 (1H, d, J = 8.2 Hz, 1′-H), 5.31 (1H, d, J = 1.2 Hz, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: 51.1, 68.8, 69.3, 72.3, 72.5, 73.9, 75.8, 77.1, 79.8, 80.9, 100.1 (1″-C, J_{C-H} = 169.9 Hz), 100.5 (1′-H, J_{C-H} = 156.8 Hz), 109.6, 173.8. *Anal.* Calcd for $C_{32}H_{58}O_{11}$: C, 62.11; H, 9.45. Found: C, 62.27; H, 9.38.

Conversion of 20 to 21 A solution of **20** (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. After usual work-up of the EtOAc extract, the solvent was evaporated under reduced pressure to give a product (150 mg). Purification of the product by column chromatography (SiO_2 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 CH_2Cl_2 (10 ml) was treated with **19** (140 mg, 0.32 mmol), boron trifluoride etherate (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 off under reduced pressure to give a product (210 mg). Then, a solution of the product (210 mg) in MeOH (2.5 ml) was treated with 1% NaOMe–MeOH (2.5 ml) and the mixture 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 (330 mg), which was purified by column chromatography (SiO_2 15 g, *n*-hexane : EtOAc = 2 : 3) to afford a triglycoside (110 mg). A solution of the triglycoside (110 mg, 0.14 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 mixture was stirred at room temperature for 2 h. It was then poured into ice-water and the whole was extracted with EtOAc. After usual work-up of the EtOAc extract, the solvent was evaporated off under reduced pressure to give a product (145 mg). Purification of the product by column chromatography (SiO_2 10 g, *n*-hexane : EtOAc = 3 : 1) afforded **21** (115 mg, 0.14 mmol).

21: A colorless oil, $[\alpha]_D$ −27° (c = 1.0, in $CHCl_3$ at 24 °C). IR ($CHCl_3$) cm^{-1}: 3500, 2990, 1725. ^1H-NMR (500 MHz, $CDCl_3$) δ: 0.88 (3H, t, J = 6.7 Hz, ω-H_3), 1.21 (3H, d, J = 6.1 Hz), 1.27 (3H, d, J = 6.1 Hz), 1.33 (6H, s), 1.35 (3H, s), 1.39 (3H, d, J = 6.7 Hz), 1.53 (3H, s), 1.55 (6H, s), 2.31 (2H, t-like, 2-H_2), 3.67 (3H, s, –$COOCH_3$), 4.22 (1H, d, J = 8.2 Hz, 1′-H), 5.51, 5.59 (1H each, both br s, 1″-H, 1‴-H). *Anal.* Calcd for $C_{44}H_{76}O_{15}$: C, 62.54; H, 9.06. Found: C, 62.43; H, 9.01.

Conversion of 21 to Mammoside I Methyl Ester (14a) A solution of **21** (30 mg, 0.036 mmol) and **19** (30 mg, 0.069 mmol) in CH_2Cl_2 (2.0 ml) was treated with boron trifluoride etherate (15 μl, 0.05 eq) and molecular sieves 4 Å (2 g), and the whole was 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 give a product (83 mg). A solution of this product in MeOH (1.0 ml) was treated with 1% NaOMe–MeOH (1.0 ml) and the reaction mixture was stirred at room temperature for 20 min, then poured into ice-water, and extracted with $CHCl_3$. After usual work-up of the $CHCl_3$ extract, the solvent was concentrated under reduced pressure to give a product (74 mg), which was purified by column chromatography (SiO_2 10 g, *n*-hexane : EtOAc = 1 : 4) to afford a product (33 mg). The product (33 mg) was treated with 1% HCl–MeOH (1.0 ml) with stirring at room temperature for 2 h, and neutralized with an $AgCO_3$ powder. After removal of the precipitate, the filtrate was concentrated under reduced pressure to give a product (55 mg). Purification of the product by column chromatography (SiO_2 7 g, $CHCl_3$: MeOH = 3 : 1) afforded **14a** (24 mg, 0.028 mmol), which was identical with mammoside I methyl ester prepared from mammoside B (**11**).

Treatment of Mammoside A (10) with 5% Aqueous KOH A solution of mammoside A (**10**, 40 mg) in acetone (2.0 ml) was treated with 5% aqueous KOH (2.0 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 (38 mg). Column chromatography [SiO_2 10 g, $CHCl_3$: MeOH : H_2O = 65 : 35 : 10 (lower phase)] of this product (30 mg) afforded mammoside I (**14**, 21 mg).

The product (1 mg) was subjected to GLC analysis and identified as methylbutyric acid by comparison with an authentic sample. GLC conditions: column, 15% FFAP on Chromosorb GAW DMCS (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;

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t_R, 12 min 46 s (methylbutyric acid).

Determination of the Absolute Configuration of Methylbutyric Acid A solution of mammoside A (**10**, 500 mg) in acetone (3.0 ml) was treated with 10% aqueous KOH (3.0 ml) and the whole was heated under reflux for 3 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 give a mixture of an organic acid (235 mg). A solution of the product in *N*,*N*-dimethylformamide (3 ml) was treated with potassium fluoride (200 mg) and α-bromoacetophenone (300 mg), and the mixture was stirred at room temperature for 1 h, then poured into ice-water and extracted with ether. After usual work-up of the ether extract, the solvent was removed under reduced pressure to give a product (540 mg). 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) of the product afforded (2*S*)-(+)-methylbutyric acid phenacyl ester (28 mg).

(2*S*)-(+)-Methylbutyric Acid Phenacyl Ester: A pale yellow oil, $[\alpha]_D$ +15° (*c* = 5.2, in $CHCl_3$ at 25 °C). ^{1}H-NMR (90 MHz, $CDCl_3$) δ: 0.99 (3H, *J* = 7.5 Hz), 1.25 (3H, d, *J* = 7.0 Hz), 1.80 (2H, m), 2.57 (1H, m), 5.34 (2H, s), 7.49 (2H, t, *J* = 7.6 Hz), 7.61 (1H, t, *J* = 7.6 Hz), 7.92 (2H, d, *J* = 7.6 Hz).

An authentic sample (469 mg, 0.5 ml) of (2*S*)-(+)-methylbutyric acid was treated with potassium fluoride (533 mg) and α-bromoacetophenone (1.1 g) in *N*,*N*-dimethylformamide (10 ml), and the whole was stirred 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 evaporated off under reduced pressure to give a product (1.7 g). Column chromatography (SiO_2 10 g, *n*-hexane : EtOAc = 15 : 1) of the product afforded (2*S*)-(+)-methylbutyric acid phenacyl ester {571 mg, $[\alpha]_D$ +15° (*c* = 5.4, in $CHCl_3$ at 25 °C)}.

Treatment of Mammoside A (10) with 5% NaOMe–MeOH A solution of mammoside A (**10**, 40 mg) in MeOH (1.0 ml) was treated with 5% NaOMe–MeOH (2.0 ml) and the mixture 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, which was purified by column chromatography (SiO_2 10 g, $CHCl_3$: MeOH = 6 : 1) to afford mammoside I methyl ester (**14a**, 24 mg).

Treatment of Mammoside H_2 (13) with 5% Aqueous KOH A solution of mammoside H_2 (**13**, 100 mg) in acetone (4.0 ml) was treated with 5% aqueous KOH (4.0 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 (73 mg). Column chromatography [SiO_2 30 g, $CHCl_3$: MeOH : H_2O = 65 : 35 : 10 (lower phase)] of the product (70 mg) afforded mammoside J (**22**, 65 mg). Furthermore, the product (1 mg) was subjected to GLC analysis to identify isobutyric acid by comparison with an authentic sample. GLC conditions: column, 15% FFAP on Chromosorb GAW DMCS (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).

Mammoside J (**22**): Colorless fine crystals from EtOH, mp 182—183 °C, $[\alpha]_D$ −70° (*c* = 1.5, in MeOH at 27 °C). IR (KBr) cm^{-1}: 3370, 2912, 1710. ^{1}H-NMR (500 MHz, pyridine-d_5 + D_2O) δ: 0.90 (3H, t, *J* = 7.2 Hz, ω-H_3), 1.50 (3H, d, *J* = 6.4 Hz), 1.54 (3H, d, *J* = 6.1 Hz), 1.58 (3H, d, *J* = 6.1 Hz), 1.59 (3H, d, *J* = 6.1 Hz) (6′-, 6″-, 6‴-, 6⁗-H_3), 2.30 (2H, m, 2-H_2), 4.76 (1H, d, *J* = 7.5 Hz, 1′-H), 5.17 (1H, d, *J* = 7.6 Hz, 1′′′′′-H), 6.09, 6.12, 6.12 (1H each, all br s, 1″-, 1‴-, 1⁗-H). *Anal.* Calcd for $C_{46}H_{82}O_{24} \cdot H_2O$: C, 53.27; H, 8.16. Found: C, 53.39; H, 8.09.

Treatment of Mammoside H_2 (13) with 5% NaOMe–MeOH Mammoside H_2 (**13**, 30 mg) in MeOH (1.0 ml) was treated with 5% NaOMe–MeOH (1.0 ml) and the mixture 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. Column chromatography (SiO_2 10 g, $CHCl_3$: MeOH = 6 : 1) of this product afforded mammoside J methyl ester (**22a**, 16 mg).

Mammoside J Methyl Ester (**22a**): Colorless fine crystals from EtOH, mp 176—177 °C, $[\alpha]_D$ −71° (*c* = 2.0, in MeOH at 20 °C). IR (KBr) cm^{-1}: 3368, 2917, 1717. ^{1}H-NMR (500 MHz, pyridine-d_5 + D_2O) δ: 0.92 (3H, t, *J* = 7.0 Hz, ω-H_3), 1.51 (3H, *J* = 6.4 Hz), 1.55 (3H, d, *J* = 6.1 Hz), 1.58 (3H, d, *J* = 6.1 Hz), 1.59 (3H, d, *J* = 6.1 Hz) (6′-, 6″-, 6‴-, 6⁗-H_3), 2.30 (2H, m, 2-H_2), 3.64 (3H, s, –$COOCH_3$), 3.65 (1H, m, 11-H), 4.81 (1H, d, *J* = 7.5 Hz, 1′-H), 5.17 (1H, d, *J* = 7.6 Hz, 1′′′′′-H), 5.82, 6.13, 6.15 (1H each, all br s, 1″-, 1‴-, 1⁗-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: 100.4, 102.0, 102.5, 102.7, 104.5 [1′-, 1″-, 1‴-, 1⁗, 1′′′′′-C, J_{C-H}: 171.0, 171.5, 171.6 Hz (rhamnopyranosyl moieties)], 173.4. Negative FAB-MS *m*/*z*: 1031 $(M-H)^-$, 885 (**xv**), 869 (**xiv**), 577 (**xiii**). *Anal.* Calcd for $C_{47}H_{84}O_{24} \cdot 2H_2O$: C, 52.80; H, 8.30. Found: C, 52.68; H, 8.38.

Methanolysis of Mammoside J Methyl Ester (22a) A solution of mammoside J methyl ester (**22a**, 40 mg) in 9% HCl–MeOH (5.0 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 (39 mg). Repeated column chromatography (SiO_2 20 g, $CHCl_3$: MeOH = 30 : 1 → 5 : 1, *n*-hexane : EtOAc = 7 : 1) of the product afforded (11*S*)-(+)-methyl jalapinolate[2a)] (5.2 mg) and a methyl glycoside mixture (27 mg). A solution of the methyl glycoside mixture (3.0 mg) in pyridine (0.3 ml) was treated with *N*,*O*-bis(trimethylsilyl)-trifluoroacetoamide (0.6 ml) at room temperature for 1 h. The reaction mixture was directly subjected to GLC analysis to identify methyl 2,3,4-*O*-tri(trimethylsilyl)-D-fucopyranoside, methyl 2,3,4-*O*-tri(trimethylsilyl)-L-rhamnopyranoside and methyl 2,3,4,6-*O*-tetra(trimethylsilyl)-D-glucopyranoside by comparison with authentic samples. GLC conditions-1: column, 15% silicone OV-1 on Chromosorb WAW DMCS (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) temperature, 180 °C; t_R, 4 min 22 s [methyl 2,3,4-*O*-tri(trimethylsilyl)-D-fucopyranoside], 4 min 01 s [methyl 2,3,4-*O*-tri(trimethylsilyl)-L-rhamnopyranoside], 16 min 34 s, 19 min 50 s [methyl 2,3,4,6-*O*-tetra(trimethylsilyl)-D-glucopyranoside]. GLC conditions-2: column, 15% silicone SE-30 on Chromosorb WAW DMCS (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) temperature, 180 °C; t_R, 4 min 02 s [methyl 2,3,4-*O*-tri(trimethylsilyl)-D-fucopyranoside], 3 min 42 s [methyl 2,3,4-*O*-tri(trimethylsilyl)-L-rhamnopyranoside], 14 min 40 s, 17 min 53 s [methyl 2,3,4,6-*O*-tetra(trimethylsilyl)-D-glucopyranoside].

Enzymatic Hydrolysis of 22a A solution of **22a** (40 mg) in H_2O (2 ml) was treated with crude hesperidinase (Sigma, 100 mg) and the whole was stirred at room temperature for 36 h. The precipitate was removed by filtration. The filtrate was evaporated under reduced pressure to give a product, which was purified by column chromatography [SiO_2 15 g, $CHCl_3$: MeOH = 3 : 1 → $CHCl_3$: MeOH : H_2O = 7 : 3 : 1 (lower phase)] to afford D-glucose ($[\alpha]_D$ +47.2°, *c* = 0.4, after 24 h in H_2O) and mammoside I methyl ester (**14a**), which was identical with an authentic sample by comparisons of TLC behavior [$CHCl_3$: MeOH : H_2O = 7 : 3 : 1 (lower phase)], $[\alpha]_D$, IR, and ^{1}H-NMR spectra.

Complete Methylation of 22a A solution of mammoside J methyl ester (**22a**, 200 mg) in DMSO (3.0 ml) was treated with a dimsylsodium reagent [5.0 ml, prepared from 60% NaH (1.0 g) and DMSO (10 ml)][8)] and the whole was stirred at room temperature for 1 h. Methyl iodide (3.0 ml) was added at 0 °C, and the whole was stirred at room temperature for 12 h. The reaction mixture was poured into ice-water and extracted with EtOAc. The EtOAc extract was washed with H_2O, and dried over $MgSO_4$. The solvent was evaporated off under reduced pressure to give a product (165 mg). A solution of this product in 9% HCl–MeOH (5.0 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 (133 mg). Repeated column chromatography (SiO_2 20 g, $CHCl_3$: MeOH = 30 : 1 and *n*-hexane : EtOAC = 7 : 1) of the product (50 mg) afforded methyl (11*S*)-(+)-jalapinolate (11 mg). Furthermore, the product (1 mg) was subjected to GLC analysis, which identified methyl 3,4-di-*O*-methyl-D-fucopyranoside (IV), methyl 2,3-di-*O*-methyl-L-rhamnopyranoside (V), methyl 2,3,4-tri-*O*-methyl-L-rhamnopyranoside (VI), methyl 2-*O*-methyl-L-rhamnopyranoside (VII), and methyl 2,3,4,6-tetra-*O*-methyl-D-glucopyranoside (VIII) in a 1 : 1 : 1 : 1 : 1 ratio. 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 49 s (VI), 6 min 38 s (V), 2 min 41 s (VI), 9 min 02 s (VII), 3 min 25 s (VIII). 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) 170 °C; t_R, 4 min 38 s (IV), 4 min 22 s (V), 3 min 44 s (VI), 4 min 09 s (VII), 6 min 57 s, 8 min

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43 s (VIII).

Treatment of Mammoside H_1 (12) with 5% Aqueous KOH A solution of mammoside H_1 (**12**, 50 mg) in acetone (2.0 ml) was treated with 5% aqueous KOH (2.0 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 (36 mg), which was purified by column chromatography [SiO_2 15 g, $CHCl_3$: MeOH : H_2O = 65 : 35 : 10 (lower phase)] to afford mammoside J (**22**, 28 mg).

Furthermore, the product (1 mg) was subjected to GLC analysis to identify isobutyric acid and (2*S*)-(+)-methylbutyric acid by comparison with authentic samples.

Treatment of Mammoside H_1 (12) with 5% NaOMe–MeOH Mammoside H_1 (**12**, 30 mg) was treated with 5% NaOMe–MeOH (1.0 ml) and the mixture 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. Column chromatography (SiO_2 10 g, $CHCl_3$: MeOH = 6 : 1) of the product afforded mammoside J methyl ester (**22a**, 16 mg).

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