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TRITERPENES FROM THE SURFACE LAYER OF *PORIA COCOS**

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Key Word Index—*Poria cocos*; Polyporaceae; triterpene; 3,4-secolanostane; lanostane.

Abstract—The surface layer of *Poria cocos* has yielded five new triterpenes; two of the lanostane type and three of the 3,4-secolanostane type. The structures of these compounds were elucidated mainly by two-dimensional NMR techniques.

INTRODUCTION

Dried sclerotia of *Poria cocos* Wolf are used as a crude drug 'Hoelen' (Chinese name: Fu-Ling), which is a renowned Chinese drug and is combined in many traditional Chinese prescriptions as a diuretic, sedative, and tonic. In China, the inner parts of the sclerotia of *P. cocos* are called 'Bai- Fu- Ling', and are reported to have an invigorating activity in addition to diuretic and sedative activities. On the contrary, 'Fu-Ling-Pi' is reported to have only a diuretic activity and no invigorating activity [1]. In recent years, almost all of the 'Hoelen' available commercially in Japan is imported from China. It should be noted that, in Japan, usually the surface part of the sclerotia is removed and only the inner part is used as 'Hoelen'. Interestingly, however, in China, the surface part including peel is called 'Fu-Ling-Pi' and used as a diuretic [1]. Previously, we reported the isolation and structure elucidation of four novel 3,4-secolanostane triterpenes from the surface layer [2]. In continuation of our work on the constitutents of the surface part of *P. cocos*, we obtained two new lanostanes (**1**, **2**) and three new 3,4-secolanostane compounds (**3**–**5**), along with two known compounds, dehydrotumulosic acid (**6**) [3] and dehydroeburiconic acid (**7**) [4].

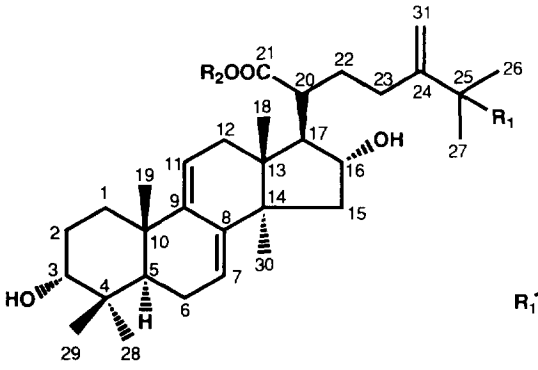
Compound **1** was obtained as an amorphous powder, $[\alpha]_D^{26}$ + 6° (pyridine). It showed a molecular ion peak at *m/z* 484 in the EI-mass spectrum and its molecular formula was determined by HR-mass spectrometry to be $C_{31}H_{48}O_4$ which is the same as that of **6**. The IR spectrum showed broad absorptions at 1707 cm^{-1} (carboxyl) and 1642 cm^{-1} (diene) and the UV spectrum showed an absorption maximum at 243 nm (log ε, 4.08), suggesting the presence of a $\Delta^{7,9(11)}$ diene grouping in the molecule [5]. The ^1H and ^{13}C NMR spectra closely resembled those of **6** except for the signal due to an oxygen-bearing methine (δ_H 3.65, *br t*, $W_{1/2}$ = 8 Hz, H-3; δ_C 75.1, *d*, C-3). Detailed analysis of the ^1H–^1H, ^{13}C–^1H and long-range ^{13}C–^1H COSY spectra of **1** led to the assumption that this compound may be the 3-epimer of **6**, which was supported by the NOE experiments. Clear NOEs were observed between the signal at δ_H 3.65 (H-3) and the signals at δ_H 1.20 (H-28) and at δ_H 0.98 (H-29), while the cross-peak between H-3 and H-5 observed in the case of **6**, was not observed in **1**.

It is of interest to note that the ^{13}C signal due to Me-29 in **1** was shifted downfield by 6.5 ppm compared with that in **6**. This finding is also consistent with the structure having the 3α-axial hydroxyl group [6].

Compound **2** was isolated as a methyl ester (**2a**), an amorphous powder, $[\alpha]_D^{26}$ + 22° (chloroform), after methylation with diazomethane. It showed a molecular ion peak at *m/z* 514 in the EI-mass spectrum and its molecular formula was determined by HR-mass spectrometry to be $C_{32}H_{50}O_5$. The UV spectrum showed an absorption maximum at 242 nm ascribable to a $\Delta^{7,9(11)}$ diene moiety. The ^1H NMR spectrum of **2a** was similar to that of **1**, but it showed two tertiary methyl signals at δ_H 1.554 and 1.547, instead of the signals due to the isopropyl group in **1**. Also, comparison of the ^{13}C NMR spectrum of **2a** with that of **1** indicated the presence of an isopropyl alcohol grouping (δ_C 30.01, 30.02, both *s*, C-26, 27; δ_C 72.4, *s*, C-25) instead of the isopropyl group in **1**. Thus the structure of **2** was determined to be 25-hydroxy-3-epidehydrotumulosic acid.

Compound **3**, an amorphous powder, $[\alpha]_D^{26}$ + 7° (pyridine) failed to show a molecular ion peak in the EI-mass spectrum, but the fragment ion peaks at *m/z* 441 $[M - CH_2CO_2Me]^+$ and 423 $[M - CH_2CO_2Me - H_2O]^+$, characteristic of 3,4-secolanostane triterpenes were observed. However, the dimethyl ester of **3** (**3a**), derived by

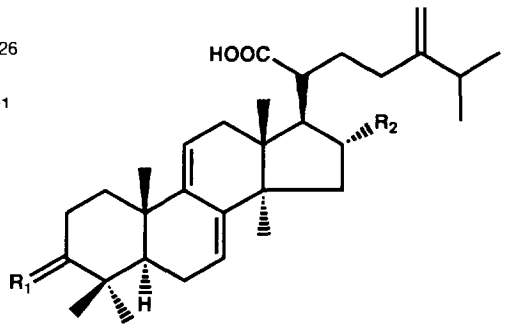
*Part 4 in the series 'Studies on the constituents of *Poria cocos*'. For part 3 see ref. [2].



1 R_1 = H, R_2 = H

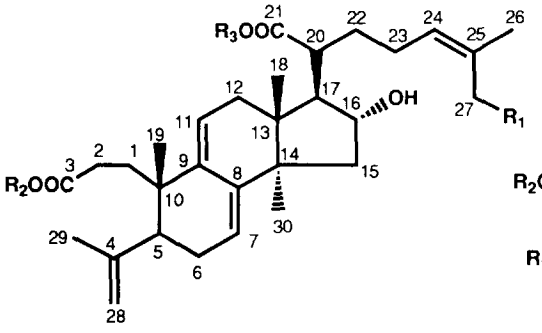
2 R_1 = OH, R_2 = H

2a R_1 = OH, R_2 = CH_3



6 R_1 =  , R_2 = OH

7 R_1 = O, R_2 = H

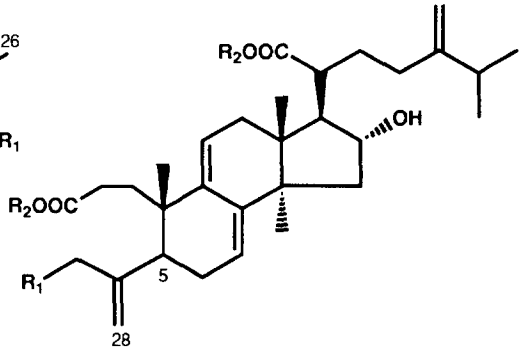


3 R_1 = OH, R_2 = H, R_3 = H

3a R_1 = OH, R_2 = CH_3, R_3 = CH_3

4 R_1 = H, R_2 = CH_3, R_3 = H

8 R_1 = H, R_2 = H, R_3 = H



5 R_1 = OH, R_2 = H

5a R_1 = OH, R_2 = CH_3

9 R_1 = H, R_2 = H

treatment with diazomethane, revealed a molecular ion peak at *m/z* 528 and its molecular formula was determined by HR-mass spectrometry to be $C_{32}H_{48}O_6$. From these results, the molecular formula of **3** was deduced to be $C_{30}H_{44}O_6$. The UV spectrum of **3** showed an absorption at 242 nm, indicative of $\Delta^{7,9(11)}$-diene moiety in the molecule. The ^1H and ^{13}C NMR spectra of **3** resembled those of poricoic acid B (**8**) [7] and suggested that one of the methyl groups C-26 and C-27 was replaced by a hydroxymethyl group. Next, a series of difference NOE experiments were carried out on **3** for the purpose of elucidating the location of the hydroxymethyl group. Irradiation of the methyl proton at δ_H 1.97 (H-26) enhanced the intensity of the signal at δ_H 5.47 (H-24, 5%) and thus the methyl group and H-24 were *cis* and the hydroxyl group must be located at C-27. Therefore, the structure of **3** was concluded to be 16α,27-dihydroxy-3,4-secolanosta-4(28),7,9(11),24-tetraen-3,21-dioic acid, named poricoic acid E.

Compound **4** was obtained as an amorphous powder, $[\alpha]_D^{26}$ + 12° (chloroform). The mass spectrum of **4** showed the molecular ion peak at *m/z* 498 and the fragment ion peaks characteristic to the 3,4-seco form (*m/z* 411 and 393) and the IR spectra showed broad absorptions due to an ester carbonyl (1734 cm^{-1}) and a carboxylic acid group (1706 cm^{-1}). The ^1H and ^{13}C NMR spectra of **4** were similar to those of **8**, except for the presence of a methoxy signal (δ_H 3.64, *s*; δ_C 51.3, *q*)

Table 1. ^{1}H NMR spectral data for compounds **1–9** (pyridine-d_5, 500 MHz)

H	**1**	**2a**	**6**	**7**	**3**	**4**	**5a**	**8**	**9**
1	2.28 *m*	2.34 *td* (13, 4)	1.5	1.6	1.91 *ddd* (9, 8, 4)	1.98 *ddd* (14, 11, 6)	2.0	1.90 *ddd* (14, 11, 6)	1.89 *ddd* (14, 11, 6)
	1.74 *dt* (13, 3)	1.82 *td* (13, 3)	2.0	2.1	2.14 *ddd* (9, 8, 3)	2.2	1.8	2.14 *ddd* (14, 11, 5)	2.14 *ddd* (14, 11, 5)
2	1.88 *ddd* (14, 7, 3)	1.9	1.9–2.0	2.3	2.5	2.5	2.4	2.5	2.5
	2.1	2.1		2.75 *td* (15, 6)	2.5	2.5	2.4	2.5	2.5
3	3.65 *br t* ($W_{1/2}$ = 8)	3.66 *br t* ($W_{1/2}$ = 8)	3.46 *dd* (7.8, 7.6)						
5	2.03 *br t* (8)	2.03 *br t* (8)	1.30 *dd* (11, 5)	1.59 *dd* (8, 4)	2.35 *br d* (4)	2.36 *d* (6)	2.43 *d* (6)	2.34 *d* (6)	2.34 *d* (6)
6	2.1	2.1	2.1–2.2	2.0	2.07 *dd* (13, 3)	2.05 *d* (19, 4)	2.2	2.07 *dd* (19, 4)	2.07 *dd* (19, 4)
	2.1	2.1		2.2	2.6	2.5	2.6	2.57 *dd* (19, 6)	2.57 *dd* (19, 6)
7	5.64 *br t* ($W_{1/2}$ = 11)	5.61 *br t* ($W_{1/2}$ = 11)	5.64 *br d* (4)	5.58 *br t* (6)	5.28 *br t* ($W_{1/2}$ = 8)	5.26 *br t* ($W_{1/2}$ = 8)	5.26 *br t* ($W_{1/2}$ = 8)	5.29 *br t* ($W_{1/2}$ = 8)	5.29 *br t* ($W_{1/2}$ = 8)
11	5.47 *br d* (6)	5.49 *br d* (6)	5.40 *br d* (6)	5.34 *br d* (6)	5.34 *br d* (3)	5.3	5.30 *br d* (5)	5.33 *br s*	5.34 *br s*
12	2.69 *br d* (19)	2.69 *br d* (19)	2.73 *br d* (18)	2.51 *br d* (18)	2.67 *br d* (12)	2.67 *d* (18)	2.4	2.69 *d* (18)	2.68 *d* (18)
	2.4	2.4	2.45 *dd* (18, 6)	2.37 *dd* (18, 6)	2.47 *dd* (12, 3)	2.5	1.95 *dd* (18, 5)	2.49 *br d* (18)	2.49 *br d* (18)
15	1.2 *d* (13)	1.89 *d* (13)	1.96 *d* (13)	1.5	1.80 *d* (9)	1.81 *d* (13)	1.78 *d* (13)	1.81 *d* (13)	1.81 *d* (13)
	2.4	2.4	2.45 *dd* (13, 8)	1.78 *td* (12, 7)	2.40 *dd* (9, 6)	2.42 *dd* (13, 9)	2.4	2.42 *dd* (13, 9)	2.42 *dd* (13, 9)
16	4.54 *dd* (8, 6)	4.54 *dd* (8, 6)	4.55 *dd* (8, 6)	1.5	4.49 *dd* (5, 4)	4.52 *dd* (8, 6)	4.43 *br t* (6)	4.51 *dd* (8, 6)	4.51 *dd* (8, 6)
				2.1					
17	2.88 *dd* (11, 6)	2.72 *dd* (11, 6)	2.90 *dd* (11, 6)	2.5	2.83 *dd* (7, 4)	2.84 *dd* (11, 6)	2.69 *dd* (11, 6)	2.84 *dd* (11, 6)	2.85 *dd* (11, 6)
18	1.10 *s*	0.92 *s*	1.09 *s*	0.99 *s*	1.06 *s*	1.08 *s*	0.97 *s*	1.09 *s*	1.09 *s*
19	1.11 *s*	1.12 *s*	1.09 *s*	1.13 *s*	1.04 *s*	0.96 *s*	1.09 *s*	1.03 *s*	1.03 *s*
20	2.96 *dt* (11, 3)	2.91 *dt* (11, 3)	2.97 *dt* (11, 3)	2.65 *td* (11, 3)	2.92 *td* (7, 2)	2.94 *td* (11, 3)	2.82 *td* (11, 3)	2.94 *td* (11, 3)	2.94 *td* (11, 3)
22	2.5	2.5–2.6	2.4–2.5	1.9	2.4–2.6	2.3–2.4	2.5	2.4–2.5	2.4
	2.7		2.68 *m*	2.1			2.5		2.6
23	2.4	2.5–2.6	2.4	2.3–2.5	2.6	2.3–2.4	2.2	2.3–2.4	2.3
	2.55 *t* (11)		2.55 *br t* (12)		2.6		2.2		2.5
24					5.47 *br t* (4)	5.34 *br s*		5.34 *br s*	
25	2.29 *m*		2.29 *m*	2.29 *m*			2.22 *m*		2.27 *m*
26	1.00 *d* (7)[a]	1.547 *s*[a]	1.00 *d* (7)[a]	1.03 *d* (7)[a]	1.97 *s*	1.61 *s*	0.99 *d* (7)[a]	1.61 *s*	0.99 *d* (7)[a]
27	1.01 *d* (7)[a]	1.554 *s*[a]	1.01 *d* (7)[a]	1.04 *d* (7)[a]	4.53 *d* (8)	159 *s*	0.98 *d* (7)[a]	1.59 *s*	0.98 *d* (7)[a]
					4.38 *d* (8)				
28	1.20 *s*	1.21 *s*	1.22 *s*	1.14 *s*	4.77 *s*	4.76 *s*	5.20 *d* (1)	4.77 *s*	4.77 *s*
					4.83 *d* (2)	4.82 *d* (2)	5.62 *d* (1)	4.83 *d* (2)	4.83 *d* (2)
29	0.98 *s*	0.99 *s*	1.14 *s*	1.07 *s*	1.74 *s*	1.71 *s*	4.39 *s*	1.73 *s*	1.74 *s*
30	1.44 *s*	1.37 *s*	1.52 *s*	1.03 *s*	1.48 *s*	1.42 *s*	1.38 *s*	1.49 *s*	1.49 *s*
31	4.85 *s*	5.09 *d* (1)	4.85 *s*	4.90 *s*			4.84 *s*		4.84 *s*
	4.99 *d* (1)	5.44 *d* (1)	4.99 *d* (1)	4.94 *d* (1)			4.91 *d* (1)		4.97 *d* (1)
OMe-3						3.64 *s*	3.64 *s*		
OMe-21		3.75 *s*					3.84 *s*		

[a]Chemical shifts in each column may be interchanged.

and for the low-field shift of the C-3 signal (2.2 ppm). In conclusion, **4** was determined to be a methyl ester of **8** at the C-3 position.

Compound **5** was also isolated as a methyl ester (**5a**), an amorphous powder, $[\alpha]_D^{26}$ + 10° (chloroform), after treatment with diazomethane. The EI-mass spectrum of **5a** showed the molecular ion peak at *m/z* 542 ($C_{33}H_{50}O_6$) and the fragment ion peaks at *m/z* 455 $[M - CH_2CO_2Me]^+$ and *m/z* 437 $[M - CH_2CO_2Me - H_2O]^+$ which are characteristic of the 3,4-seco form. The ^1H NMR spectrum of **5a** revealed the signals due to three tertiary methyls, two secondary methyls, an oxygen-bearing methine and two sp^2 methines. DEPT NMR analysis showed the presence of an sp^2 methylene and an oxygen-bearing methylene (Tables 1 and 2). Careful analyses of the ^1H–^1H and ^1H–^{13}C COSY spectra of **5a** revealed that **5a** has a similar structure to that of poricoic acid A (**9**). However, the signals due to a vinyl methyl observed in the ^1H and ^{13}C NMR spectra of **9** had disappeared and instead of them, signals of a hydroxymethyl grouping were observed. From these data and the results of the NOESY spectra, the structure of **5** was determined to be 29-hydroxyporicoic acid A and to this triterpene we gave the name poricoic acid F.

EXPERIMENTAL

General. Mps: uncorr.; UV: EtOH; IR: KBr; MS and HRMS: 70 eV: ^1H and ^{13}C NMR: pyridine-d_5 or $CDCl_3$ at 500 and 125 MHz, with TMS as int. standard. Analytical TLC and prep. TLC: Kieselgel 60 F_{254} plate (0.2, 0.5, 1.0, 2.0 mm) detected with 10% H_2SO_4; prep. HPLC: Develosil ODS 7 (20 × 250 mm) column employing a UV monitoring flow system (210 nm) at a flow rate of 10.0 ml min^{-1}.

Fungal material. Fresh sclerotia of *P. cocos*, collected at Ishikawa Prefecture, Japan, in April 1990 were peeled off and the surface layers were air-dried.

Extraction and fractionation. The surface layers of sclerotia of *P. cocos* (1 kg, dried) were extracted 2 × with MeOH (each 5 l) under reflux. The combined MeOH soln was evapd under red. pres. at 40° to afford a brown residue (75 g), which was suspended in H_2O (1 l) and extracted with Et_2O (1 l × 3). The Et_2O soln was concd,

Table 2. ^{13}C NMR spectral data for compounds **1**–**9** (pyridine d_5, 125 MHz)

C	1	2a	6	7	3	4	5a	8	9
1	30.6 *t*	30.7 *t*	36.3 *t*	36.8 *t*	36.4 *t*	35.9 *t*	35.9 *t*	36.4 *t*	36.4 *t*
2	26.7 *t*	26.7 *t*	28.7 *t*	34.9 *t*	30.3 *t*	29.5 *t*	29.6 *t*	30.2 *t*	30.2 *t*
3	75.1 *d*	75.1 *d*	78.0 *d*	215.0 *s*	176.6 *s*	174.4 *s*	174.5 *s*	176.6 *s*	176.4 *s*
4	38.0[a] *s*	37.9[a] *s*	39.3 *s*	47.4 *s*	149.2 *s*	149.0 *s*	153.8 *s*	149.2 *s*	149.1 *s*
5	43.7 *d*	43.7 *d*	49.8 *d*	51.0 *d*	50.7 *d*	50.7 *d*	46.4 *d*	50.7 *d*	50.7 *d*
6	23.4 *t*	23.4 *t*	23.5 *t*	23.9 *t*	28.6 *t*	28.5 *t*	29.3 *t*	28.6 *t*	28.6 *t*
7	121.2 *d*	121.4 *d*	121.2 *d*	120.7 *d*	117.9 *d*	117.9 *d*	118.3 *d*	117.9 *d*	117.9 *d*
8	142.8 *s*	142.5 *s*	142.7 *s*	142.9 *s*	141.9 *s*	141.8 *s*	141.7 *s*	141.7 *s*	141.6 *s*
9	146.6 *s*	146.7 *s*	146.4 *s*	144.9 *s*	137.5 *s*	137.2 *s*	137.2 *s*	137.5 *s*	137.5 *s*
10	37.9[a] *s*	37.90[a] *s*	37.9 *s*	37.5 *s*	38.9 *s*	38.8 *s*	39.4 *s*	38.9 *s*	38.8 *s*
11	116.1 *d*	115.8 *d*	116.5 *d*	117.7 *d*	120.3 *d*	120.4 *d*	120.5 *d*	120.2 *d*	120.2 *d*
12	36.3 *t*	36.1 *t*	36.3 *t*	36.0 *t*	37.0 *t*	37.0 *t*	36.8 *t*	37.0 *t*	37.0 *t*
13	45.2 *s*	44.9 *s*	45.1 *s*	44.2 *s*	45.7 *s*	45.6 *s*	45.3 *s*	45.6 *s*	45.6 *s*
14	49.5 *s*	49.3 *s*	49.4 *s*	50.4 *s*	49.3 *s*	49.2 *s*	49.1 *s*	49.2 *s*	49.3 *s*
15	44.4 *t*	44.4 *t*	44.4 *t*	31.5 *t*	43.7 *t*	43.7 *t*	43.7 *t*	43.7 *t*	43.8 *t*
16	76.5 *d*	76.1 *d*	76.4 *d*	27.2 *t*	76.3 *d*	76.4 *d*	76.1 *d*	76.4 *d*	76.4 *d*
17	57.6 *d*	57.5 *d*	57.6 *d*	48.1 *d*	57.6 *d*	57.7 *d*	57.5 *d*	57.6 *d*	57.5 *d*
18	17.7 *q*	17.6 *q*	17.6 *q*	16.2 *q*	18.4 *q*	18.3 *q*	18.4 *q*	18.3 *q*	18.3 *q*
19	23.0 *q*	23.0 *q*	23.0 *q*	22.0[a] *q*	22.3[a] *q*	22.2[a] *q*	22.1 *q*	22.3 *q*	22.2 *q*
20	48.5 *d*	47.9 *d*	48.5 *d*	49.0 *d*	48.3 *d*	48.3 *d*	47.6 *d*	48.3 *d*	48.3 *d*
21	178.6 *s*	176.5 *s*	178.6 *s*	178.3 *s*	179.0 *s*	178.5 *s*	176.4 *s*	178.6 *s*	178.4 *s*
22	31.5 *t*	32.2 *t*	31.5 *t*	31.7 *t*	33.1 *t*	33.0 *t*	31.1 *t*	33.0 *t*	31.3 *t*
23	33.2 *t*	29.8 *t*	33.2 *t*	32.7 *t*	26.6 *t*	27.1 *t*	32.9 *t*	27.1 *t*	33.2 *t*
24	156.0 *s*	157.5 *s*	156.0 *s*	155.8 *s*	126.8 *d*	125.1 *d*	155.5 *s*	125.1 *s*	156.0 *s*
25	34.1 *d*	72.4 *s*	34.1 *d*	34.2 *d*	136.9 *s*	131.5 *s*	33.9 *d*	131.4 *s*	34.1 *d*
26	22.0[b] *q*	30.01[b] *q*	22.0[a] *q*	22.0[a] *q*	21.9 *q*	25.8 *q*	22.0[a] *q*	25.7 *q*	22.0[a] *q*
27	21.9[b] *q*	30.02[b] *q*	21.9[a] *q*	21.9[a] *q*	60.8 *t*	17.7 *q*	21.8[a] *q*	17.7 *q*	21.9[a] *q*
28	29.2 *q*	29.1 *q*	28.8 *q*	25.6 *q*	112.1 *t*	112.2 *t*	109.1 *t*	112.1 *t*	112.1 *t*
29	23.1 *q*	23.1 *q*	16.6 *q*	22.3 *q*	22.26[a] *q*	22.1[a] *q*	65.3 *t*	22.3 *q*	22.2 *q*
30	26.6 *q*	26.5 *q*	26.6 *q*	25.6 *q*	24.9 *q*	24.8 *q*	24.8 *q*	24.9 *q*	24.8 *q*
31	107.0 *t*	107.1 *t*	107.0 *t*	107.0 *t*			107.2 *t*		107.0 *t*
OMe-3						51.3 *q*	51.4 *q*		
OMe-21		51.1 *q*					51.2 *q*		

[a,b]Chemical shifts in each column may be interchanged.

and the residue (45 g) chromatographed on a silica gel (3 kg) column and eluted with $CHCl_3$ (5 l) and MeOH–$CHCl_3$ gradient mixtures (1:99, 4 l; 1:49, 10 l; 1:19, 4 l; 7:93, 6 l; 1:9, 8 l; 1:4, 8 l) and to give 8 fractions.

Fr. 2 (9.5 g) was rechromatographed on a silica gel (2 kg) column with MeOH–$CHCl_3$ (1:499) and separated into 3 frs (fr. 2-1, 300 mg; fr. 2-2, 2.0 g; fr. 2-3, 2.5 g). Fr. 2-1 was purified repeatedly by prep. TLC using MeOH–$CHCl_3$ (1:199) to yield dehydroeburiconic acid (**7**, 80 mg) which was identified based on the spectroscopic data [4].

Fr. 4 (3.1 g) was rechromatographed on a silica gel (1 kg) column with MeOH–$CHCl_3$ (3:97) to afford 4 frs (fr. 4-1, 1.0 g; fr. 4-2, 1.5 g; fr. 4-3, 250 mg; fr. 4-4, 210 mg). Fr. 4-2 was further purified by reversed phase prep. HPLC with MeCN–H_2O (3:2) to yield dehydrotumulosic acid (**6**, 300 mg), while fr. 4-3 was purified repeatedly by prep. TLC with MeOH–$CHCl_3$ (1:19) to yield **1** (160 mg).

Fr. 5 (3.8 g) was rechromotographed on a silica gel (500 g) column with MeOH–$CHCl_3$ (3:97) and the eluate was further purified by a combination of prep. TLC (1:19) and reversed phase prep. HPLC with MeCN–H_2O (1:1), yielding **4** (30 mg).

Fr. 8 (1.9 g) was further purified by reversed phase prep. HPLC with MeCN–H_2O (2:3) to give 5 frs (fr. 8-1, 50 mg; fr. 8-2, 30 mg; fr. 8-3, 460 mg; fr. 8-4, 100 mg; 8-5, 550 mg). Fr. 8-1 was treated with CH_2N_2 and the product purified on prep. TLC to afford **5a** (20 mg). Fr. 8-2 was purified by reversed phase HPLC repeatedly to afford **3** (30 mg). Fr. 8-4 was also treated with CH_2N_2 and the product was chromatographed with silica gel to afford **2a** (20 mg).

Compound **1** (*3-epidehydrotumulosic acid*). Amorphous powder, $[\alpha]_D^{26}$ + 6° (pyridine; *c* 0.6). IR ν_{max}^{KBr} cm^{-1}: 1707, 1642. UV λ_{max}^{EtOH} nm (log ε); 243 (4.08). EIMS *m/z* (rel. int.): 484 $[M]^+$ (64), 466 (83), 448 (60), 433 (93), 295 (100). HRMS *m/z* 484.3662 $[M]^+$, $C_{31}H_{48}O_4$ requires 484.3553.

Compound **2a** (*methyl 25-hydroxy-3-epidehydrotumulosate*). Amorphous powder, $[\alpha]_D^{26}$ + 22° ($CHCl_3$; *c* 1.0). IR ν_{max}^{KBr} cm^{-1}: 1719, 1639. UV λ_{max}^{EtOH} nm (log ε): 242.0 (4.02). EIMS *m/z* (rel. int.): 514 $[M]^+$ (2), 496 (100), 478 (68), 382 (93). HRMS *m/z* 496.3592 $[M-H_2O]^+$, $C_{32}H_{48}O_4$ requires; 496.3553.

Compound **3** (*poricoic acid E*). Amorphous powder $[\alpha]_D^{26}$ + 7° (Pyridine; *c* 1.0). IR ν_{max}^{KBr} cm^{-1}: 1708, 1639. UV λ_{max}^{EtOH} nm (log ε): 242.0 (4.06). EIMS *m/z* (rel. int.): 482 $[M-H_2O]^+$ (17), 435 (20), 407 (36), 391 (21), 354 (17), 309 (24), 235 (20), 55 (100). Compound **3** (1 mg) was treated with CH_2N_2 to yield a dimethyl ester (**3a**). EIMS *m/z* (rel. int.): 528 $[M]^+$ (5), 510 (16), 441 (47), 423 (100). HRMS *m/z* 528.3375 $[M]^+$, $C_{32}H_{48}O_6$ requires; 528.3451.

Compound **4** (*poricoic acid BM*). Amorphous powder. $[\alpha]_D^{26}$ + 12° ($CHCl_3$; *c* 0.1). IR ν_{max}^{KBr} cm^{-1}: 1734, 1706. UV λ_{max}^{EtOH} nm (log ε): 242.0 (4.07). EIMS *m/z* (rel. int.): 498 $[M]^+$ (7), 411 (100), 393 (75). HRMS *m/z* 498.3389 $[M]^+$, $C_{31}H_{46}O_5$ requires; 498.3345.

Compound **5a** (*dimethyl poricoate F*). Amorphous powder. $[\alpha]_D^{26}$ + 10° ($CHCl_3$; *c* 0.1). IR ν_{max}^{KBr} cm^{-1}: 1734, 1718. UV λ_{max}^{EtOH} cm^{-1} nm (log ε): 241.0 (4.05). EIMS *m/z* (rel. int.): 542 $[M]^+$ (33), 524 (40), 506 (24), 455 (25) 437 (100). HRMS *m/z* 542.3701 $[M]^+$, $C_{33}H_{50}O_6$ requires; 542.3608.

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