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 $CHCl_3$-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-inflammatory[1] and antitumor activities[2] 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 $CHCl_3$-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] 7β,9α-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-1α,2α-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 $CHCl_3$-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-diene[13] 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 $C_{20}H_{32}O$ from the HREIMS and ^{13}C 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-5α), 4.33, br t (J = 4.2 Hz, H-6α), 1.74, br t (J = 7.6 Hz, H-9α)]; six methylenes; and four methyl groups [δ_H 1.09, s (H_3-17), 1.24, s (H_3-18), 1.00, s (H_3-19), 1.12, s (H_3-20)]. The ^{13}C 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-6α) to C-5/C-8/C-10 located the hydroxy group at C-6 (Figure 2). According to the NOESY correlations between H-6α and H-5α/H_3-19, and biosynthetic considerations, C-6 hydroxy group was assigned as β orientation and the structure was elucidated as 6β-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 ^{13}C NMR data suggested a molecular formula of $C_{22}H_{34}O_3$. The IR spectrum exhibited absorption bands at 3508, 1714, and 1632 cm^{-1} due to the presence of hydroxy, ester, and olefinic groups. The ^{1}H and ^{13}C 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 (*Me*OCO-1), δ_C 170.2 (Me*OC*O-1)] and two oxygenated methines [δ_H 4.78, br t (J = 2.1 Hz, H-1β), 4.38, br s (H-6α)], characterizing **2** as a $\Delta^{8(14),15}$-isopimaradiene carrying a hydroxy and an acetoxy substituents. On the basis of the HMBC correlations from *Me*OCO-1 to Me*OC*O-1/C-1, from H_3-20 (δ_H 1.16, s)/H-5α (δ_H 1.49, d, J = 1.7 Hz)/H-9α (δ_H 2.18, br t, J = 5.3 Hz) to C-1, from H-5α/H_2-7 to C-6 (δ_C 68.3),

and from H-6α 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-1β and H_3-20 and of H-6α and H-5α/H_3-19 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 1α-acetoxy-6β-hydroxyisopimara-8(14),15-diene.

Kaempulchraol R (**3**) was isolated as an amorphous solid, and its molecular formula, $C_{22}H_{34}O_3$, was determined from the ^{13}C NMR data and protonated molecular ion at *m/z* 347.2586. The ^{1}H and ^{13}C 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 ^{1}H NMR spectrum of **3**, whereas the presence of two oxygenated carbons in the ^{13}C 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-5α (δ_H 1.92, dd, J = 13.6, 2.8)/H-7β (δ_H 5.42, t, J = 3.3 Hz)/H_2-11 (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-7β) and C-5 (δ_C 39.5)/C-8 (δ_C 133.3)/C-9/C-14 (δ_C 141.3) and of *Me*OCO-7 (δ_H 2.04, s) and Me*OC*O-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-5α and between H-7β and H-6β (δ_H 1.56, m)/H_3-17 (δ_H 1.03, s). Thus, the structure of kaempulchraol R (**3**) was assigned as 7α-acetoxy-9α-hydroxyisopimara-8(14),15-diene.

Kaempulchraol S (**4**) was obtained as an amorphous solid, and its molecular formula was determined as $C_{20}H_{30}O_2$ by HREIMS and ^{13}C NMR data. The ^{1}H and ^{13}C 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-5α (δ_H 1.66, dd, J = 14.2, 3.5 Hz)/H-14β (δ_H 4.28, s) to the carbonyl carbon and from H-14β 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-14β and H_3-17 (δ_H 1.12, s) established the α orientation of the C-14 hydroxy group. Accordingly, kaempulchraol S (**4**) was characterized as 7-oxo-14α-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 $C_{22}H_{34}O_3$. The ^{1}H 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-6α (δ_H 4.17, m) and H-7β (δ_H 5.03, d, J = 2.9 Hz) to C-5 (δ_C 51.8)/C-8 (δ_C 132.0) and from *Me*OCO-7 (δ_H 2.04, s) to Me*OC*O-7 (δ_C 169.8)/C-7 (δ_C 79.0) (Figure 2). The NOESY correlations between H-6α and H-5α (δ_H 1.36, d, J = 1.9 Hz)/H_3-19 (δ_H 0.96, s) and between H-7β and H_3-17 (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 6β-hydroxy-7α-acetoxyisopimara-8(14),15-diene.

The two known compounds were identified as 7α-hydroxyisopimara-8(14),15-diene[13] and ethyl 4-methoxy-*trans*-cinnamate[1] 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 (^{1}H 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 Bü chi Sepacore system (Büchi Labortechnik AG, Flawil, Switzerland). TLC was conducted on precoated silica gel 60F_{254} and RP-18 F_{254} 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, ×3) at 35 °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),

7α-hydroxyisopimara-8(14),15-diene (30 mg),[13] and ethyl 4-methoxy-*trans*-cinnamate[1] (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–H_2O (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–H_2O (2:2:2:1) afforded kaempulchraols S (**4**, 65 mg) and T (**5**, 5 mg).

*Kaempulchraol P (**1**)*: amorphous solid; $[\alpha]^{25}_D$ –20 (*c* 0.1, MeOH); IR (KBr) ν_{max} 3483, 2920, 1635, 1542, 1458, 1036, 997 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; EIMS *m/z* 288 $[M]^+$ (38); HREIMS *m/z* 288.2457 $[M]^+$ (calculated for $C_{20}H_{32}O$, 288.2453).

*Kaempulchraol Q (**2**)*: amorphous solid; $[\alpha]^{25}_D$ –39 (*c* 0.1, MeOH); IR (KBr) ν_{max} 3508, 2954, 1714, 1632, 1262, 1035, 989 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; CIMS *m/z* 345 $[M–H]^+$ (10); HRCIMS *m/z* 345.2431 $[M–H]^+$ (calculated for $C_{22}H_{33}O_3$, 345.2430).

*Kaempulchraol R (**3**)*: amorphous solid; $[\alpha]^{25}_D$ –36 (*c* 0.1, MeOH); IR (KBr) ν_{max} 3596, 2951, 1743, 1634, 1372, 1227, 1014, 991 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; CIMS *m/z* 346 $[M]^+$ (6); HRCIMS *m/z* 347.2586 $[M+H]^+$ (calculated for $C_{22}H_{35}O_3$, 347.2586).

*Kaempulchraol S (**4**)*: amorphous solid; $[\alpha]^{25}_D$ +30 (*c* 0.1, MeOH); IR (KBr) ν_{max} 3461, 2928, 1652, 1617, 1375, 1253, 1046, 1005 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; EIMS *m/z* 302 $[M]^+$ (15); HREIMS *m/z* 302.2242 $[M]^+$ (calculated for $C_{20}H_{30}O_2$, 302.2246).

*Kaempulchraol T (**5**)*: amorphous solid; $[\alpha]^{25}_D$ –32 (*c* 0.1, MeOH); IR (KBr) ν_{max} 3503, 2923, 1718, 1636, 1367, 1236, 1041, 953 cm^{-1}; ^1H and ^{13}C NMR data, see Tables 1 and 2; CIMS *m/z* 346 $[M]^+$ (18); HRCIMS *m/z* 347.2601 $[M+H]^+$ (calculated for $C_{22}H_{35}O_3$, 347.2586).

ASSOCIATED CONTENT

Supporting Information

The ^{1}H and ^{13}C NMR, $^{1}H-^{1}H$ 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.

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REFERENCES

(1) Tuchinda, P.; Udchachon, J.; Reutrakul, V.; Santisuk, T.; Skelton, B. W.; White, A. H.; Taylor, W. C. *Phytochemistry* **1994**, *36*, 731–734.

(2) Prasad, S.; Yadav, V. R.; Sundaram, C.; Reuter, S.; Hema, P. S.; Nair, M. S.; Chaturvedi, M. M.; Aggarwal, B. B. *J. Biol. Chem.* **2010**, *285*, 26987–26997.

(3) Win, N. N.; Awale, S.; Esumi, H.; Tezuka, Y.; Kadota, S. *J. Nat. Prod*. **2007**, *70*, 1582−1587.

(4) Win, N. N.; Awale, S.; Esumi, H.; Tezuka, Y.; Kadota, S. *Chem. Pharm. Bull*. **2008**, *56*, 491−496.

(5) Win, N. N.; Awale, S.; Esumi, H.; Tezuka, Y.; Kadota, S. *Bioorg. Med. Chem. Lett*. **2008**, *18*, 4688−4691.

(6) Win, N. N.; Awale, S.; Esumi, H.; Tezuka, Y.; Kadota, S. *Bioorg. Med. Chem*. **2008**, *16*, 8653−8660.

(7) Win, N. N.; Ito, T.; Aimaiti, S.; Imagawa, H.; Ngwe, H.; Abe, I.; Morita, H. *J. Nat. Prod.* **2015**, *78*, 1113−1118.

(8) Win, N. N.; Ito, T.; Aimaiti, S.; Kodama, T.; Imagawa, H.; Ngwe, H.; Asakawa, Y.; Abe, I.; Morita, H. *Tetrahedron*, **2015**, *71*, 4707−4713.

(9) Chang, C. I.; Tseng, M. H.; Kuo, Y. H. *Chem. Pharm. Bull.* **2005**, *53*, 286−289.

(10) Xia, X.; Zhang, J.; Zhang, Y.; Wei, F.; Liu, X.; Jia, A.; Liu, C.; Li, W.; She, Z.; Lin, Y. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 3017−3019.

(11) Thongnest, S.; Mahidol, C.; Sutthivaiyakit, S.; Ruchirawat, S. *J. Nat. Prod.* **2005**, *68*, 1632−1636.

(12) Nagashima, F.; Murakami, M.; Takaoka, S.; Asakawa, Y. *Phytochemistry* **2003**, *64*, 1319−1325.

(13) Touchè, E. M. G.; Lopez, E. G.; Reyes, A. P.; Sánchez, H.; Honecker, F.; Achenbach, H. *Phytochemistry* **1997**, *45*, 387−390.

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

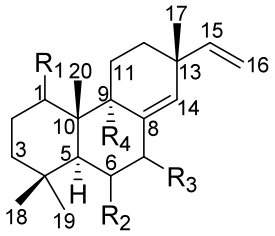
position	**1**	**2**	**3**	**4**	**5**
1α	1.73, m		1.71, m	1.19, m	1.10, m
1β	1.05, m	4.78, br t (2.1)	1.39, m	1.83, m	1.74, m
2α	1.46[a], m	1.70, ddd (14.6, 6.8, 3.7)	1.50[a], m	1.56, m	1.48, m
2β	1.46[a], m	1.84, tdd (14.6, 3.7, 2.1)	1.50[a], m	1.67, m	1.61, m
3α	1.20, m	1.56, m	1.41, m	1.20, m	1.26, m
3β	1.41, m	1.15, m	1.25, m	1.47[a], m	1.41, m
5α	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)
6α	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
6β			1.56, m	2.39, dd (17.9, 14.2)	
7α	2.35, m	2.35, m			
7β	2.27, dd (14.4, 2.7)	2.26, dd (14.4, 2.7)	5.42, t (3.3)		5.03, d (2.9)
9α	1.74, br t (7.6)	2.18, br t (5.3)			2.00, t (5.7)
11α	1.59, m	1.40, m	1.78, m	2.23[a], m	1.61[a], m
11β	1.62, m	1.54, m	1.58, m	2.23[a], m	1.61[a], m
12α	1.38, m	1.37, m	1.75, m	1.70, m	1.39, m
12β	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)
14α					
14β				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		
*Me*OCO-1		2.07, s			
*Me*OCO-7			2.04, s		2.04, s

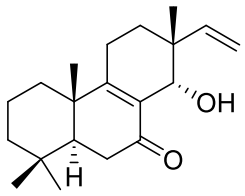
[a]Overlapping resonances within the same column.

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
*Me*OCO-1		21.2			
Me*OC*O-1		170.2			
*Me*OCO-7			21.7		21.4
Me*OC*O-7			169.2		169.8

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

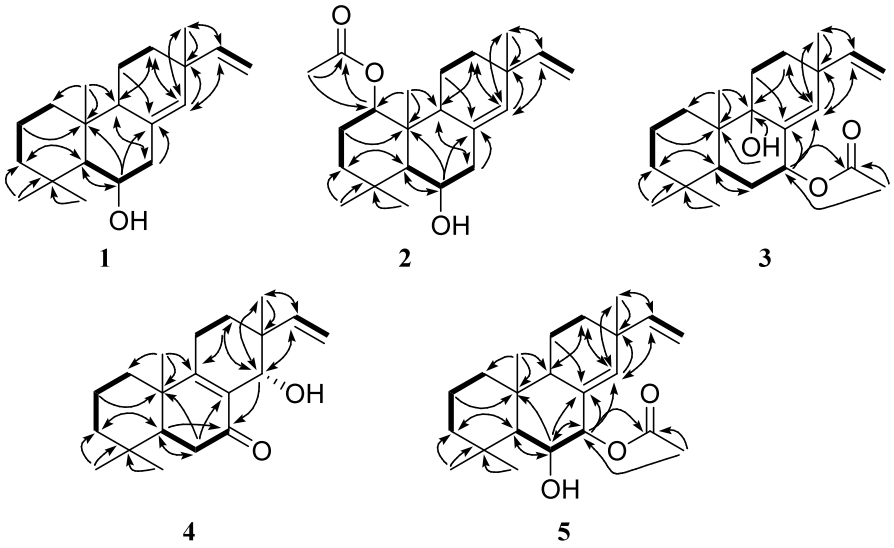




4

	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

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



1 **2** **3**

4 **5**

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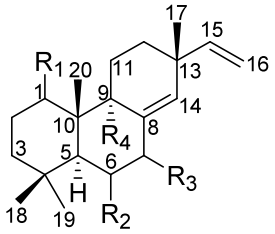

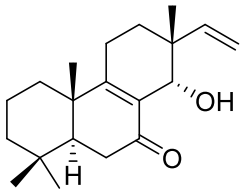

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	R_1	R_2	R_3	R_4
1	H	β-OH	H	H
2	α-OAc	β-OH	H	H
3	H	H	α-OAc	OH
5	H	β-OH	α-OAc	H