

Kaempulchraols P–T, Diterpenoids from *Kaempferia pulchra* Rhizomes Collected in Myanmar

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ABSTRACT: The isolation of the oily fraction obtained from the CHCl₃-soluble extract of the rhizomes of *Kaempferia pulchra* (Zingiberaceae) afforded five new isopimarane diterpenoids, kaempulchraols P–T (**1–5**), along with two known analogues. The structures were elucidated using spectroscopic techniques, including 2D NMR spectroscopy.

Kaempferia pulchra Ridl. [syn. *Kaempferia elegans* (Wall.) Baker], a member of the Zingiberaceae family, is known as “Shan-pan-oot” in Myanmar. The rhizomes have been reported to possess anti-inflammatory¹ and antitumor activities² and are popular for self-medication among patients with cancer and AIDS in Myanmar. In the ongoing research on the discovery of anticancer agents from Myanmar medicinal plants,³⁻⁸ the crude extracts were screened against a panel of five human cancer cell lines (A549, human lung cancer; HeLa, human cervix cancer; PANC-1 and PSN-1, human pancreatic cancer; and MDA-MB-231, human breast cancer) and TIG-3, a normal human primary fibroblast cell line. Because the CHCl₃-soluble fraction of the rhizomes of *K. pulchra* exhibited reasonable antiproliferative activity against the tested cancer cell lines, we proceeded with the isolation of its secondary metabolites. In the two preceding papers, 15 new isopimarane-type diterpenoids were reported, *i.e.*, kaempulchraols A–O, together with six known compounds [9α -hydroxyisopimara-8(14),15-dien-7-one,⁹ $7\beta,9\alpha$ -dihydroxypimara-8(14),15-diene,¹⁰ (1*S*,5*S*,9*S*,10*S*,11*R*,13*R*)-1,11-dihydroxypimara-8(14),15-diene,¹¹ sandaracopimaradien-1*α*,2*α*-diol,¹ (2*R*)-*ent*-2-hydroxyisopimara-8(14),15-diene,¹² and (1*R*,2*S*,5*S*,9*S*,10*S*,11*R*,13*R*)-1,2,11-trihydroxypimara-8(14),15-diene]¹¹ as well as their antiproliferative activities.^{7, 8} Further investigation of the remaining oily fractions obtained from the CHCl₃-soluble extract led to the isolation of five new components, which were named kaempulchraols P–T (**1–5**) (Figure 1), along with the known 7α -hydroxyisopimara-8(14),15-diene¹³ and ethyl 4-methoxy-*trans*-cinnamate.¹ Herein, we describe the isolation and structural elucidation of the isolated compounds.

Kaempulchraol P (**1**) was obtained as an amorphous solid, and its molecular formula was established as C₂₀H₃₂O from the HREIMS and ¹³C NMR data. The IR spectrum of **1** showed absorption bands at 3483 and 1635 cm⁻¹ due to the presence of hydroxy and olefinic groups, respectively. The ¹H NMR data (Table 1) exhibited signals corresponding to the presence of a

terminal vinyl group [δ_{H} 5.78, dd ($J = 17.7, 10.2$ Hz, H-15), 4.93, dd ($J = 17.7, 1.5$ Hz, H-16a), 4.91, dd ($J = 10.2, 1.5$ Hz, H-16b)]; three methines, including an oxygenated methine [δ_{H} 1.08, d ($J = 1.4$ Hz, H-5 α), 4.33, br t ($J = 4.2$ Hz, H-6 α), 1.74, br t ($J = 7.6$ Hz, H-9 α)]; six methylenes; and four methyl groups [δ_{H} 1.09, s (H₃-17), 1.24, s (H₃-18), 1.00, s (H₃-19), 1.12, s (H₃-20)]. The ¹³C NMR data (Table 2) revealed the presence of four olefinic carbons [δ_{C} 148.2 (C-15), 133.4 (C-8), 132.3 (C-14), 110.6 (C-16)]; three methine carbons, including an oxymethine carbon [δ_{C} 68.4 (C-6), 56.8 (C-5), 50.4 (C-9)]; three quaternary carbons [δ_{C} 39.4 (C-10), 37.6 (C-13), 34.22 (C-4)]; six methylenes [δ_{C} 45.8 (C-7), 43.9 (C-3), 42.4 (C-1), 34.25 (C-12), 19.1 (C-2), 18.4 (C-11)]; and four methyl carbons [δ_{C} 33.8 (C-19), 26.6 (C-17), 23.9 (C-18), 18.8 (C-20)]. These data suggested that **1** is a monohydroxy derivative of a $\Delta^{8(14),15}$ -isopimaradiene. The key HMBC correlations from an oxygenated methine (δ_{H} 4.33, H-6 α) to C-5/C-8/C-10 located the hydroxy group at C-6 (Figure 2). According to the NOESY correlations between H-6 α and H-5 α /H₃-19, and biosynthetic considerations, C-6 hydroxy group was assigned as β orientation and the structure was elucidated as 6 β -hydroxyisopimara-8(14),15-diene.

Kaempulchraol Q (**2**) was isolated as an amorphous solid and exhibited a deprotonated molecular ion at m/z 345.2431 in HRCIMS, which, in conjunction with the ¹³C NMR data suggested a molecular formula of C₂₂H₃₄O₃. The IR spectrum exhibited absorption bands at 3508, 1714, and 1632 cm⁻¹ due to the presence of hydroxy, ester, and olefinic groups. The ¹H and ¹³C NMR spectroscopic data (Tables 1 and 2) of **2** were similar to those of **1** except for the presence of an acetoxy group [δ_{H} 2.07, s; δ_{C} 21.2 (MeOCO-1), δ_{C} 170.2 (MeOCO-1)] and two oxygenated methines [δ_{H} 4.78, br t ($J = 2.1$ Hz, H-1 β), 4.38, br s (H-6 α)], characterizing **2** as a $\Delta^{8(14),15}$ -isopimaradiene carrying a hydroxy and an acetoxy substituents. On the basis of the HMBC correlations from MeOCO-1 to MeOCO-1/C-1, from H₃-20 (δ_{H} 1.16, s)/H-5 α (δ_{H} 1.49, d, $J = 1.7$ Hz)/H-9 α (δ_{H} 2.18, br t, $J = 5.3$ Hz) to C-1, from H-5 α /H₂-7 to C-6 (δ_{C} 68.3),

and from H-6 α to C-5 (δ_C 51.0)/C-8 (δ_C 133.2)/C-10 (δ_C 42.0) (Figure 2), the acetoxy and hydroxy groups were located at C-1 and C-6, respectively. The NOESY correlations of H-1 β and H₃-20 and of H-6 α and H-5 α /H₃-19 suggested α and β orientations of the C-1 acetoxy and C-6 hydroxy groups, respectively. Hence, the structure of kaempulchraol Q (**2**) was elucidated as 1 α -acetoxy-6 β -hydroxyisopimara-8(14),15-diene.

Kaempulchraol R (**3**) was isolated as an amorphous solid, and its molecular formula, C₂₂H₃₄O₃, was determined from the ¹³C NMR data and protonated molecular ion at *m/z* 347.2586. The ¹H and ¹³C NMR spectroscopic data (Tables 1 and 2) of **3** were similar to those of **2**. Important differences included the absence of the resonance of one oxygenated methine proton in the ¹H NMR spectrum of **3**, whereas the presence of two oxygenated carbons in the ¹³C NMR spectrum of **3** suggested that one of the oxygen bearing groups is attached to a tertiary carbon. The key HMBC correlations (Figure 2) between a hydroxy proton (δ_H 2.63, s) and C-9 (δ_C 74.8)/C-10 (δ_C 41.6)/C-11 (δ_C 25.6) and between H-5 α (δ_H 1.92, dd, *J* = 13.6, 2.8)/H-7 β (δ_H 5.42, t, *J* = 3.3 Hz)/H₂-11 (δ_H 1.58, 1.78, both m)/H-14 (δ_H 5.78, s) and C-9 indicated that the hydroxy group was located at C-9. Further HMBC correlations of an oxygenated methine (δ_H 5.42, t, *J* = 3.3 Hz, H-7 β) and C-5 (δ_C 39.5)/C-8 (δ_C 133.3)/C-9/C-14 (δ_C 141.3) and of MeOCO-7 (δ_H 2.04, s) and MeOCO-7 (δ_C 169.2)/C-7 (δ_C 77.1) located the acetoxy group at C-7. The α orientations of the C-9 hydroxy and C-7 acetoxy groups were confirmed by the NOESY correlations between HO-9 and H-5 α and between H-7 β and H-6 β (δ_H 1.56, m)/H₃-17 (δ_H 1.03, s). Thus, the structure of kaempulchraol R (**3**) was assigned as 7 α -acetoxy-9 α -hydroxyisopimara-8(14),15-diene.

Kaempulchraol S (**4**) was obtained as an amorphous solid, and its molecular formula was determined as C₂₀H₃₀O₂ by HREIMS and ¹³C NMR data. The ¹H and ¹³C NMR spectroscopic data of **4** (Tables 1 and 2) were similar to those of kaempulchraol G.⁷ The presence of an oxygenated methine proton (δ_H 4.28, s) and a carbonyl carbon (δ_C 201.6) suggested **4** to be a

$\Delta^{8(9),15}$ -isopimaradiene with a hydroxy and carbonyl group. However, the locations of these hydroxy and carbonyl groups in **4** were different from those of kaempulchraol G. The HMBC correlations (Figure 2) from H-5 α (δ_{H} 1.66, dd, $J = 14.2, 3.5$ Hz)/H-14 β (δ_{H} 4.28, s) to the carbonyl carbon and from H-14 β to C-7/C-8 (δ_{C} 131.6)/C-9 (δ_{C} 169.6)/C-12 (δ_{C} 28.3)/C-13 (δ_{C} 38.4)/C-15 (δ_{C} 143.5)/C-17 (δ_{C} 23.4) located the carbonyl group at C-7 and the hydroxy group at C-14. The NOESY correlations between H-14 β and H₃-17 (δ_{H} 1.12, s) established the α orientation of the C-14 hydroxy group. Accordingly, kaempulchraol S (**4**) was characterized as 7-oxo-14 α -hydroxyisopimara-8(9),15-diene.

Kaempulchraol T (**5**) was obtained as an amorphous solid. The HRCIMS spectrum of **5** exhibited a protonated molecular ion at m/z 347.2601, which, in conjunction with the ^{13}C NMR data, indicated a molecular formula of $\text{C}_{22}\text{H}_{34}\text{O}_3$. The ^1H and ^{13}C NMR spectroscopic data together with the COSY and HMQC correlations (Figure 2) resembled those of **2**. The differences were the positions of the hydroxy and acetoxy groups, which were located at C-6 and C-7 based on the HMBC correlations from H-6 α (δ_{H} 4.17, m) and H-7 β (δ_{H} 5.03, d, $J = 2.9$ Hz) to C-5 (δ_{C} 51.8)/C-8 (δ_{C} 132.0) and from MeOCO-7 (δ_{H} 2.04, s) to MeOCO-7 (δ_{C} 169.8)/C-7 (δ_{C} 79.0) (Figure 2). The NOESY correlations between H-6 α and H-5 α (δ_{H} 1.36, d, $J = 1.9$ Hz)/H₃-19 (δ_{H} 0.96, s) and between H-7 β and H₃-17 (δ_{H} 1.09, s) established the orientations of the C-6 hydroxy and the C-7 acetoxy groups as β and α , respectively. Therefore, the structure of kaempulchraol T (**5**) was defined as 6 β -hydroxy-7 α -acetoxyisopimara-8(14),15-diene.

The two known compounds were identified as 7 α -hydroxyisopimara-8(14),15-diene¹³ and ethyl 4-methoxy-*trans*-cinnamate¹ based on the observed and reported NMR data.

EXPERIMENTAL SECTION

General Experimental Procedures. Optical rotations were recorded on a JASCO P2100

polarimeter. Infrared spectra were recorded using KBr pellets on a Jasco FT/IR-460 Plus spectrometer. NMR spectra were recorded at 600 MHz (^1H NMR) and 150 MHz (^{13}C NMR) on a Varian UNITY 600 spectrometer. Chemical shift values were expressed in δ (ppm) downfield from TMS as an internal standard. The mass spectra, HRMS data, were recorded on a JEOL MStation JMS-700 spectrometer. Open-column chromatography was performed with normal-phase silica gel (silica gel 60N, spherical, neutral, 40–50 μm , Kanto Chemical Co., Inc., Japan) and Cosmosil 75C18-OPN (Nacalai Tesque Inc., Kyoto, Japan). MPLC was performed with a Büchi Sepacore system (Büchi Labortechnik AG, Flawil, Switzerland). TLC was conducted on precoated silica gel 60F₂₅₄ and RP-18 F₂₅₄ plates (Merck; 0.25 or 0.50 mm thickness).

Plant Material. Rhizomes of *K. pulchra* were collected from Pindaya Township, Shan State, Myanmar, in September 2013 and were identified by the authorized botanist of the Department of Botany, University of Yangon. A voucher specimen (TMPW 28301) was deposited at the Museum for Materia Medica, Analytical Research Center for Ethnomedicines, Institute of Natural Medicine, University of Toyama, Japan.

Extraction and Isolation. The rhizomes of *K. pulchra* (500 g) were extracted with CHCl_3 under sonication (1 L, 90 min, $\times 3$) at 35 $^\circ\text{C}$, and the solvent was evaporated under reduced pressure to yield 30 g of extract.

The chloroform extract (30 g) was chromatographed on silica gel with an EtOAc–*n*-hexane solvent system to provide seven fractions. The isolation and purification of subfraction 2-2 to fraction 6 by various chromatographic techniques afforded kaempulchraols A–O and six known compounds.^{7,8}

Subfraction 2-1 (645 mg) was rechromatographed on silica gel with *n*-hexane–EtOAc (4:1) to afford three subfractions [2-1-1: 200 mg; 2-2-2: 146 mg; 2-1-3: 200 mg]. The purification of subfraction 2-1-1 (200 mg) by normal-phase preparative TLC with C_6H_6 – CHCl_3 (1:1) afforded kaempulchraol P (**1**, 80 mg),

7 α -hydroxyisopimara-8(14),15-diene (30 mg),¹³ and ethyl 4-methoxy-*trans*-cinnamate¹ (50 mg). Subfraction 2-1-2 (146 mg) was purified by normal-phase preparative TLC with *n*-hexane–EtOAc (3:1) followed by reverse-phase preparative TLC with MeOH–MeCN–H₂O (7:2:1) to give kaempulchraols Q (**2**, 38 mg) and R (**3**, 68 mg). The purification of subfraction 2-1-3 (200 mg) by normal-phase preparative TLC with *n*-hexane–EtOAc (3:1) followed by reverse-phase preparative TLC with MeOH–MeCN–acetone–H₂O (2:2:2:1) afforded kaempulchraols S (**4**, 65 mg) and T (**5**, 5 mg).

Kaempulchraol P (1): amorphous solid; $[\alpha]_D^{25}$ –20 (*c* 0.1, MeOH); IR (KBr) ν_{\max} 3483, 2920, 1635, 1542, 1458, 1036, 997 cm⁻¹; ¹H and ¹³C NMR data, see Tables 1 and 2; EIMS *m/z* 288 [M]⁺ (38); HREIMS *m/z* 288.2457 [M]⁺ (calculated for C₂₀H₃₂O, 288.2453).

Kaempulchraol Q (2): amorphous solid; $[\alpha]_D^{25}$ –39 (*c* 0.1, MeOH); IR (KBr) ν_{\max} 3508, 2954, 1714, 1632, 1262, 1035, 989 cm⁻¹; ¹H and ¹³C NMR data, see Tables 1 and 2; CIMS *m/z* 345 [M–H]⁺ (10); HRCIMS *m/z* 345.2431 [M–H]⁺ (calculated for C₂₂H₃₃O₃, 345.2430).

Kaempulchraol R (3): amorphous solid; $[\alpha]_D^{25}$ –36 (*c* 0.1, MeOH); IR (KBr) ν_{\max} 3596, 2951, 1743, 1634, 1372, 1227, 1014, 991 cm⁻¹; ¹H and ¹³C NMR data, see Tables 1 and 2; CIMS *m/z* 346 [M]⁺ (6); HRCIMS *m/z* 347.2586 [M+H]⁺ (calculated for C₂₂H₃₅O₃, 347.2586).

Kaempulchraol S (4): amorphous solid; $[\alpha]_D^{25}$ +30 (*c* 0.1, MeOH); IR (KBr) ν_{\max} 3461, 2928, 1652, 1617, 1375, 1253, 1046, 1005 cm⁻¹; ¹H and ¹³C NMR data, see Tables 1 and 2; EIMS *m/z* 302 [M]⁺ (15); HREIMS *m/z* 302.2242 [M]⁺ (calculated for C₂₀H₃₀O₂, 302.2246).

Kaempulchraol T (5): amorphous solid; $[\alpha]_D^{25}$ –32 (*c* 0.1, MeOH); IR (KBr) ν_{\max} 3503, 2923, 1718, 1636, 1367, 1236, 1041, 953 cm⁻¹; ¹H and ¹³C NMR data, see Tables 1 and 2; CIMS *m/z* 346 [M]⁺ (18); HRCIMS *m/z* 347.2601 [M+H]⁺ (calculated for C₂₂H₃₅O₃, 347.2586).

ASSOCIATED CONTENT

Supporting Information

The ^1H and ^{13}C NMR, ^1H - ^1H COSY, HMQC, HMBC, NOESY, and HRMS spectra of compounds **1–5** (Figure S1–Figure S35). This material is available free of charge at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (H.M. and I.A.); by a grant from the Tokyo Biochemical Research Foundation (H.M. and N.N.W.); and by a grant from the Kobayashi International Scholarship Foundation (H.M.). We also thank Y. Okamoto (Tokushima Bunri University, Tokushima, Japan) for her technical assistance with the MS measurements.

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Table 1. ^1H NMR Spectroscopic Data (600 MHz, CDCl_3) of Kaempulchraols P–T (1–5), (δ in ppm and J values in (Hz) in parentheses)

position	1	2	3	4	5
1 α	1.73, m		1.71, m	1.19, m	1.10, m
1 β	1.05, m	4.78, br t (2.1)	1.39, m	1.83, m	1.74, m
2 α	1.46 ^a , m	1.70, ddd (14.6, 6.8, 3.7)	1.50 ^a , m	1.56, m	1.48, m
2 β	1.46 ^a , m	1.84, tdd (14.6, 3.7, 2.1)	1.50 ^a , m	1.67, m	1.61, m
3 α	1.20, m	1.56, m	1.41, m	1.20, m	1.26, m
3 β	1.41, m	1.15, m	1.25, m	1.47 ^a , m	1.41, m
5 α	1.08, d (1.4)	1.49, d (1.7)	1.92, dd (13.6, 2.8)	1.66, dd (14.2, 3.5)	1.36, d (1.9)
6 α	4.33, br t (4.2)	4.38, br s	1.81, dt (12.8, 2.8)	2.52, dd (17.9, 3.5)	4.17, m
6 β			1.56, m	2.39, dd (17.9, 14.2)	
7 α	2.35, m	2.35, m			
7 β	2.27, dd (14.4, 2.7)	2.26, dd (14.4, 2.7)	5.42, t (3.3)		5.03, d (2.9)
9 α	1.74, br t (7.6)	2.18, br t (5.3)			2.00, t (5.7)
11 α	1.59, m	1.40, m	1.78, m	2.23 ^a , m	1.61 ^a , m
11 β	1.62, m	1.54, m	1.58, m	2.23 ^a , m	1.61 ^a , m
12 α	1.38, m	1.37, m	1.75, m	1.70, m	1.39, m
12 β	1.51, m	1.46, m	1.42, m	1.47 ^a , m	1.51, m
14	5.39, br s	5.44, br t (1.72)	5.78, s		5.80, d (1.8)
14 α					
14 β				4.28, s	
15	5.78, dd (17.7, 10.2)	5.76, dd (17.2, 10.7)	5.81, dd (17.4, 10.6)	5.67, dd (17.7, 11.0)	5.74, dd (17.4, 10.5)
16a	4.93, dd (17.7, 1.5)	4.90, dd (17.2, 1.5)	4.99, dd (17.5, 1.1)	4.94, dd (17.7, 1.1)	4.89, dd (17.4, 1.4)
16b	4.91, dd (10.2, 1.5)	4.92, dd (10.7, 1.5)	4.95, dd (10.6, 1.1)	4.98, dd (11.0, 1.1)	4.93, dd (10.5, 1.4)
17	1.09, s	1.08, s	1.03, s	1.12, s	1.09, s
18	1.24, s	1.27, s	0.87, m	0.93, s	1.24, s
19	1.00, s	1.04, s	0.88, m	0.89, s	0.96, s
20	1.12, s	1.16, s	0.89, m	1.13, s	1.12, s
HO-7					
HO-9			2.63, s		
MeOCO-1		2.07, s			
MeOCO-7			2.04, s		2.04, s

^aOverlapping resonances within the same column.

Table 2. ^{13}C NMR Spectroscopic Data (150 MHz, CDCl_3) of Kaempulchraols P–T (1–5), (δ in ppm)

position	1	2	3	4	5
1	42.4	76.0	31.6	35.2	42.0
2	19.1	22.9	18.5	18.4	19.1
3	43.9	36.5	41.4	41.0	43.9
4	34.22	33.8	32.7	33.1	33.8
5	56.8	51.0	39.5	49.9	51.8
6	68.4	68.3	27.5	35.5	69.9
7	45.8	45.6	77.1	201.6	79.0
8	133.4	133.2	133.3	131.6	132.0
9	50.4	42.7	74.8	169.6	46.0
10	39.4	42.0	41.6	39.8	39.1
11	18.4	17.9	25.6	23.2	18.0
12	34.25	33.9	30.9	28.3	34.0
13	37.6	37.6	38.1	38.4	37.8
14	132.3	133.0	141.3	68.1	139.4
15	148.2	148.0	147.3	143.5	147.2
16	110.6	110.7	111.1	112.6	111.6
17	26.6	26.7	23.3	23.4	26.5
18	23.9	24.1	21.8	21.3	24.4
19	33.8	33.6	33.4	32.3	33.6
20	18.8	18.7	17.9	17.9	18.5
<i>MeOCO-1</i>		21.2			
<i>MeOCO-1</i>		170.2			
<i>MeOCO-7</i>			21.7		21.4
<i>MeOCO-7</i>			169.2		169.8

Figure 1. Structures of Kaempulchraols P–T (1–5).

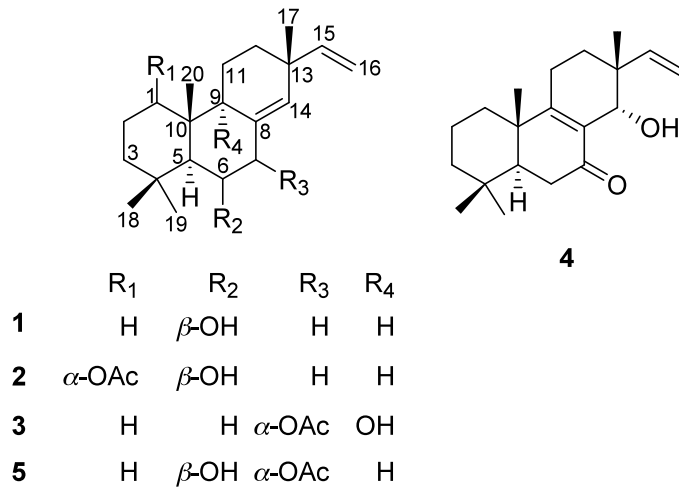


Figure 2. COSY (bold lines) and key HMBC ($^1\text{H} \rightarrow ^{13}\text{C}$) (arrows) correlations in compounds 1–5.

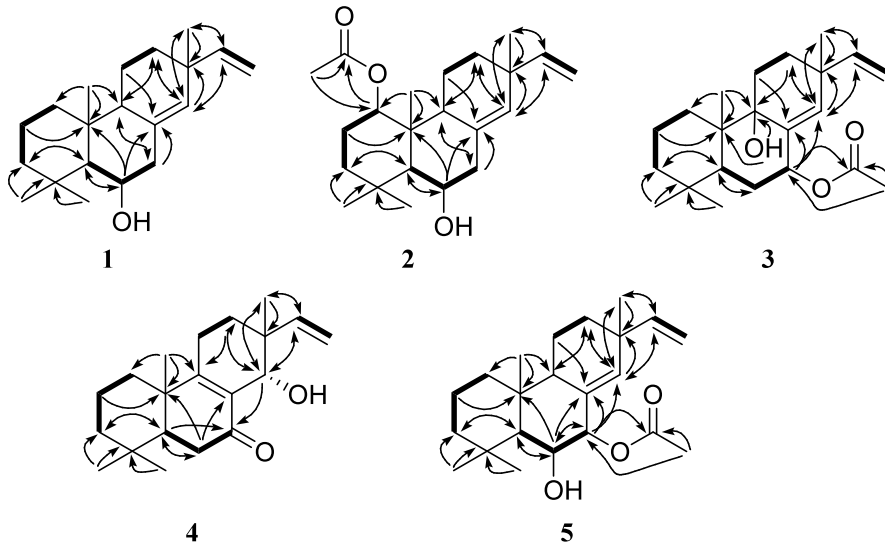
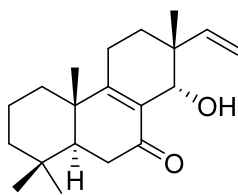
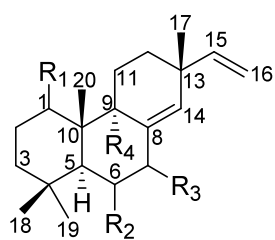


Table of Contents/Abstract Graphic



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	R ₁	R ₂	R ₃	R ₄
1	H	β -OH	H	H
2	α -OAc	β -OH	H	H
3	H	H	α -OAc	OH
5	H	β -OH	α -OAc	H