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Triterpenoids from *Pyrethrum tatsienense*

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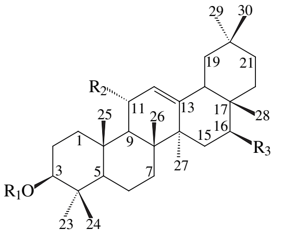
Two novel and eight known triterpenoids were isolated from alcoholic extract of the whole plant of *Pyrethrum tatsienense*. The structures of new compounds were elucidated as olean-12-en-3β,11α,16β-triol-3-*O*-palmitate (**1**), ursa-12-en-3β,11β,16β-triol-3-*O*-palmitate (**2**) by spectroscopic methods including intensive 2D NMR techniques (H^1–H^1 COSY, gHMQC, gHMBC) and FAB-MS, and the known compounds were identified on the basis of comparing their NMR data with those of corresponding compounds in the literature.

1. Introduction

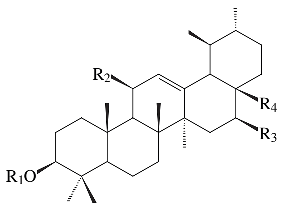
The genus *Pyrethrum* (Compositae) consists of about 100 species distributed throughout European, North Africa and middle of Asia (TNPIB 1991). There are about ten species grown in northwest of China. *P. tatsienense* is an important herbal plant, which has been used as a traditional folk medicine for the treatment of hepatitis, diminishing inflammation and acesodyne in China (Delectis 1979). Up to now, its chemical constituents have not been investigated. In continuing our investigation on natural products for terpenoids and steroids (Feng et al. 2005; Jin et al. 2004; Li et al. 2003), ten triterpenoids compounds were isolated from an alcoholic extract of the whole plant of this species. We report herein the isolation and structural elucidation of the two new and eight known triterpenoid compounds.

2. Investigations, results and discussion

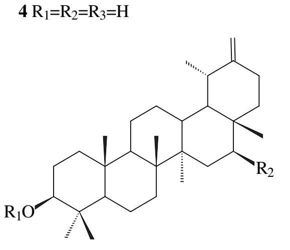
From an alcoholic extract of the whole plant of *P. tatsienense*, two new triterpenoids, olean-12-en-3β,11α,16β-triol-3-*O*-palmitate (**1**), ursa-12-en-3β,11β,16β-triol-3-*O*-palmitate (**2**), as well as eight known triterpenoids, olean-12-en-3β,16β-diol-3-*O*-palmitate (**3**) (Ukiya et al. 2001), β-amyrin (**4**) (Mahato et al. 1994; Seo et al. 1981), α-amyrin (**5**) (Mahato et al. 1994; Seo et al. 1981), methylursolate (**6**) (Mahato et al. 1994), taraxasterol (**7**) (Mahato et al. 1994; Reynolds et al. 1986), taraxast-20 (30)-ene-3β,16β-diol-3-*O*-palmitate (**8**) (Ukiya et al. 2001), pseudotaraxasterol (**9**) (Mahato et al. 1994; Reynolds et al. 1986), lup-3β-*O*-palmitate (**10**) (Guo et al. 1998) were isolated and purified by repeated chromatography over silica gel column. Every compound obtained was subjected to detail spectroscopic analysis to establish their chemical structures. To the best of our knowledge, compounds **1** and **2** are previously unreported naturally occurring. The structures of known compounds were identified by direct comparison of their spectral data (^{1}H NMR and ^{13}C NMR and DEPT) with those reported values in the corresponding literature.



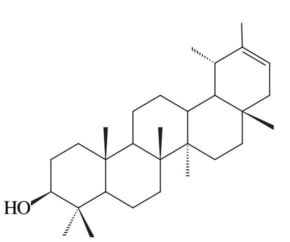
1 R_1=CO$(CH_2)_{14}CH_3$, R_2=R_3=OH
3 R_1=CO$(CH_2)_{14}CH_3$, R_2=H, R_3=OH
4 R_1=R_2=R_3=H



2 R_1=CO$(CH_2)_{14}CH_3$, R_2=R_3=OH, R_4=CH_3
5 R_1=R_2=R_3=H, R_4=CH_3
6 R_1=R_2=R_3=H, R_4=$COOCH_3$



7 R_1=R_2=H
8 R_1=CO$(CH_2)_{14}CH_3$, R_2=OH



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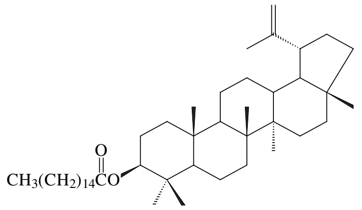

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Compound **1** was obtained as colorless gum, $[\alpha]_D^{20} + 8.0°$ (C, 0.96, $CHCl_3$). Its molecular formula was assigned as $C_{46}H_{80}O_4$ on the basis of FAB-MS data $[M]^+$ at m/z 696, indicated seven degrees of unsaturation. The IR spectrum showed absorption bands for hydroxyl (3385 cm^{-1}) and es-

Table: ^{13}C NMR (100.13 MHz) data for compound 1, 2 and 4

Carbon	**1**	**2**	**4**	Carbon	**1**	**2**	**4**
C-1	38.9	38.7	38.2	C-20	31.1	39.3	30.9
C-2	22.9	22.6	22.7	C-21	33.8	31.5	34.8
C-3	80.4	80.1	80.5	C-22	37.3	38.4	30.5
C-4	39.3	39.1	37.7	C-23	28.3	28.1	28.0
C-5	55.3	55.2	55.2	C-24	16.9	16.6	16.7
C-6	18.4	18.3	18.2	C-25	18.1	17.6	15.6
C-7	33.1	31.9	32.6	C-26	17.1	16.8	16.8
C-8	44.0	44.0	39.8	C-27	24.1	23.2	27.1
C-9	49.0	48.1	46.8	C-28	21.8	21.3	21.5
C-10	37.9	37.7	37.3	C-29	33.3	17.6	33.2
C-11	81.4	81.5	23.6	C-30	23.7	21.9	23.9
C-12	121.9	125.3	122.2	C-1′	173.9	173.6	173.7
C-13	151.0	144.3	143.5	C-2′	34.2	34.8	33.2
C-14	43.7	43.3	43.7	C-3′	25.3	25.1	25.1
C-15	26.1	25.1	35.5	C-4′ to	29.4–	29.2–	29.2–
C-16	65.7	66.6	65.9	C-13′	29.9	29.6	29.7
C-17	35.0	33.4	36.8	C-14′	31.8	31.5	31.9
C-18	48.8	60.1	49.1	C-15′	22.9	23.7	23.5
C-19	46.6	39.3	46.5	C-16′	14.3	14.1	14.1

Assignments were aided by spin splitting patterns, DEPT, ^{1}H–^{1}H COSY, gHMQC, gHMBC experiments, and chemical shift values (δ. The δ values are in ppm and are referenced to either the residual $CHCl_3$ (7.26 ppm) or $CDCl_3$ (77.00 ppm)

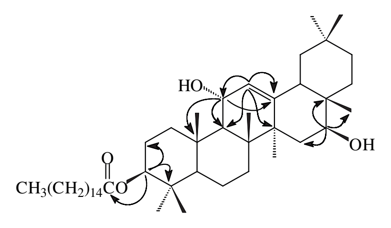

Fig. 1: Key cross peaks in gHMBC of **1** (from H to C)

ter carbonyl (1731 and 1265 cm^{-1}) groups. The ester group in **1** could be further deduced as a palmitoyl moiety because of the characteristic signal δ 173.9 (C-1′) in the downfield region of the ^{13}C NMR spectrum, as well as a saturated long chain feature: a methyl signal δ 0.82 (t, J = 7.2 Hz, H-16′), several methylene signals δ 1.28 (brs, H-15′ to H-4′, 24 H) and δ 1.65 (m, H-3′) and δ 2.26 (t, J = 7.2 Hz, H-2′ in the ^{1}H NMR spectrum (Chaturvedula et al. 2002; Barreiros et al. 2002). In addition to the long chain ester group, it implied that compound **1** was a pentacyclic triterpene that the left 30 carbon signals (8 × CH_3, 7 × CH_2, 8 × CH, 7 × C) in ^{13}C NMR combined with DEPT experiment (Table), which could be supported by eight methyl groups for triterpenes δ 0.76, 0.82, 0.83, 0.85, 0.90, 1.01, 1.04, 1.27 in the ^{1}H NMR spectrum. The typical double bond signals at δ 151.0, 121.9 and three carbons bearing-oxygen at δ 81.5, 80.4 and 65.7 further show that **1** has an olean-12-en carbon skeleton with one palmitoyl moiety and two secondary hydroxyl functions (Barreiros et al. 2002; Ukiya et al. 2001), and this can be confirmed by ^{1}H NMR data, an olefinic proton (5.49, d, J = 3.2 Hz) and three oxymethine proton (δ 4.50, dd, J = 5.6, 11.8 Hz; 4.46, dd, J = 3.2, 9.2 Hz; 4.19, dd, J = 4.8, 11.2 Hz). The ester group (palmitoyl) is linked at C-3β position because of the correlation between H-3 (4.50, dd, J = 5.6, 11.8 Hz) and C-1′ (δ 173.9), C-2 (δ 22.9), C-4 (δ 39.3) in the HMBC, together with comparison of the chemical shift (δ 4.50) and peak pattern (double doublet) and coupling constant (Jae = 5.6 and Jaa = 11.8 Hz) of **1** with those of known triterpenoids (Barreiros et al. 2002; Ukiya et al. 2001). One hydroxyl group was attached at C-11 in α-orientation because of following evidence: the olefinic proton signal (H-12) was as doublet (δ 5.49) ascribed to the methine carbon of C-11; the comparison of the NMR data of H-11β (δ_H 4.46, dd, J = 3.2, 9.2 Hz; δ_C 81.5) for **1** to those of a known compound olean-12-ene-3β,11α-diol (Barreiros et al. 2002); the cross peaks between H-11 with H-12 (δ 5.20) and H-9 (1.82) in the ^{1}H–^{1}H COSY experiment, as well as H-11 with C-9, C-10, C-12 and C-13, and H-12 with C-9, C-11, C-13 and C-14 in the gHMBC experiment (Fig. 1). Another hydroxyl group was linked at C-16 in β-orientation by careful comparison of the NMR data (δ 4.19, dd, Jae = 4.8 and Jaa = 11.2 Hz) with those of the known compound **3** (olean-12-ene-3β,16β-diol-3-*O*-palmitate) (Ukiya et al. 2001), and the results of H-16 showing correlation with C-15, C-17 and C-28 in the gHMBC (Fig. 1). Hence, compound **1** was identified as olean-12-en-3β,11α,16β-triol-3-*O*-palmitate.

Compound **2** was obtained as colorless oil, $[\alpha]_D^{20} + 6.0°$ (C, 0.4, $CHCl_3$). Its molecular formula was assigned as $C_{46}H_{80}O_4$ on the basis of FAB-MS data $[M]^+$ at m/z 696, indicating seven degrees of unsaturation. The IR spectrum showed absorption bands for hydroxyl (3312 cm^{-1}) and ester carbonyl (1714 and 1220 cm^{-1}) groups. Like compound **1**, the palmitoyl ester group in **2** was also elucidated by the typical saturated long chain signal δ_C 173.6 (C-1′) and δ_H 2.29 (2 H, t, J = 7.2 Hz, H-2′), δ 1.66 (2 H, m, H-3′), δ 1.25 (brs, H-4′ to H-15′, 24H) and δ 0.86 (3 H, t, J = 7.2 Hz, H-16′) (Barreiros et al. 2002; Ukiya et al. 2001). Besides the ester group, the presence of eight methyl groups (six singlets: δ 0.77, 0.88, 0.93, 1.09, 1.09, 1.23; two doublets: δ 0.90, d, J = 6.0 Hz and 0.82, d, J = 6.0 Hz) in the ^{1}H NMR and 30 carbon signals (8 × CH_3, 7 × CH_2, 8 × CH, 7 × C) in the ^{13}C NMR combined with DEPT experiment suggested that compound **2** was a triterpenoid. The above results and typical double bond resonances at δ_C 144.3 (C-13) and 125.3 (C-12) indicated that **2** was a pentacyclic triterpene with an ursa-12-en carbon skeleton (Bhaumik et al. 1981; Mahato et al. 1994). The ester group (palmitoyl) was linked at C-3β position because the correlation between H-3 (4.55, m) and C-1′ (δ 173.6), C-2 (δ 22.6), C-4 (δ 39.1) in the HMBC, together with comparison of the chemical shifts (δ_H 4.55 and δ_C 80.1) of **2** with those of known triterpenoids (Ukiya et al. 2001). One hydroxyl group was attached at C-11 and as β-orientation because of some evidence: firstly, the olefinic proton signal (H-12) was as doublet (δ 5.41, d, J = 3.2 Hz) described to the methine carbon of C-11; then, the differences from the NMR data of H-11α (δ_H 4.53, dd, J = 3.2, 9.2 Hz; δ_C 81.5) for **2** with those of the known compound 3α,11α-dihydroxy-urs-12-ene (δ 4.26, dd J = 3.2, 8.8 Hz; δ_C 68.4) (Torre et al. 1990; Mahato et al. 1994); thirdly, the changes of chemical shift of C-9 and C-12 from δ 48.1 and 125.3 in **2** to δ 55.8 (C-9) and 128.8 in 3α,11α-dihydroxy-urs-12-ene; and eventually the cross peaks between H-11 with H-12 (δ 5.41) and H-9 (1.87) in the ^{1}H–^{1}H COSY experiment, as well as H-11 with C-9, C-10, C-12 and C-13, and H-12 with C-9, C-11, C-13 and C-18 in the gHMBC experiment (Fig. 2). Another hydroxyl group was linked at C-16 in β-orientation by careful comparison of the NMR data (δ 4.25, dd, Jae = 5.2 and Jaa = 11.2 Hz) with those of urs-12-en-3β,16β-diol-3-*O*-palmitate (Ukiya et al. 2001), and the results of H-16 showing correlations with C-15, C-17, C-18 and C-28 in the gHMBC (Fig. 2). Consequently, compound **2** was identified as urs-12-en-3β,11β, 16β-triol-3-*O*-palmitate.

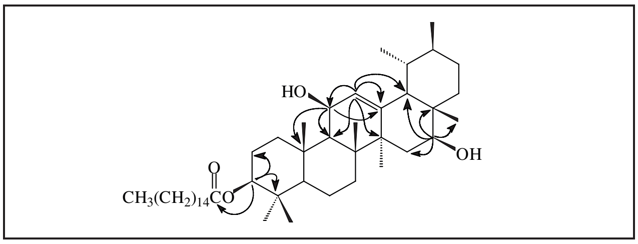

Fig. 2: Key cross peaks in gHMBC of **2** (from H to C)

3. Experimental

3.1. *Equipment*

Melting points: X-4 Digital Display Micro-Melting point apparatus, uncorr. Optical rotations: Perkin Elmer 241 polarimeter, solvent $CHCl_3$. IR-spectra were measured on an FTS 165-IR spectrometer (Bio-Rad, USA). ^1H NMR (400.13 MHz), ^{13}C NMR (100.62 MHz) and 2D NMR were recorded on a Varian INOVA-400 FT-NMR spectrometer (USA) in $CDCl_3$ with TMS as internal standard. FAB-MS was recorded on a VG ZAB-HS mass spectrometer. Separation and purification were performed by chromatographic column (CC) over silica gel. Silica gel (200–300 mesh) used for CC and silica gel (GF_{254}) for TLC were obtained from the Qingdao Marine Chemical Factory, Qingdao, P. R. China. Spots were detected on the TLC under UV light or by heating over 110 °C after spraying with 98% H_2SO_4-EtOH (v : v = 5 : 95).

3.2. *Plant material*

The fresh air-dried plant material of *P. tatsienense* (No. 2004-02) was bought from Huangzhong Tibetan Hospital of Qinghai province, China, in January 2004 and was identified by Prof. Guo-Liang Zhang, College of Biology, Lanzhou University, Lanzhou, P. R. China. A voucher specimen has been deposited at key Laboratory of Natural Medicine for Gansu Province.

3.3. *Extraction and isolation*

The air-dried whole plant of *P. tatsienense* (3.5 kg) was powdered and extracted with 95% EtOH at room temperature (20 l × 4, each extraction lasted 7 days). The combined extracts were evaporated to dryness under reduced pressure. The residue (350 g) was then suspended in H_2O (1.0 L), and extracted with petroleum ether (60–90 °C) (1.0 L × 4), EtOAc (1.0 L × 4) and *n*-BuOH (1.0 L × 4), respectively. The petroleum ether (60–90 °C) extract (65 g) was subjected to column chromatography on silica gel (200 ~ 300 mesh, 700 g) using petroleum ether (60–90 °C) with increasing volume of EtOAc (v : v = 40 : 1, 20 : 1, 15 : 1, 10 : 1, 7 : 1, 4 : 1, 2 : 1, 1 : 1, each about 3.5 l) as eluent. The fractions PT1-PT10 were collected according to TLC analysis. Fraction PT2 (4.0 g) was further fractionated on a silica gel column (200 ~ 300 mesh, 100 g) using petrolemn ether-EtOAc (v : v, 25 : 1) to give a mixture of compounds **3** and **6** (30 mg), that was further isolated and purified on a silica gel column (200 ~ 300 mesh, 10 g) using ether (60–90 °C)-EtOAc (v : v, 20 : 1) to give **3** (8 mg) and **6** (10 mg); Fraction PT4 (3.0 g) was further fractionated on a silica gel column (200 ~ 300 mesh, 90 g) eluting with petroleum ether-EtOAc (v : v, 10 : 1,) and to give three subfractions (Fr. PT4a, 0.5 g, Fr. PT4b, 0.6 g, Fr. PT4c, 0.3 g). Fr. PT4a (0.5 g) was subjected to column chromatography on silica gel column (200 ~ 300 mesh, 20 g) eluting with ether-EtOAc (20 : 1) to give a mixture of **7** and **9** (70 mg), that was further isolated and purified by CC over a silica gel, eluting with petroleum ether-acetone (v : v, 15 : 1) to yield pure **7** (25 mg) and **9** (15 mg); Fr. PT4b (0.6 g) gave compound **4** after a CC on a silica gel column eluting with petroleum ether-EtOAc (v : v, 15 : 1); Fr. PT4c (0.3 g), mixture of **1** and **2**, was repeated fractionated on a silica gel column (200 ~ 300 mesh, 10 g) eluting with petroleum ether-EtOAc (v : v, 10 : 1) to give pure **1** (5 mg) and **2** (15 mg). Fraction PT5 (0.3 g) was purified by CC on a silica gel column (200 ~ 300 mesh, 10 g) eluting with petroleum ether-EtOAc (v : v, 12 : 1) to yield **8** (60 mg). Fraction PT6 (0.5 g) was purified by CC on a silica gel column (200 ~ 300 mesh, 15 g) eluting with petroleum ether-acetone (v : v, 10 : 1) to give **10** (30 mg). Fraction PT9 (0.6 g) was purified by CC on a silica gel (200 ~ 300 mesh, 18 g) column eluting with $CHCl_3$-acetone (v : v, 30 : 1) to yield **5** (6 mg).

3.4. *Compounds isolated*

3.4.1. *Olean-12-en-3β,11α,16β-triol-3-palmitate* (**1**)

Colorless gum, $[\alpha]_D^{20} + 8.0°$ (C, 0.96, $CHCl_3$). IR (film, ν_{max}, cm^{-1}) 3385 (OH), 2924, 2853, 1731 (ester carbonyl), 1708, 1645, 1462, 1385, 1265, 1115, 1027, 985, 927, 857, 813, 721. FAB-MS m/z: 696 $[M]^+$, 679 $[M + 1 - H_2O]^+$, 634, 473, 439, 423, 351. ^1H NMR (400 MHz, TMS, $CDCl_3$) δ ppm: 5.49 (1 H, d, J = 3.2 Hz, H-12), 4.50 (1 H, dd, J = 11.8, 5.6 Hz, H-3α), 4.46 (1 H, dd, J = 9.2, 3.2 Hz, H-11β), 4.19 (1 H, dd, J = 11.2, 4.8 Hz, H-16α), 2.26 (t, J = 7.2, H-2′), 1.83 (1 H, d, J = 9.2 Hz, H-9), 1.27, 1.04, 1.01, 0.90, 0.85, 0.83, 0.82, 0.76 (each 3 H, s, H-23, 24, 25, 26, 27, 28, 29, 30). ^{13}C NMR: see Table.

3.4.2. *Urs-12-en-3β,11β,16β-triol-3-palmitate* (**2**)

Colorless oil, $[\alpha]_D^{20}$ +6.0° (C, 0.4, $CHCl_3$). IR IR (film, ν_{max}, cm^{-1}) 3312 (OH), 2919, 2850, 1778, 1714 (ester carbonyl function), 1571, 1462, 1362, 1220, 1180, 1118, 1048, 986, 905, 839, 755, 722. FAB-MS m/z: 696, 679, 678, 667, 662, 651, 623, 608, 565, 508, 473, 463, 455, 439, 423. ^1H NMR (400 MHz, TMS, $CDCl_3$) δ ppm: 5.41 (1 H, d, J = 3.2 Hz, H-12), 4.55 (m, H-3α), 4.53 (1 H, dd, J = 9.2, 3.2 Hz, H-11α), 4.25 (1 H, dd, J = 11.2, 5.2 Hz, H-16α), 2.29 (2 H, t, J = 7.2 Hz, H-2′), 1.87 (1 H, d, J = 9.2 Hz, H-9), 1.23, 1.09, 1.09, 0.93, 0.88, 0.77 (each 3 H, s, H-23, 24, 25, 26, 27, 28), 0.90 (3 H, d, J = 6.0 Hz) and 0.82 (3 H, d, J = 6.0 Hz, H-29, 30). ^{13}C NMR: see Table.

3.4.3. *Olean-12-en-3β,16β-diol-3-O-palmitate* (**3**)

^1H NMR (400 MHz, TMS, $CDCl_3$) δ ppm: 5.15 (1H, t, J = 4.0 Hz, H-12), 4.99 (1 H, t, J = 8.4 Hz, H-3), 4.20 (1 H, dd, J = 4.8, 11.2, H-16), 2.25 (2 H, t, J = 7.2, H-2′), 1.17, 0.95, 0.92, 0.87, 0.85, 0.83, 0.83, 0.75 (s, each 3 H, H-23, 24, 25, 26, 27, 28, 29, 30). ^{13}C NMR: see Table.

3.4.4. *β-Amyrin* (**4**)

Colorless needles, ^1H NMR (400 MHz, TMS, $CDCl_3$) δ ppm: 5.15 (1 H, t, J = 4.0 Hz, H-12), 3.22 (1 H, m, H-3), 1.14, 1.00, 0.97, 0.94 (each 3 H, s, H-27, 26, 23, 25), 0.88 (6 H, s, H-30, 29), 0.83, 0.79 (each 3 H, s, H-28, 24). ^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ ppm (order C-1 ~ C-30): 38.6, 27.2, 79.1, 38.8, 55.2, 18.4, 32.8, 38.8, 47.7, 37.0, 23.5, 121.7, 145.2, 41.7, 26.2, 27.0, 32.5, 47.2, 46.8, 31.1, 34.7, 37.2, 28.1, 15.5. 15.7, 16.9, 26.0, 28.4, 33.4, 23.7.

3.4.5. *α-Amyrin* (**5**)

Colorless needles. M.p. 184 ~ 185 °C. ^1H NMR (400 MHz, TMS, $CDCl_3$) δ ppm: 3.32 (1 H, m, H-3), 5.13 (1 H, t, J = 4.0 Hz, H-12), 0.78 (3 H, d, J = 6.0 Hz, H-29). ^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ ppm (order C-1 ~ C-30): 38.3, 27.2, 79.1, 38.8, 55.2, 18.4, 32.8, 40.0, 47.7, 36.9, 23.4, 124.4, 139.6, 42.1, 26.6, 28.1, 33.8, 59.1, 39.8, 39.6, 31.1, 41.6, 28.1, 15.6, 15.6, 16.8, 23.3, 28.8, 17.5, 21.4.

3.4.6. *Methylursolate* (**6**)

White needles, ^1H NMR (400 MHz, TMS, $CDCl_3$) δ ppm: 5.19 (t, J = 3.6 Hz, H-12), 3.12 (dd, J = 11.2, 4.8 Hz, H-3α), 0.92 (d, J = 6.0 Hz, H-30), 0.85 (d, J = 6.4 Hz, H-29), ^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ ppm (order C-1 ~ C-30): 32.6, 27.9, 78.8, 37.6, 56.1, 19.0, 33.9, 39.7, 48.1, 37.5, 23.8, 125.5, 139, 42.8, 28.6, 24.9, 48.1, 53.8, 39.4, 37.7, 30.4, 37.5, 28.6, 15.8, 16.3, 17.5, 23.9, 17.4, 178.6, 16.3, 21.4.

3.4.7. *Taraxasterol* (**7**)

White needles. M.p. 221 ~ 222 °C. ^1H NMR (400 MHz, TMS, $CDCl_3$) δ ppm: 3.22 (1 H, dd, J = 9.2, 5.0 Hz, H-3), 0.96 (3 H, d, J = 7.0 Hz, H-29), 4.66 (1 H, brs, H-30), 4.60 (1 H, brs, H-30′), 0.71, 0.77, 0.86, 0.97, 0.98, 1.06 (s, each 3 H, H-23, 24, 25, 26, 27, 28). ^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ ppm (order C-1 ~ C-30): 38.9, 27.4, 79.2, 38.9, 55.5, 18.2, 33.9, 40.5, 50.7, 37.1, 21.5, 26.8, 38.7, 42.2, 26.8, 38.5, 34.3, 48.8, 39.8, 15.7, 25.2, 39.0, 28.1, 15.7, 17.0, 15.9, 14.6, 19.3, 25.2, 107.3.

3.4.8. *Taraxast-20(30)-ene-3β,16β-diol-3-O-palmitate* (**8**)

Colorless oil. ^1H NMR (400 MHz, TMS, $CDCl_3$) δ ppm: 4.49 (1 H, dd, J = 10.8, 5.6 Hz, H-3), 3.39 (1 H, dd, J = 11.0, 5.2 Hz, H-16), 4.63 (2 H, d, J = 7.2 Hz, H-30). ^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ ppm (order C-1 ~ C-30): 38.3, 23.7, 80.5, 39.7, 55.4, 18.1, 34.8, 40.9, 49.9, 36.9, 21.4, 25.8, 38.9, 42.3, 25.2, 77.6, 36.9, 47.6, 39.0, 153.6, 25.1, 36.0, 27.9, 16.3, 16.3, 15.8, 14.1, 21.3, 25.0, 107.4; 173.7(C-1′), 34.8 (C-2′), 25.2 (C-3′), 29.24 (C-4′), 29.66 (C-13′), 31.91 (C-14′), 22.68 (C-15′), 14.11 (C-16′).

3.4.9. *Pseudotaraxasterol* (**9**)

White needles. M.p. 188 ~ 189 °C. ^1H NMR (400 MHz, TMS, $CDCl_3$) δ ppm: 3.22 (1 H, dd, J = 11.4, 5.8 Hz, H-3), 5.20 (1 H, d, J = 6.1 Hz, H-21), 0.99 (3 H, d, J = 7.0 Hz, H-29), 1.64 (3 H, brs, H-30). ^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ ppm (order C-1 ~ C-30): 39.1, 27.1, 79.2, 39.8, 55.5, 18.5, 34.0, 41.7, 50.7, 37.3, 21.6, 27.6, 39.8, 42.3, 27.5, 37.0, 34.0, 48.5, 36.3, 139.8, 119.0, 41.8, 28.5, 15.7, 15.8, 15.9, 14.6, 17.7, 22.7, 21.6.

3.4.10. *Lup-3β-O-palmitate* (**10**)

Colorless gum. ^1H NMR (400 MHz, TMS, $CDCl_3$) δ ppm: 4.44 (1 H, dd, J = 10.3, 5.4 Hz), 4.67 (1 H, brs, H-29), 4.59 (1 H, brs, H-29′), 1.67 (3 H, s, H-30), 2.25 (2 H, t, J = 7.6, H-2′). ^{13}C NMR (100 MHz, TMS, $CDCl_3$)

δ ppm (order C-1 ~ C-30): 38.3, 22.6, 80.5, 37.8, 55.3, 18.1, 34.1, 40.9, 49.8, 37.2, 20.8, 25.1, 37.6, 40.8, 27.9, 36.8, 44.0, 48.5, 47.6, 149.9, 29.8, 40.0, 27.9, 15.9, 16.1, 16.1, 15.9, 16.5, 18.1, 109.8, 19.2, 173.7 (C-1′), 34.8 (C-2′), 25.1 (C-3′), 29.24 (C-4′), 29.85 (C-13′), 31.90 (C-14′), 22.67 (C-15′), 14.10 (C-16′).

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