THE MNIOPETALS, NEW INHIBITORS OF REVERSE TRANSCRIPTASES
FROM A Mniopetalum SPECIES (BASIDIOMYCETES)

II. STRUCTURE ELUCIDATION

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The structures of six new drimane sesquiterpenoids, mniopetals A~F, were elucidated by a combination of chemical and spectroscopic methods. The mniopetals are inhibitors of RNA-directed DNA-polymerases.

In our search for novel inhibitors of RNA-directed DNA-polymerases of human immunodeficiency, avian myeloblastosis and murine leukemia viruses1~4, six new antibiotics, mniopetals A~F (1~6), as well as the biologically inactive sesquiterpenoids 1z,15-dihydroxymarasmene (11) and (−)-11,12-dihydroxydrimene (14) were isolated from fermentations of a Canadian Mniopetalum species. 11 had been previously found in cultures of Marasmius oreades5 whereas 14 is a known intermediate in the total synthesis of polygodial6,7.

The production, isolation and biological characterization of the mniopetals A~F has been described in the preceding paper8. In this study we report the structural elucidation of these compounds.

Structural Elucidation of the Mniopetals

Mniopetals A~F (1~6) are closely related to marasmal (7), a drimane derivative recently isolated by AYER et al.5 from cultures of the basidiomycete Marasmius oreades.

Fig. 1. Structures of mniopetal A~F (1~6) and marasmal (7).
Table 1. $^1$H NMR spectral data for mniopetals A~F (1~6) (400 MHz, $\delta$ in ppm).

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1: $J$ (Hz): 1,2$\beta$ = 2.2; 2$\beta$,3$\alpha$ = 12.7; 2$\beta$,3$\beta$ = 4.1; 3a,3$\beta$ = 12.5; 5,6$\alpha$ = 3.4; 5,6$\beta$ = 12.7; 6x,6$\beta$ = 19.2; 6x,7 = 6.7; 2',3$\alpha$a = 6.5; 2',3$\beta$b = 6.5; 9',10' = 6.9.

2: $J$ (Hz): e.g. 2',3'a = 7.8; 2',3'b = 4.2.

6: $J$ (Hz): e.g., 1,2$\beta$ = 2.5; 2x,2$\alpha$ = 14.1; 2x,3$\alpha$ = 3.4; 2x,3$\beta$ = 7.1; 2$\beta$,3$\alpha$ = 14.2; 2$\beta$,3$\beta$ = 2.5; 3a,3$\beta$ = 14.1.

Table 2. $^{13}$C NMR spectral data for mniopetals A (1), B (2) and F (6) (100.62 MHz, $\delta$ in ppm, $J$ in Hz).

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<td>33.19 (qm, 126°)</td>
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$^a$ $^1$$J_{CH}$ (Hz).

$^b$ $^2$$J_{CH}$ (Hz).

$^c$ $^3$$J_{CH}$ (Hz).

As is indicated by the $^1$H and $^{13}$C NMR data (Tables 1 and 2) all mniopetals contain the same structural pattern at rings B and C. The presence of the $\alpha$,\$unsaturated aldehyde unit is confirmed by a strong IR absorption at $\sim$1675 cm$^{-1}$ (KBr), signals at $\delta$ $\sim$9.45 (CHO) and $\sim$7.2 (br d, 7-H) in the
The 1H NMR spectrum, and signals at δ ~ 194 (C-12), ~ 156 (C-7), and ~ 139 (C-8) in the 13C NMR spectrum. The lactone and lactol groups of the mnioptals give rise to 13C NMR signals and δ ~ 177 (C-15) and ~ 100 (C-11), respectively, and absorptions at ~ 1760 and ~ 3430 cm⁻¹ in the IR spectrum. In all cases, the 11-H signal in the 1H NMR spectrum appears as a broad singlet, which is characteristic for an α-orientation of the 11-hydroxy group.

In mnioptal A (1), C27H40O9, the presence of a sequence (C)-CH(OH)-CH(OCOR)-CH2-(C) can be deduced from the 1H NMR spectrum. It forms part of ring A, which is connected with the rest of the molecule by the 1H-13C long range correlations given in Fig. 2.

The stereochemistry of ring A follows from the 1H NMR spectrum. Since 2-H at δ 5.35 shows a diaxial coupling of J = 12.7 Hz to H-3a, the acyloxy substituent must occupy an equatorial position. The 1-H resonance appears as a broad singlet indicating that the hydroxy group at this carbon must be axial. This is supported by the strong deshielding of the protons in 3- and 9-positions, due to 1,3-interaction with the axial hydroxy group.

The remaining 1H and 13C NMR data of mnioptal A (1) are consistent with the presence of a 2-acetoxydecanoyloxy residue at C-2. The absolute configuration at the side chain stereogenic center was determined by methanolysis of 1 to methyl 2-hydroxydecanoate (8) which subsequently was converted into the (S)-MTPA ester 9 ([MTPA = α-methoxy-α(trifluoromethyl)-(phenylacetic acid)]) by treatment with

![Fig. 2. Important 1H-13C long-range couplings (COLOC experiments) of mnioptal A (1), arrows are directing from H to C.](image)

![Fig. 3. Conversion of mnioptal A (1) into the (S)-MTPA ester of methyl (R)-2-hydroxydecanoate [(R,S)-9].](image)

![Fig. 4. Characteristic fragmentations of 1 in the EI-MS.](image)
(R)-(−)-MTPA-Cl\(^{10,11}\). For comparison, a mixture of \((S,R)\)-9 and \((S,S)\)-9 was prepared by esterification of racemic \(8\) with \((R)-(−)-MTPA-Cl\). As was demonstrated by Yasuhara and Yamaguchi\(^{11}\), the \(^1\)H NMR data of the MTPA-derivatives of \(\alpha\)-hydroxycarboxylic acid esters allow an unambiguous assignment of their absolute configuration. In the present case, the \((S, R)\)-diastereomer of MTPA ester 9 was obtained, which proves the \((2'R)\)-configuration of the acetoxyacyl side chain in mniopetal A (1).

On electron impact, mniopetal A (1) and other acylated compounds of this series undergo McLafferty rearrangement with loss of the acyloxy chain yielding an intense ‘drimane’ ion at \(m/z\) 278 (C\(_{15}\)H\(_{16}\)O\(_5\)) in the MS. In the case of 1, \(\alpha\)-cleavage of the 2-acetoxydecanoyl side chain leads to a diagnostic fragment ion \(m/z\) 213 (C\(_{12}\)H\(_{22}\)O\(_3\)) as shown in Fig. 4.

Mniopetal B (2) shows a peak at \(m/z\) 448 (C\(_{23}\)H\(_{36}\)O\(_8\)) due to the loss of water from the molecular ion. The presence of a strong [M + Na]\(^+\) peak at \(m/z\) 489 in the (+)-FAB-MS confirms C\(_{23}\)H\(_{36}\)O\(_8\) as the molecular formula. The \(^1\)H and \(^{13}\)C NMR spectra of 2 lack the signals of the acetyl residue, and show an upfield shift of the 2′-H resonance to \(\delta\) 4.17. Therefore, mniopetal B (2) is the deacetyl derivative of 1.

The MS and NMR spectra of mniopetal C (3), C\(_{23}\)H\(_{34}\)O\(_8\), demonstrate that this compound is the lower homologue of mniopetal B (2) and contains a 2-hydroxyoctanoyloxy residue at C-2.

Mniopetal D (4), C\(_{25}\)H\(_{38}\)O\(_8\), is an isomer of mniopetal B (2) in which the 2-acetoxydecanoyl residue is attached to the OH-group in 1-position. This cases deshielding of 1-H to \(\delta\) 5.84 and an upfield shift of the 2-H resonance to \(\delta\) 4.39. The acyl residue in 1-position effects an upfield shift of 9-H to \(\delta\) 3.24 whereas in the 2-acylated compounds 1 ~ 3 the corresponding signal occurs at \(\delta\) ~ 3.8.

Mniopetal E (5), C\(_{15}\)H\(_{20}\)O\(_6\), is the basic diol from which the mniopetals 1 ~ 4 are derived by esterification. In the \(^1\)H NMR spectrum of 5 the resonances of 1-H and 2-H appear at \(\delta\) 4.40 and 4.14, respectively.

Mniopetal F (6), C\(_{15}\)H\(_{20}\)O\(_5\), contains only one axial hydroxy group at ring A. The location of this substituent and the relative stereochemistry of 6 were established by NOE experiments given in Fig. 5. It should be noted that during NMR measurements in CD\(_3\)OD the pseudoaxial \(\beta\)-proton in the pseudoaxial 6-\(\beta\)-proton in 6 was smoothly exchanged against deuterium. Kuehneromycin A (10), the 1-oxo derivative corresponding to mniopetal F (6) has been recently found in cultures of a Tasmanian Kuehneromyces sp.\(^3\).

One of the major metabolites of Mniopetalum sp., \(1\alpha,15\)-dihydroxymarasmene (11), has already been described as a cometabolite of marasmal (7) from Marasmius oreades\(^5\). 11, C\(_{15}\)H\(_{22}\)O\(_4\), shows complex \(^1\)H NMR and \(^{13}\)C NMR spectra reflecting an equilibrium between the two epimeric hemiacetals. On acetylation, 11 yielded a mixture of...

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**Fig. 5.** NOE correlations for mniopetal F (6).

**Fig. 6.** Structures of kuehneromycin (10), \(1\alpha,15\)-dihydroxymarasmene (11), diacetate 12, and diacetoxyaldehyde 13.
diacetate 12 and diacetoxyaldehyde 13 which could be separated by chromatography. In contrast to the free hemiacetal 11, only one single epimer of 12 was observed.

The absolute stereochemistry of 11 given in the formula, was determined by high field NMR application of the Mosher method and will be topic of a separate publication12).

A second biologically inactive compound from *Mniopetalum* was identified as the known \((-\)-)11,12-dihydroxy-7-drimene (14), C\textsubscript{15}H\textsubscript{26}O\textsubscript{2}. Its spectral and physical data were in agreement with those reported in the literature7,8). Since the absolute configuration of \((-\)-)11,12-dihydroxy-7-drimene has been established by total syntheses7,8), the natural product 14 possesses the absolute stereochemistry given in the formula. It corresponds to that of 11 and most of the natural occurring drimane derivatives of known absolute configuration13). Since the mniopetals A~F (1~6) are produced by the same fungus, an identical stereochemistry can be assumed for these compounds. All mniopetals exhibit nearly the same CD curves which resemble closely that of kuehneromycin A (10)3).

**Experimental**

**General**

Spectral data were recorded on the following instruments: \(^1\)H and \(^{13}\)C NMR, Bruker AC-200, AMXR-300 and AM-400; EI-MS, A.E.I. MS-50 and Finnigan MAT 90 and 95Q; FAB-MS, Kratos Concept H-System; IR, Bruker FT-IR IFS 48 and Perkin-Elmer 1420; UV, Perkin-Elmer Lambda 1420; Varian Cary 17; CD, Jobin Yvon CNRS Roussel-Jouan Dicbrographe III. Optical rotations were recorded with a Perkin Elmer 241 polarimeter. The mp's were determined with a Reichert hot-plate microscope and are uncorrected. Merck silica gel 60 (230~400 mesh) was used for flash chromatography. TLC was carried out on aluminium foils coated with silica gel Merck 60 F\textsubscript{254}. Solvent systems used for flash chromatography and TLC: I, toluene-acetone-HOAc, 70:30:1; II, petroleum ether\textsubscript{40~60} - EtOAc, 5:1; III, petroleum ether\textsubscript{40~60} - EtOAc, 10:1; IV, petroleum ether\textsubscript{40~60} - EtOAc, 2:1. All solvents were distilled prior to use.

*Mniopetal A (1)*

Colorless oil; Rf 0.53 (I); [\alpha]\textsubscript{D}\textsuperscript{20} -63\textdegree (c 1.33, CHCl\textsubscript{3}); UV \(\lambda\textsubscript{max}^{MeOH}\) nm (log e) 228 (3.70); CD \(\lambda\textsubscript{max}^{MeCN}\) nm (de) 230 (−5.83), 263 (0), 323 (+0.87), 370 (0); IR (KBr) cm\textsuperscript{-1} 3440, 2956, 2928, 2857, 1750, 1674, 1645, 1373, 1202, 1117, 1094, 1059, 947; \(^1\)H NMR, Table 1; \(^{13}\)C NMR, Table 2; EI-MS (direct inlet, 180\textdegreeC) \(m/z\) (relative intensity %) 508.2669 (1, M\textsuperscript{+}, calcd for C\textsubscript{27}H\textsubscript{40}O\textsubscript{9} 508.2672), 490 (15, C\textsubscript{27}H\textsubscript{38}O\textsubscript{8}), 278 (41, C\textsubscript{15}H\textsubscript{18}O\textsubscript{5}), 260 (20, C\textsubscript{15}H\textsubscript{16}O\textsubscript{4}), 234 (36, C\textsubscript{14}H\textsubscript{18}O\textsubscript{3}), 216 (54, C\textsubscript{14}H\textsubscript{16}O\textsubscript{2}), 215 (47, C\textsubscript{14}H\textsubscript{15}O\textsubscript{2}), 213 (65, C\textsubscript{12}H\textsubscript{13}O\textsubscript{2}), 205 (22, C\textsubscript{13}H\textsubscript{17}O\textsubscript{2}), 204 (37, C\textsubscript{13}H\textsubscript{16}O\textsubscript{2}), 188 (29, C\textsubscript{13}H\textsubscript{16}O), 187 (22, C\textsubscript{13}H\textsubscript{15}O), 186 (57, C\textsubscript{13}H\textsubscript{14}O), 185 (24, C\textsubscript{11}H\textsubscript{12}O\textsubscript{2}), 125 (60, C\textsubscript{9}H\textsubscript{17}), 69 (24), 43 (100).

**Determination of the Absolute Configuration at C-2' of Mniopetal A**

To a stirred solution of 1 (5.0 mg) in THF (4 ml) and MeOH (2 ml) were added five drops of 30\% methanolic NaOMe. After stirring at 20\textdegreeC for 1 hour, the reaction mixture was diluted with CHCl\textsubscript{3} (30 ml) and washed successively with saturated aqueous NH\textsubscript{4}Cl (20 ml) and brine (25 ml). The organic layer was dried over Na\textsubscript{2}SO\textsubscript{4} and evaporated to dryness to give an oil, which was chromatographed on a silica gel column. Elution with solvent system II (Rf 0.40) afforded methyl 2-hydroxydecanoate (8) (1.5 mg, 75\%).

A mixture of \((R)-(-)\)-MTPA-Cl (15 mg), 8 (1.5 mg) and pyridine (0.3 ml) in CCL\textsubscript{4} (0.8 ml) was stirred at 20\textdegreeC for 5 hours. The mixture was poured into Et\textsubscript{2}O (40 ml) and the solution washed consecutively
with saturated aqueous NH₄Cl (2 x 30 ml), saturated aqueous NaHCO₃ (30 ml) and brine (30 ml). The organic phase was dried over Na₂SO₄ and evaporated in vacuo. The resulting oil was chromatographed on a silica gel column. Elution with solvent system III afforded (S, R)-9 (2.3mg, 74%) as colorless oil; Rf0.57 (III); [α]D° 0° (c0.10, CHCl₃); UV λmax nm (log ε) 206 (sh, 4.88), 262 (sh, 3.69); IR (KBr) cm⁻¹ 2950, 2925, 1750, 1215, 1168, 1115, 1074, 1013, 760, 716, 692; ¹H NMR (200MHz, CDCl₃) δ 0.87 (3H, t, J = 7.0 Hz, 10-H), 1.15 - 1.45 (12H, m), 1.90 (2H, m, 3-H), 3.56 (3H, q, J = 1.1 Hz, OCH₃), 3.74 (3H, s, CO₂CH₃), 5.17 (1H, t, J = 6.3 Hz, 2-H), 7.40 (3H, m, Ph), 7.58 (2H, m, Ph); EI-MS (180°C) m/z (%) 418.1956 (2, M⁺, calcd for C₂₁H₂₉F₃O₅ 418.1967), 349 (6), 216 (12), 190 (50), 189 (100), 186 (5), 185 (43), 153 (48), 149 (24), 135 (25), 105 (28), 83 (24), 55 (28).

(S)-MTPA-esters (S,R)-9 and (S,S)-9 from Racemic Methyl 2-Hydroxydecanoate (8)

A mixture of the diastereomeric MTPA-esters (S,R)-9 and (S,S)-9 (8.6mg, 83%) was obtained from rac. methyl 2-hydroxy-decanoate (8) (5.0 mg) and (R)-(−)-MTPA-Cl according to the previous procedure. The ¹H NMR signals of the diastereomers were assigned according to Lit.8,9).

Colorless oil; Rf 0.57 [(S,R)-9] and 0.62 [(S,S)-9] (III); ¹H NMR (200MHz, CDCl₃) (50.87 (3H, t, J = 7.0 Hz, 10-H), 1.15 - 1.45 (12H, m), 1.77 -1.98 (2H, m, 3-H), 3.56 (3/2H, q, J = 1.1 Hz, OCH₃ of [(S,R)-9]), 3.65 (3/2H, q, J = 1.1 Hz, OC₂H₃ of [(S,S)-9]), 3.74 (3/2H, s, CO₂CH₃ of [(S,R)-9]), 3.77 (3/2H, s, CO₂CH₃ of 9), 5.15 (1/2H, t, J = 6.3 Hz, 2-H of [(S,R)-9]), 5.17 (1/2H, t, J = 6.3 Hz, 2-H of [(S,S)-9]), 7.40 (3H, m, Ph), 7.58 (2/2H, m, Ph of [(S,R)-9]), 7.63 (2/2H, m, Ph of [(S,S)-9]).

Mniopetal B (2)

Colorless oil; Rf 0.45 (I); [α]D° −46° (c 0.28, CHCl₃); UV λmax nm (log ε) 230 (−7.32), 265 (0), 323 (+1.07), 380 (0); IR (KBr) cm⁻¹ 3410, 2955, 2927, 2856, 1763, 1735, 1676, 1653, 1458, 1370, 1244, 1203, 1126, 1096, 1057, 945; ¹H NMR, Table 1; ¹³C NMR, Table 2; EI-MS (180°C) m/z (%) 448.2478 (2, M⁺ -H₂O, calcd for C₂₅H₃₆O₇ 448.2461), 278 (38), 261 (27), 234 (65), 216 (60), 215 (42), 205 (29), 204 (55), 188 (44), 186 (39), 159 (28), 148 (33), 83 (42, C₅H₉), 57 (43), 55 (43); (+)-FAB-MS (mNBA = 3-nitrobenzoic acid) m/z 489 (M + Na⁺) 449 (M – H₂O + H⁺), 279, 261.

Mniopetal C (3)

Colorless oil; Rf 0.41 (toluene:HCO₂Et:HCO₂H, 10:5:3); [α]D° −45° (c 0.05, CHCl₃); UV λmax nm (log ε) 228 (3.91); IR (KBr) cm⁻¹ 3430, 2955, 2928, 2857, 1770, 1749, 1676, 1649, 1207, 1184, 1123, 1094; ¹H NMR, Table 1; EI-MS (180°C) m/z (%) 420.2153 (3, M⁺ -H₂O, calcd for C₂₃H₃₂O₇ 420.2148), 278 (72), 261 (34), 234 (41), 233 (33), 216 (69), 215 (100), 210 (37), 204 (63), 188 (55), 187 (34), 186 (42), 159 (35), 148 (25), 97 (36), 83 (42), 69 (40), 57 (52), 55 (64), 44 (31), 43 (67), 41 (27); (+)-FAB-MS (mNBA = 3-nitrobenzoic acid) m/z 461 (M + Na⁺) 421 (M – H₂O + H⁺), 279, 261.

Mniopetal D (4)

Colorless oil; Rf 0.39 (I); [α]D° −40° (c 0.05, CHCl₃); UV λmax nm (log ε) 228 (3.95); IR (KBr) cm⁻¹ 3420, 2956, 2928, 2856, 1765, 1735, 1676, 1649, 1371, 1202, 1166, 1117, 1095, 1059, 948; ¹H NMR, Table 1; EI-MS (180°C) m/z (%) 420.2153 (3, M⁺ -H₂O, calcd for C₂₅H₃₆O₇ 420.2148), 278 (72), 261 (34), 234 (41), 233 (33), 216 (69), 215 (100), 210 (37), 204 (63), 188 (55), 187 (34), 186 (42), 159 (35), 148 (25), 97 (36), 83 (42), 69 (40), 57 (52), 55 (64), 44 (31), 43 (67), 41 (27); (+)-FAB-MS (mNBA = 3-nitrobenzoic acid) m/z 461 (M + Na⁺) 421 (M – H₂O + H⁺), 279, 261.

Mniopetal E (5)

Colorless oil; Rf 0.19 (I); [α]D° −57° (c 0.10, CHCl₃); UV λmax nm (log ε) 228 (3.84); CD λmax nm (Ac) 230 (−5.01), 250 (0), 320 (+0.94), 380 (0); IR (KBr) cm⁻¹ 3400, 2934, 1769, 1676, 1649, 1172, 1116, 1096, 1052; ¹H NMR, Table 1; EI-MS (180°C) m/z (%) 296.1263 (0.2, M⁺, calcd for C₁₅H₂₀O₂ 296.1260), 278 (5), 234 (23), 205 (24), 204 (45), 148 (100, C₅H₈O₂), 121 (36, C₆H₁₂O), 120 (37, C₆H₈O), 105 (23, C₈H₁₈), 91 (40), 57 (27), 43 (58).

Mniopetal F (6)

Colorless oil; Rf 0.45 (I); [α]D° −29° (c 0.22, MeOH); UV λmax nm (log ε) 228 (4.26); CD λmax nm (Ac)
(Δσ) 207 (−5.26), 232 (−4.57), 258 (+0.05), 326 (+0.79); IR (KBr) cm⁻¹ 3429, 2930, 1457, 1170, 1115, 1089, 1058; ¹H NMR, Table 1; ¹³C NMR, Table 2; EI-MS (190°C) m/z (%): 280.1273 (3, M⁺, calcd for C₁₅H₂₀O₅ 280.1311), 262 (44, C₁₅H₁₈O₄), 244 (10, C₁₅H₁₆O₃), 234 (22, C₁₄H₁₈O₃), 217 (52, C₁₄H₁₇O₂), 188 (64, C₁₃H₁₆O), 159 (31, C₁₂H₁₅), 132 (64, C₉H₈O), 117 (40, C₉H₉), 105 (54, C₈H₉O), 91 (100, C₇H₇), 79 (52), 55 (30).

1α,15-Dihydroxymarasmene (11)

Colorless microcristals: MP 150~154°C, MP (5) 152~155; Rf 0.35 (I); [α]D+ 92° (c 0.60, MeOH); UV (CHCl₃) no absorption above 220nm; IR (KBr) cm⁻¹ 3400, 2931, 2867, 1457, 1391, 1367, 1170, 1124, 1059, 1044, 956, 923; ¹H NMR (400MHz, CD₃OD) (50.93-1.08 (6H, m), 1.23 (1H, m), 1.55-1.90 (3H, m), 1.95-2.55 (3H, m), 3.25-3.55 (1H, m), 3.90-4.60 (3H, m), 5.10-5.90 (3H, m); ¹³C NMR (100.6MHz, CD₃OD) δ 20.32, 21.79, 31.91, 32.45, 39.68, 40.67, 49.36, 52.08, 66.56, 69.47, 99.18, 103.78, 105.02, 121.93, 123.55 (CH₃, CH₂); 24.41, 26.60, 27.16, 28.33, 36.33, 72.24, 73.67 (CH₂); 33.57, 34.14, 134.94, 135.64 (C); EI-MS (180°C) m/z (%) 266.1521 (2, M⁺, calcd for C₁₅H₂₂O₄ 266.1518), 248 (43, C₁₅H₂₀O₃), 220 (31, C₁₄H₂₀O₂), 201 (62, C₁₄H₁₇O), 173 (50, C₁₃H₁₇), 149 (78, C₉H₈O₂), 131 (32, C₁₀H₁₁), 119 (32, C₉H₉O), 118 (25, C₉H₁₀), 117 (25), 105 (35), 91 (38), 81 (35, C₇H₈O₆), 69 (28).

Acetylation of 1α,15-Dihydroxymarasmene (11)

Treatment of 1α,15-dihydroxymarasmene (11, 35 mg) with acetic anhydride (1.0 ml) in pyridine (2.0 ml) for 24 hours, followed by removal of the solvents, gave an oil, which was chromatographed on a silica gel column. Elution with petroleum ether 40~60 °EtOAc (3 : 1) afforded 1α,15-diacetoxymarasmene (12, 15 mg, 33%), followed by diacetoxyaldehyde 13 (18 mg, 39%).

1α,15-Diacetoxymarasmene (12)

Colorless oil; Rf 0.50 (IV); [α]D+ 66° (c 0.70, CHCl₃); UV (CHCl₃) nm (log ε) 228 (sh, 3.63), 274 (3.16); IR (KBr) cm⁻¹ 2945, 2920, 1747, 1730, 1366, 1237, 1221, 1210, 1199, 1152, 1030, 985, 931; ¹H NMR (200MHz, CDC₁₃) δ 0.73 (3H, s, 14-H), 0.97 (3H, s, 14-H), 1.27 (1H, ddd, J = 13.0, 4.5 and 2.5Hz), 1.56 (1H, dd, J = 14.1 and 4.0 Hz), 1.60~1.80 (2H, m), 2.00~2.27 (2H, m) 2.10 (3H, s, CH₃CO₂), 2.12 (3H, s, CH₃CO₂), 2.36 (1H, m), 2.95 (1H, m, 9-H), 4.41 (2H, m, 12-H), 5.32 (1H, dd, J = 2.8 and 2.8 Hz, 1-H), 5.67 (1H, d, J = 3.7 Hz, 11-H), 5.79 (1H, m, 7-H), 6.08 (1H, s, 15-H); ¹³C NMR (100.6MHz, CDC₁₃) δ 19.03, 21.23, 21.26, 23.20, 24.81, 31.56, 32.39, 35.35, 40.31, 47.97, 50.90, 69.13, 71.43, 95.44, 103.85, 121.84, 133.19, 169.25, 170.11; EI-MS (180°C) m/z (%) M⁺ not detected, 290.1510 (13, M⁺ - HOAc, calcd for C₁₇H₂₂O₄ 290.1518), 262 (29, C₁₅H₂₀O₃), 244 (10, C₁₄H₁₈O₃), 234 (22, C₁₄H₁₈O₃), 217 (52, C₁₄H₁₇O₂), 188 (64, C₁₃H₁₆O), 159 (31, C₁₂H₁₅), 132 (64, C₉H₈O), 117 (40, C₉H₉), 105 (54, C₈H₉O), 91 (100, C₇H₇), 79 (52), 69 (35), 55 (30).

(+)-FAB-MS (mNBA+NaOAc) m/z 723 (2M⁺Na)+, 373 (M⁺Na)+, 313 (M-HOAc+Na)+, 291 (M-HOAc+H)+, 231 (M-2HOAc+H)+.
(-)-11,12-Dihydroxydrimene (14)

Colorless oil; Rf 0.47 (I); [α]D 23 -6.5° (c 0.16, CHCl3); UV λmax no absorption above 220 nm; IR (KBr) cm⁻¹ 3390, 2924, 2849, 1631, 1459, 1388, 1366, 1346, 1209, 1167, 1119, 1079, 1041, 996; ¹H NMR (400 MHz, CD3OD) δ 0.85 (3H, s, 15-H), 0.93 (3H, s, 14-H), 0.96 (3H, s, 13-H), 1.20 (1H, ddd, J = 13.2, 13.0 and 3.9 Hz, 1α-H), 1.27 (1H, ddd, J = 13.6, 13.0 and 3.6 Hz, 3α-H), 1.29 (1H, dd, J = 12.3 and 4.6 Hz, 5-H), 1.48 (1H, ddd, J = 13.0, 3.2, 3.1 and 1.8 Hz, 3β-H), 1.53 (1H, dddd, J = 13.8, 7.1, 3.6 and 3.2 Hz, 2α-H), 1.66 (dddd, J = 13.8, 13.6, 13.2, 3.4 and 3.1 Hz, 2β-H), 1.98 (1H, m, 6β-H), 2.06 (1H, dddd, J = 13.0, 3.5, 3.4 and 1.8 Hz, 1β-H), 2.10 (1H, m, 9-H), 2.12 (1H, m, 6α-H), 3.66 (1H, dd, J = 11.0 and 7.5 Hz, 11-H), 3.89 (1H, dd, J = 11.0 and 2.6 Hz, 11-H), 3.99 (1H, d, J = 12.7 Hz, 12-H), 4.30 (1H, ddd, J = 12.7, 2.2 and 1.1 Hz, 12-H), 5.83 (1H, dm, J = 5.7 Hz, 7-H); ¹³C NMR (75 MHz, CD3OD) δ 14.94 (C-15), 19.85 (C-2), 22.32 (C-13), 24.56 (C-6), 33.77 (C-4α), 33.90 (C-14α), 36.81 (C-10), 40.62 (C-1), 43.27 (C-3), 51.08 (C-5), 55.88 (C-9), 61.36 (C-11), 67.04 (C-12), 126.42 (C-7), 138.20 (C-8), assignments may be interchanged; EI-MS (70°C) m/z (%) 238.1952 (6, M⁺, calcd for C15H26O2 238.1933), 220 (6, C15H24O), 207 (4, C14H23O), 205 (2, C14H21O), 190 (47, C14H22), 175 (11), 124 (24), 109 (100, C8H13), 105 (15), 91 (14), 81 (12), 69 (12), 55 (10).

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References