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### **Poriacosones A and B: two new lanostane triterpenoids from *Poria cocos***

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## Poriacosones A and B: two new lanostane triterpenoids from *Poria cocos*

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Two new lanostane triterpenoids, poriacosones A (**8**) and B (**9**), together with eight known compounds were isolated from the sclerotia of *Poria cocos* (Schw.) Wolf (Polyporaceae), and identified by spectroscopic analysis, including IR, UV, CD, ESI-TOF-MS, HR-SIMS, 1D-, and 2D-NMR spectra. The structures of the new compounds were established as 3 $\alpha$ ,16 $\alpha$ -dihydroxy-24-oxolanost-7,9(11)-dien-21-oic acid (**8**) and 3 $\beta$ ,16 $\alpha$ -dihydroxy-24-oxolanost-7,9(11)-dien-21-oic acid (**9**).

**Keywords:** *Poria cocos*; lanostane triterpenoids; poriacosone A; poriacosone B

### 1. Introduction

Dried sclerotium of *Poria cocos* (Schw.) Wolf (Polyporaceae) is a well-known traditional Chinese medicine used for the treatment of insomnia, water retention, and diarrhea [1]. Various triterpenoids of lanostane type from the sclerotia of *P. cocos* have been reported [2]. Some of them exhibit anti-inflammatory effect [3], antiemetic property [4], and cytotoxic activity [5]. The aim of our study was to further investigate the chemical constituents of the sclerotia of *P. cocos*. Herein, we describe the isolation and structural elucidation of two new triterpenoids, named poriacosones A (**8**) and B (**9**), together with eight known compounds, 3-epidehydrotumulosic acid (**1**) [6], 3-*O*-acetyl-16 $\alpha$ -hydroxytrametenolic acid (**2**) [7], polyporenic acid C (**3**) [8], dehydropachymic acid (**4**) [7], pachymic acid (**5**) [7], dehydrotumulosic acid (**6**) [6], tumulosic acid (**7**) [9], and 3 $\beta$ ,16 $\alpha$ -dihydroxylanosta-7,9(11), 24-trien-21-oic acid (**10**) [3] (Figure 1).

### 2. Results and discussion

Compound **8** was obtained as white amorphous powder with  $[\alpha]_D^{20} + 41.8$  (*c* 0.0240, MeOH). The molecular formula was inferred as C<sub>30</sub>H<sub>46</sub>O<sub>5</sub> from HR-SIMS, DEPT, and <sup>13</sup>C NMR (Table 2) spectral data. The IR spectrum showed an absorption band at 1642 cm<sup>-1</sup> and the UV spectrum showed an absorption maximum at 243 nm (log  $\epsilon$ , 2.76), suggesting the presence of a  $\Delta^{7,9(11)}$  diene moiety in **8** [6,9]. Its <sup>1</sup>H NMR spectrum (Table 1) showed signals of two secondary methyl groups [ $\delta_H$  0.97 (3H, d, *J* = 7.0 Hz) and 1.01 (3H, d, *J* = 7.0 Hz)], five tertiary methyl groups ( $\delta_H$  0.95, 1.05, 1.07, 1.17, and 1.41), two oxygen-bearing methines [ $\delta_H$  3.61 (1H, br s/*W*<sub>1/2</sub> = 8.0 Hz) and 4.58 (1H, t, *J* = 7.0 Hz)], and two olefinic methines [ $\delta_H$  5.44 (1H, d, *J* = 5.0 Hz) and 5.60 (1H, br s)]. And the <sup>13</sup>C NMR spectrum of **8** confirmed the presence of seven methyl carbons, two oxygenated carbons ( $\delta_C$  75.0 and 76.1) and four olefinic carbons ( $\delta_C$  116.0, 121.1, 142.7, and 146.5). In addition, a ketone group ( $\delta_C$  213.7) and a

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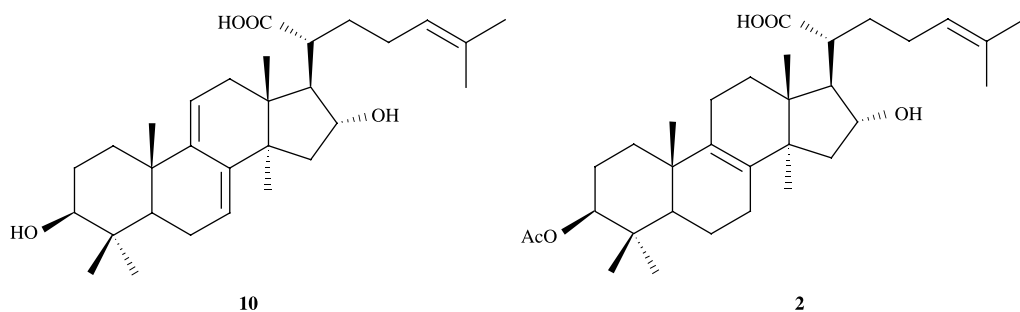
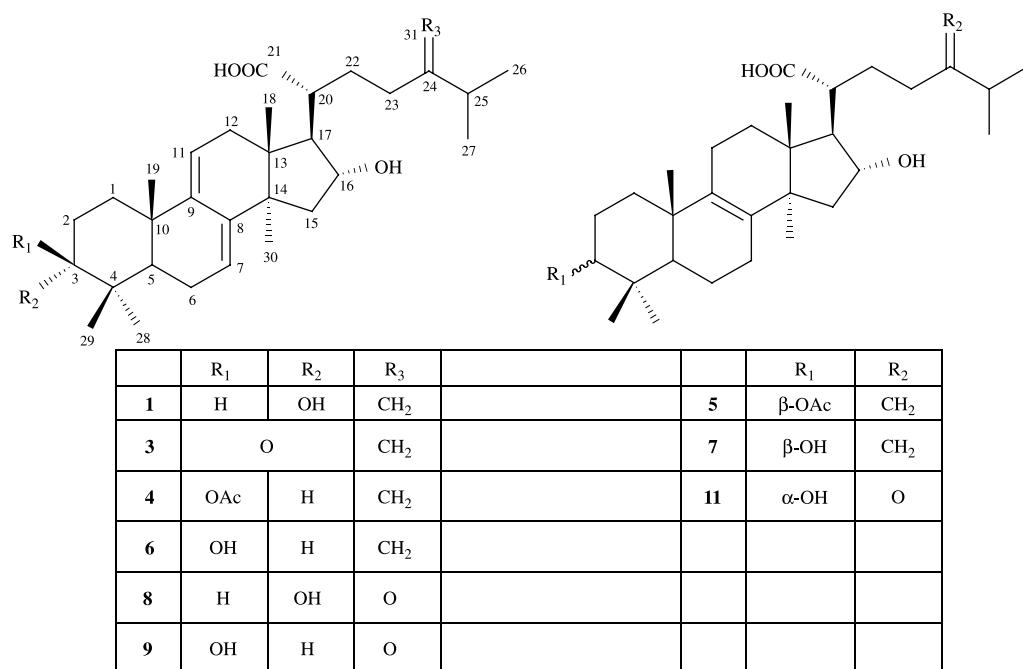


Figure 1. Structures of compounds 1–11.

carboxyl group ( $\delta_C$  178.9) were observed. The ketone group was deduced to be located at C-24 based on the HMBC correlations between C-24 and H-23, H-25, Me-26, and Me-27, and compared with the NMR spectral data of daedaleanic acid B (**11** in Figure 1) [10], which had an identical side chain at C-17. The signals observed in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **8** were closely related to those of compound **1** (3-epidehydrotumulosic acid) [6], indicating that **8** also had a similar lanostane structure and an  $3\alpha$ -axial hydroxyl group [ $\delta_{\text{H-3}}$  3.61 (1H, br  $s/W_{1/2} = 8.0\text{ Hz}$ ) in **8** and  $\delta_{\text{H-3}}$  3.63 (1H, br  $s/W_{1/2} = 8.0\text{ Hz}$ ) in **1** for H-3 $\beta$ , and  $\delta_{\text{H-3}}$  3.44

(1H, dd,  $J = 7.0, 7.5\text{ Hz}$ ) for H-3 $\alpha$  in dehydrotumulosic acid (**6**) as 3-epidehydrotumulosic acid (**1**), except for the presence of the ketone group at C-24. Detailed analysis of the  $^1\text{H}$ – $^1\text{H}$  COSY (Figure 2), HMBC (Figure 3), and HSQC spectra of **8** led to the assignment of all proton and carbon signals of **8**. Therefore, the structure of **8** was elucidated to be  $3\alpha,16\alpha$ -dihydroxy-24-oxolanost-7,9(11)-dien-21-oic acid, named poriacosone A.

Compound **9** was obtained as white amorphous powder with  $[\alpha]_{\text{D}}^{20} + 26.2$  ( $c$  0.0765, MeOH). The molecular formula was deduced as  $\text{C}_{30}\text{H}_{46}\text{O}_5$  from HR-SIMS and

Table 1.  $^1\text{H}$  NMR spectral data for compounds **8** and **9** (500 MHz, in  $\text{C}_5\text{D}_5\text{N}$ ).

| H  | <b>8</b>                          | <b>9</b>                                    |
|----|-----------------------------------|---|
| 1  | 1.71 dd (3.0, 13.0) 2.26 m        | 1.43 m 1.95 m                               |
| 2  | 1.85 dd (3.0, 13.0) 2.03 m        | 1.66 m 1.82 m                               |
| 3  | 3.61 br s ( $W_{1/2} = 8.0$ )     | 3.44 dd (7.0, 7.5)                          |
| 5  | 1.99 br d (8.5)                   | 1.28 dd (4.5, 11.5)                         |
| 6  | 2.09 br d (8.5)                   | 2.10 br d (17.5) 2.17 ddd (4.5, 11.5, 17.5) |
| 7  | 5.60 br s                         | 5.60 d (4.5)                                |
| 11 | 5.44 d (5.0)                      | 5.36 br s                                   |
| 12 | 2.34 m 2.66 dd (5.0, 18.0)        | 2.38 dd (5.4, 16.5) 2.65 br d (16.5)        |
| 15 | 1.89 d (13.0) 2.39 dd (7.0, 13.0) | 1.91 br d (13.0) 2.42 dd (8.5, 13.0)        |
| 16 | 4.58 t (7.0)                      | 4.59 dd (6.0, 9.0)                          |
| 17 | 2.80 m                            | 2.86 m                                      |
| 18 | 1.05 s                            | 1.02 s                                      |
| 19 | 1.07 s                            | 1.04 s                                      |
| 20 | 2.87 m                            | 2.92 m                                      |
| 22 | 2.43 m 2.92 m                     | 2.45 m 2.94 m                               |
| 23 | 2.86 m 2.87 m                     | 2.84 m 2.89 m                               |
| 25 | 2.52 d (7.0)                      | 2.52 d (7.0)                                |
| 26 | 0.97 d (7.0)                      | 0.98 d (7.0)                                |
| 27 | 1.01 d (7.0)                      | 1.01 d (7.0)                                |
| 28 | 1.17 s                            | 1.19 s                                      |
| 29 | 0.95 s                            | 1.11 s                                      |
| 30 | 1.41 s                            | 1.49 s                                      |

All values are in ppm, coupling constants ( $J$ ) in Hz; assignments were made by  $^1\text{H}$ - $^1\text{H}$  COSY, HSQC, and HMBC spectral data.

$^{13}\text{C}$  NMR (Table 2) spectral data. Compared with **8**, an intense UV absorption band at 243 nm ( $\log \epsilon$ , 2.43) and IR absorption band at  $1642\text{ cm}^{-1}$  were also observed, suggesting the presence of a  $\Delta^{7,9(11)}$  diene group in **9** [6,9]. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data (Tables 1 and 2) of **9** were similar to those of **8** except for the signals due to ring A. Nevertheless, comparison of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data of **9** with those of **6** (dehydrotumulosic acid) and daedalenic acid B (**11** in Figure 1) [10] revealed that **9**, **6**, and **11** had identical substitution

pattern in ring A, namely, having the  $3\beta$ -hydroxyl group. Detailed analysis of the  $^1\text{H}$ - $^1\text{H}$  COSY, HMBC and HSQC spectra of **9** led to the assignment of all proton and carbon signals of **9**. Thus, the structure of **9** was determined to be  $3\beta,16\alpha$ -dihydroxy-24-oxolanost-7,9(11)-dien-21-oic acid, named poriacosone B.

Compounds **8** and **9** are a pair of epimers, and could be separated by high-pressure liquid chromatography (HPLC) with an achiral column (see the Experimental section).

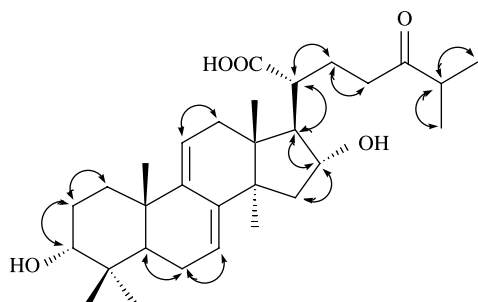
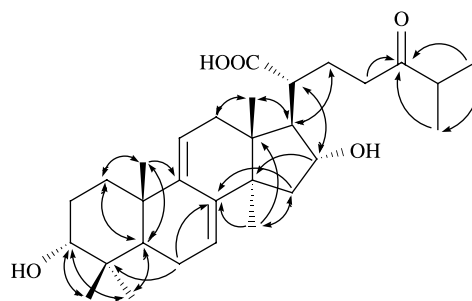
Figure 2.  $^1\text{H}$ - $^1\text{H}$  COSY correlations of **8**.Figure 3. Key HMBC correlations of **8** (from H to C).

Table 2.  $^{13}\text{C}$  NMR spectral data for compounds **1**, **6**, **8**, **9**, and **11** (125 MHz, in  $\text{C}_5\text{D}_5\text{N}$ ).

| C  | <b>8</b> * | <b>1</b> | <b>11</b> [10] | <b>9</b> * | <b>6</b> |
|----|------------|----------|----------------|------------|----------|
| 1  | 30.5 t     | 30.6     | 30.7           | 36.3 t     | 36.3     |
| 2  | 26.6 t     | 26.7     | 26.8           | 28.6 t     | 28.7     |
| 3  | 75.0 d     | 75.1     | 75.0           | 78.0 d     | 78.0     |
| 4  | 37.7 s     | 37.9     | 38.1           | 39.3 s     | 39.3     |
| 5  | 43.6 d     | 43.7     | 44.6           | 49.8 d     | 49.8     |
| 6  | 23.3 t     | 23.4     | 18.5           | 23.5 t     | 23.5     |
| 7  | 121.1 d    | 121.3    | 26.6           | 121.3 d    | 121.2    |
| 8  | 142.7 s    | 142.8    | 134.5          | 142.7 s    | 142.8    |
| 9  | 146.5 s    | 146.6    | 135.0          | 146.4 s    | 146.3    |
| 10 | 37.8 s     | 37.9     | 37.4           | 37.8 s     | 37.8     |
| 11 | 116.0 d    | 116.1    | 20.9           | 116.5 d    | 116.6    |
| 12 | 36.1 t     | 36.2     | 29.7           | 36.3 t     | 36.3     |
| 13 | 45.0 s     | 45.1     | 46.2           | 45.0 s     | 45.1     |
| 14 | 49.5 s     | 49.5     | 48.8           | 49.4 s     | 49.8     |
| 15 | 44.3 t     | 44.4     | 43.6           | 44.4 t     | 44.4     |
| 16 | 76.1 d     | 76.4     | 76.4           | 76.2 d     | 76.4     |
| 17 | 57.1 d     | 57.6     | 56.9           | 57.3 d     | 57.7     |
| 18 | 17.6 q     | 17.6     | 17.8           | 17.7 q     | 17.6     |
| 19 | 23.0 q     | 23.1     | 19.3           | 23.0 q     | 23.0     |
| 20 | 47.8 d     | 48.5     | 47.8           | 47.7 d     | 49.4     |
| 21 | 178.9 s    | 178.7    | 178.6          | 178.4 s    | 178.7    |
| 22 | 26.5 t     | 31.4     | 26.8           | 26.7 t     | 31.6     |
| 23 | 38.5 t     | 33.2     | 38.6           | 38.6 t     | 33.2     |
| 24 | 213.7 s    | 156.0    | 213.8          | 213.7 s    | 156.1    |
| 25 | 40.8 d     | 34.1     | 40.9           | 40.9 d     | 34.1     |
| 26 | 18.2 q     | 22.0     | 18.3           | 18.3 q     | 22.0     |
| 27 | 18.3 q     | 21.9     | 18.4           | 18.4 q     | 21.8     |
| 28 | 29.1 q     | 29.2     | 29.0           | 28.8 q     | 28.8     |
| 29 | 22.8 q     | 23.0     | 22.5           | 16.6 q     | 16.6     |
| 30 | 26.5 q     | 26.6     | 25.3           | 26.6 q     | 26.6     |
| 31 |            | 107.0    |                |            | 106.9    |

\*Assignments were made by  $^1\text{H}$ - $^1\text{H}$  COSY, HSQC and HMBC data; multiplicity was established from HSQC and DEPT data; s, C; d, CH; t,  $\text{CH}_2$ ; q,  $\text{CH}_3$ .

The spectral data of  $^1\text{H}$  and  $^{13}\text{C}$  NMR of **7** and  $^1\text{H}$  NMR of **10** were reported for the first time in this paper.

### 3. Experimental

#### 3.1 General experimental procedures

Optical rotations were measured on a Perkin-Elmer 243B polarimeter with MeOH as solvent. UV spectra were obtained on a Varian Cary-300 UV-vis photometer in MeOH solution. IR spectra were recorded on a Thermo Nicolet Nexus 470 FT-IR spectrometer. Mass spectra were recorded on a MDS SCIEX API ASTAR spectrometer (for ESI-TOF-MS) and

an APEX II FT-ICR-MS spectrometer (for HR-SIMS). 1D- and 2D-NMR spectra were recorded on a Varian Inova 500 NMR spectrometer (500 MHz for  $^1\text{H}$  NMR and 125 MHz for  $^{13}\text{C}$  NMR) using  $\text{C}_5\text{D}_5\text{N}$  as solvent and TMS as internal standard. Preparative HPLC was performed on a P680 chromatograph (Dionex Co., Sunnyvale, CA, USA), equipped with UVD170U detector using a Phenomenex Luna 10 C18 (2) column (250 mm  $\times$  21.2 mm, 10  $\mu\text{m}$ ) at a flow rate of 10 ml/min. Open column chromatography was carried out using silica gel (200–300 mesh, Qingdao Marine Chemical Co., Qingdao, China) as stationary phase. TLC was conducted on silica gel GF<sub>254</sub> plates (Merck, Whitehouse Station, NJ, USA) and reverse-phase C18 silica gel plates (Merck).

#### 3.2 Plant material

The sclerotia of *P. cocos* were collected from 'The China National GAP Base of Chinese Materia Medica for *Poria cocos*' at Luotian County, Hubei Province, China, in September 2002. The fungus was identified at the site by Professor Xiu-wei Yang who is a co-author of this paper, and a voucher specimen (No. 20020920) has been deposited in the State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, China.

#### 3.3 Extraction and isolation

Dried sclerotia of *P. cocos* (10 kg) were powdered and extracted with 95% ethanol (401  $\times$  5 times, 1 h/time) under reflux. The ethanolic extract was concentrated under reduced pressure to afford an extract (130.7 g, yield 1.31%), which was suspended in water (1.25 l) and partitioned successively with cyclohexane (2.51  $\times$  7 times), EtOAc (2.51  $\times$  5 times), and *n*-BuOH (2.51  $\times$  5 times). The cyclohexane solution was concentrated *in vacuo* to yield a green residue (16.2 g, 0.162%), which was chromatographed on a silica gel column and eluted with cyclohexane-EtOAc mixture of increas-

ing polarity. A total of 151 fractions (*ca.* 100 ml each) were collected and combined on the basis of TLC analysis. The fractions 85–89 were purified by preparative reverse-phase HPLC with MeOH–H<sub>2</sub>O–HCOOH (76:24:0.05) as mobile phase at a flow rate of 10 ml/min to yield compound **1** (18 mg).

The EtOAc solution was concentrated *in vacuo* to give a brown residue (36.8 g, 0.368%), and fractionated on silica gel column chromatograph, eluting with EtOAc–MeOH gradient mixtures to give 258 fractions (*ca.* 100 ml each), which were combined on the basis of TLC analysis leading to four main fractions (A–D). Fraction A was subjected to preparative reverse-phase HPLC eluting with MeOH–H<sub>2</sub>O–HCOOH (80:20:0.05) at a flow rate of 10 ml/min to give compounds **2** (13 mg) and **3** (24 mg). Fraction B was purified by preparative reverse-phase HPLC eluting with MeOH–H<sub>2</sub>O–HCOOH (80:20:0.05) at a flow rate of 10 ml/min to afford compounds **4** (90 mg) and **5** (240 mg). Fraction C was subjected to preparative reverse-phase HPLC using MeOH–H<sub>2</sub>O–HCOOH (75:25:0.06) as solvent system at a flow rate of 10 ml/min to yield compounds **6** (90 mg) and **7** (44 mg). Compounds **8** (12 mg), **9** (8 mg), and **10** (10 mg) obtained from subfraction D, which were separated by preparative reverse-phase HPLC eluting with MeOH–H<sub>2</sub>O–HCOOH (60:40:0.05) at a flow rate of 10 ml/min.

### 3.3.1 3-Epidehydrotumulosic acid (**1**)

$[\alpha]_D^{20} + 33.4$  (*c* 0.03, MeOH); negative ESI-TOF-MS *m/z*: 483.3 [M – H]<sup>–</sup>; IR, UV, and NMR spectral data were in agreement with those reported for 3-epidehydrotumulosic acid [6].

### 3.3.2 3-O-Acetyl-16 $\alpha$ -hydroxytrametenolic acid (**2**)

Positive ESI-TOF-MS *m/z*: 515.3 [M + H]<sup>+</sup>; IR and NMR spectral data were in agreement with those reported for 3-*O*-acetyl-16 $\alpha$ -hydroxytrametenolic acid [7].

### 3.3.3 Polyporenic acid C (**3**)

$[\alpha]_D^{20} + 7.1$  (*c* 0.14, MeOH); positive ESI-TOF-MS *m/z*: 483.3 [M + H]<sup>+</sup>; IR, UV, and NMR spectral data were in agreement with those reported for polyporenic acid C [8,11].

### 3.3.4 Dehydropachymic acid (**4**)

$[\alpha]_D^{20} + 101.1$  (*c* 0.12, MeOH); positive ESI-TOF-MS *m/z*: 527.3 [M + H]<sup>+</sup>; IR, UV, and NMR spectral data were in agreement with those reported for dehydropachymic acid [7,12].

### 3.3.5 Pachymic acid (**5**)

$[\alpha]_D^{20} + 34.3$  (*c* 0.12, MeOH); negative ESI-TOF-MS *m/z*: 527.3 [M – H]<sup>–</sup>; IR and NMR spectral data were in agreement with those reported for pachymic acid [7,12].

### 3.3.6 Dehydrotumulosic acid (**6**)

$[\alpha]_D^{20} + 49.7$  (*c* 0.12, MeOH); negative ESI-TOF-MS *m/z*: 483.3 [M – H]<sup>–</sup>; IR, UV, and NMR spectral data were in agreement with those reported for dehydrotumulosic acid [6].

### 3.3.7 Tumulosic acid (**7**)

$[\alpha]_D^{20} + 37.8$  (*c* 0.13, MeOH); <sup>1</sup>H NMR (500 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$ : 1.18 (1H, m, H<sub>a</sub>-1), 1.61 (1H, br d, *J* = 13.0 Hz, H<sub>b</sub>-1), 1.60 (1H, m, H<sub>a</sub>-2), 1.70 (1H, m, H<sub>b</sub>-2), 3.42 (1H, dd, *J* = 7.5, 8.5 Hz, H-3 $\alpha$ ), 1.17 (1H, br d, *J* = 12.5 Hz, H-5 $\alpha$ ), 1.66 (2H, m, H-6), 2.04 (2H, m, H-7), 1.96 (2H, m, H-11), 1.97 (1H, m, H<sub>a</sub>-12), 2.15 (1H, m, H<sub>b</sub>-12), 1.69 (1H, br d, *J* = 13.0 Hz, H<sub>a</sub>-15), 2.40 (1H, dd, *J* = 8.0, 13.0 Hz, H<sub>b</sub>-15), 4.51 (1H, dd, *J* = 6.0, 8.0 Hz, H-16 $\beta$ ), 2.80 (1H, dd, *J* = 6.0, 10.0 Hz, H-17 $\alpha$ ), 1.22 (3H, s, CH<sub>3</sub>-18), 1.01 (3H, s, CH<sub>3</sub>-19), 2.95 (1H, m, H-20), 2.50 (1H, m, H<sub>a</sub>-22), 2.62 (1H, m, H<sub>b</sub>-22), 2.40 (1H, m, H<sub>a</sub>-23), 2.51 (1H, br t, *J* = 12.0 Hz, H<sub>b</sub>-23), 2.26 (1H, m, H-25), 0.95 (3H, d, *J* = 7.0 Hz, CH<sub>3</sub>-26), 0.97 (3H, d, *J* = 7.0 Hz, CH<sub>3</sub>-27), 1.13 (3H, s, CH<sub>3</sub>-28), 1.05 (3H, s, CH<sub>3</sub>-29), 1.46 (3H, s, CH<sub>3</sub>-30), 4.81 (1H, s, H<sub>a</sub>-31), 4.95 (1H, s, H<sub>b</sub>-31); <sup>13</sup>C



NMR (125 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$ : 36.0 (C-1), 28.6 (C-2), 78.0 (C-3), 39.5 (C-4), 50.9 (C-5), 18.7 (C-6), 27.0 (C-7), 134.8 (C-8), 135.2 (C-9), 37.4 (C-10), 20.9 (C-11), 29.7 (C-12), 46.3 (C-13), 48.8 (C-14), 43.7 (C-15), 76.6 (C-16), 57.3 (C-17), 17.8 (C-18), 19.4 (C-19), 48.7 (C-20), 178.8 (C-21), 31.6 (C-22), 33.2 (C-23), 156.1 (C-24), 34.1 (C-25), 22.0 (C-26), 21.8 (C-27), 28.6 (C-28), 16.4 (C-29), 25.4 (C-30), 107.0 (C-31); negative ESI-TOF-MS  $m/z$ : 485.4 [M - H]<sup>-</sup>; IR and UV spectral data were in agreement with those reported for tumulosic acid [9].

### 3.3.8 *Poriacosone A (3 $\alpha$ ,16 $\alpha$ -dihydroxy-24-oxolanost-7,9(11)-dien-21-oic acid) (8)*

White amorphous powder; C<sub>30</sub>H<sub>46</sub>O<sub>5</sub>; [ $\alpha$ ]<sub>D</sub><sup>20</sup> + 41.8 (*c* 0.02, MeOH); UV (MeOH)  $\lambda_{\max}$  (nm, log  $\epsilon$ ): 202 (2.92), 236 (2.72), 243 (2.76), 251 (2.69); IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3420, 2923, 2854, 1707, 1680, 1642, 1610, 1458, 1381, 1261, 1111, 1055, 863, 793, 557, 409; <sup>1</sup>H NMR (500 MHz, C<sub>5</sub>D<sub>5</sub>N) and <sup>13</sup>C NMR (125 MHz, C<sub>5</sub>D<sub>5</sub>N) spectral data were shown in Tables 1 and 2; negative ESI-TOF-MS  $m/z$ : 485.3 [M - H]<sup>-</sup>; HR-SIMS  $m/z$ : 485.3269 [M - H]<sup>-</sup> (calcd for C<sub>30</sub>H<sub>45</sub>O<sub>5</sub>, 485.3272).

### 3.3.9 *Poriacosone B (3 $\beta$ ,16 $\alpha$ -dihydroxy-24-oxolanost-7,9(11)-dien-21-oic acid) (9)*

White amorphous powder; C<sub>30</sub>H<sub>46</sub>O<sub>5</sub>; [ $\alpha$ ]<sub>D</sub><sup>20</sup> + 26.2 (*c* 0.08, MeOH); UV (MeOH)  $\lambda_{\max}$  (nm, log  $\epsilon$ ): 202 (2.36), 236 (2.39), 243 (2.43), 252 (2.28); IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3425, 2962, 2929, 2855, 2715, 1704, 1673, 1642, 1616, 1452, 1365, 1380, 1288, 1263, 1097, 1036, 775; <sup>1</sup>H NMR (500 MHz, C<sub>5</sub>D<sub>5</sub>N) and <sup>13</sup>C NMR (125 MHz, C<sub>5</sub>D<sub>5</sub>N) spectral data were shown in Tables 1 and 2; negative ESI-TOF-MS  $m/z$ : 485.3 [M - H]<sup>-</sup>; HR-SIMS  $m/z$ : 485.3270 [M - H]<sup>-</sup> (calcd for C<sub>30</sub>H<sub>45</sub>O<sub>5</sub>, 485.3272).

### 3.3.10 *3 $\beta$ ,16 $\alpha$ -dihydroxylanosta-7,9(11),24-trien-21-oic acid (10)*

White amorphous powder; C<sub>30</sub>H<sub>46</sub>O<sub>4</sub>; [ $\alpha$ ]<sub>D</sub><sup>20</sup> + 35.8 (*c* 0.06, MeOH); UV (MeOH)

$\lambda_{\max}$  (nm, log  $\epsilon$ ): 202 (2.53), 235 (2.27), 243 (2.30), 251 (2.13); IR (KBr)  $\nu_{\max}$  (cm<sup>-1</sup>): 3420, 2929, 2874, 2742, 1642, 1607, 1385, 1363, 1102, 789; <sup>1</sup>H NMR (500 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$ : 1.46 (1H, m, H<sub>a</sub>-1), 2.12 (1H, m, H<sub>b</sub>-1), 1.68 (1H, m, H<sub>a</sub>-2), 1.87 (1H, m, H<sub>b</sub>-2), 3.44 (1H, dd, *J* = 7.0, 7.5 Hz, H-3 $\alpha$ ), 1.28 (1H, dd, *J* = 4.5, 11.0 Hz, H-5 $\alpha$ ), 2.15 (2H, m, H-6), 5.61 (1H, br s, H-7), 5.37 (1H, br s, H-11), 2.38 (1H, br d, *J* = 18.0 Hz, H<sub>a</sub>-12), 2.70 (1H, br d, *J* = 18.0 Hz, H<sub>b</sub>-12), 1.92 (1H, br d, *J* = 13.0 Hz, H<sub>a</sub>-15), 2.45 (1H, dd, *J* = 8.0, 13.0 Hz, H<sub>b</sub>-15), 4.51 (1H, dd, *J* = 6.0, 8.0 Hz, H-16 $\beta$ ), 2.86 (1H, m, H-17 $\alpha$ ), 1.05 (3H, s, CH<sub>3</sub>-18), 1.05 (3H, s, CH<sub>3</sub>-19), 2.92 (1H, m, H-20), 2.50 (1H, m, H<sub>a</sub>-22), 2.40 (1H, m, H<sub>b</sub>-22), 2.50 (1H, m, H<sub>a</sub>-23), 2.41 (1H, m, H<sub>b</sub>-23), 5.31 (1H, br s, H-24), 1.59 (3H, s, CH<sub>3</sub>-26), 1.58 (3H, s, CH<sub>3</sub>-27), 1.20 (3H, s, CH<sub>3</sub>-28), 1.11 (3H, s, CH<sub>3</sub>-29), 1.48 (3H, s, CH<sub>3</sub>-30); negative ESI-TOF-MS  $m/z$ : 469.3 [M - H]<sup>-</sup>; <sup>13</sup>C NMR spectral data were in agreement with those reported for 3 $\beta$ ,16 $\alpha$ -dihydroxylanosta-7,9(11),24-trien-21-oic acid [3].

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