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BITTER TRITERPENOIDS FROM THE FUNGUS *GANODERMA APPLANATUM*

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Key Word Index—*Ganoderma applanatum*; Polyporaceae; triterpenoids; ganoderenic acid; furanoganoderic acid; ganoderic acid.

Abstract—Six novel triterpenoids, ganoderenic acid, furanoganoderic acid and ganoderic acid derivatives, some of which are bitter principles, were isolated from the fruiting body of the fungus *Ganoderma applanatum*. Their structures were determined mainly by spectroscopic and chemical methods.

INTRODUCTION

Recently, a great number of triterpenoids have been isolated from *Ganoderma lucidum*, some of them exhibiting a bitter taste or useful biological activities [1–28]. In our continuing study of fungal bitter constituents, we investigated *G. applanatum*, which has been used as a home remedy in China and Japan and from which only two triterpenoids, alnusenone and friedelin, had been isolated [29]. In the present paper, we describe the structural elucidation of novel triterpenoid components of *G. applanatum*, ganoderenic acids F, G, H and I, furanoganoderic acid and ganoderic acid AP, along with the identification of ganoderenic acid A [16] and Compound B8 [19]. We also report on their bitterness.

RESULTS AND DISCUSSION

The chloroform layer of the ethanol extract of *G. applanatum* was chromatographed on a silica gel column to separate it into several fractions. Some of them were subjected to silica gel column chromatography and reverse-phase LC, after methylation if needed, to give eight triterpenoids (**1**–**8**).

Compound **1**, ganoderenic acid G, (*m/z* 512, $C_{30}H_{40}O_7$ by HRMS) showed in its ^{1}H NMR spectrum (Table 1) the signals due to a secondary hydroxyl group [δ 4.41 (1H, *dd*, J = 9.8, 5.9)], an olefinic proton [δ 5.86 (1H, *s*)] and seven methyl groups [δ 0.45 (*s*), 0.76 (*s*), 0.84 (*s*), 0.96 (*s*), 1.13 (*d*, J = 7.3), 1.14 (*s*) and 2.01 (*s*)]. Its ^{13}C NMR spectrum (Table 2) showed the presence of an unconjugated carbonyl group (δ 213.0), three conjugated carbonyl groups (δ 204.5, 199.8 and 197.4), a carboxyl group (δ 181.2), three tertiary olefinic carbons (δ 152.6, 150.3 and 155.6), an olefinic methine carbon (δ 124.5) and a methine carbon (δ 72.9) bearing a hydroxyl group, in addition to seven methyl carbons, six methylene carbons, three methine carbons and four tertiary carbons. The presence of the α,β-unsaturated carbonyl groups was indicated by the absorption maxima at 246 nm (ε = 8900) and 277 nm (sh, ε = 4040) in the UV spectrum. ^{1}H NMR spin decoupling and the ^{1}H–^{13}C shift correlated spectrum of **1** revealed the partial structures (I–VI) and the correlations between the carbons and the attached protons (Fig. 1).

The partial structures were connected by measuring the HMBC spectrum [30]. For instance, the methyl protons observed at δ 1.13 in the partial structure V showed a cross-peak between the carboxyl carbon at δ 181.2, as well as between the carbons at δ 35.2 and 47.6, which indicated that the carboxylic acid was adjacent to the carbon at δ 35.2. The methyl protons at δ 2.01 in the partial structure VI showed a cross-peak with the methine carbon at δ 52.0 in IV, so that partial structures IV and VI were connected by the bond between the carbons at δ 52.0 and 155.6. On the other hand, the olefinic proton at δ 5.86 in VI showed a cross-peak with the conjugated carbonyl carbon at δ 197.4, with which the methylene protons at δ 2.78 and 2.2 in V also gave cross-peaks. This observation indicated that the partial structures V and VI were connected by locating the carbonyl carbon (δ 197.4) between them. In a similar manner, all of the partial structures were connected with one another and structure **1** was proposed for ganoderenic acid G. The configur-

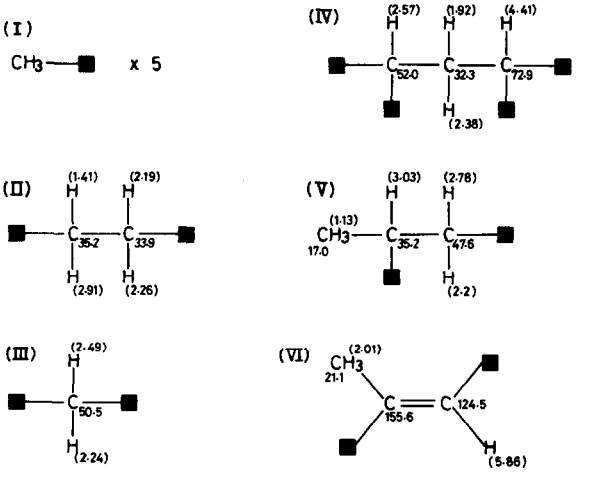


Fig. 1. Partial structures of ganoderenic acid G (**1**).

ation of the hydroxyl group at C-15 was determined to be α by measuring the NOE between H-15β (δ 4.41) and Me-18 (δ 0.74). The signal of Me-21 was observed at δ 2.12 in $CDCl_3$, which indicated the *E* configuration of the double bond between C-20 and C-22 by analogy with those of ganoderenic acids A–D [16]. On the basis of these observations, the structure of ganoderenic acid G was concluded to be 15α-hydroxy-3,7,11,23-tetraoxo-5α-lanosta-8,20*E*-dien-26-oic acid (**1**). This structure was confirmed by converting **1** to **1a** on treatment with ozone followed by pyridinium dichromate (PDC). **1a** was also prepared from the known lucidone B [5, 12] by PDC oxidation.

Compound **2**, ganoderenic acid F, was formulated to be $C_{30}H_{38}O_7$. Its ^1H NMR (Table 1) was similar to that of **1**, but **2** did not show any signal due to H-15β which was observed at δ 4.41 in **1**. The ^{13}C NMR spectrum (Table 2) of **2** also resembled that of **1**, and indicated the presence of an additional carbonyl group (δ 204.9) at C-15 instead of the α-hydroxyl group. Thus, the structure of

Table 1. ^1H NMR spectral data of compounds **1**–**4**, **6** and **7**. (500 MHz, C_6D_6, TMS as int. standard)

H	1	2	3	4	6	7
1α	2.41 *ddd* (14.5, 9.3, 6.8)*	1.41 *ddd* (14.2, 9.5, 6.6)		1.4	1.38 *ddd* (14.2, 7.3, 7.3)	0.95
1β	2.91 *ddd* (14.5, 8.0, 6.1)	2.88 *ddd* (14.2, 8.3, 6.6)	2.88	2.99 *ddd* (13.2, 3.4, 3.4)	2.90 *ddd* (14.2, 8.1, 6.1)	2.55 *ddd* (13, 7.3, 4.9)
2α	2.19 *ddd* (14.5, 9.3, 6.1)				2.2	2.11 *ddd* (15.7, 7.8, 5.4)
2β	2.26 *ddd* (14.5, 8.0, 6.8)	2.23 *ddd* (15.1, 8.6, 6.5)			2.2	2.23 *ddd* (15.7, 9.3, 7.3)
3α	—	—	2.88	2.85	—	—
5α	1.80 *dd* (15.2, 2.7)	1.96 *dd* (14.4, 3.2)	1.43 *dd* (14.7, 2.9)	1.28 *dd* (15.1, 2.3)	1.79 *dd* (15.1, 2.9)	1.62 *dd* (15.1, 2.9)
6α	2.10 *dd* (14.8, 2.4)		2.44 *dd* (15.6, 2.9)	2.36 *dd* (16.3, 2.3)	2.09 *dd* (15.1, 2.9)	2.06 *dd* (16.6, 2.9)
6β	1.95 *dd* (15.2, 14.8)		2.25 *dd* (15.6, 14.7)	2.11 *dd* (16.3, 15.1)	1.93 *dd* (15.1, 15.1)	1.92 *dd* (16.6, 15.1)
12α	2.49 *d* (17)	2.36	2.39 *d q* (15.6, 1.0)	2.48 *d* (16.1)	2.49 *d q* (17.0, 1.0)	4.14 *s*
12β	2.24 *d* (17)	2.36	2.30 *d* (15.6)	2.24 *d* (16.1)	2.26 *d* (17.0)	—
15β	4.41 *dd* (9.8, 5.9)	—	—	4.48 *ddd* (7.8, 5.9, 2.0)	4.51 *dd* (9.5, 5.6)	4.31 *ddd* (8.3, 6.8, 2.0)
16	1.92 *ddd* (15, 10.3, 5.9)		2.04 *dd* (18.3, 8.8)	1.88 *ddd* (14.6, 10.3, 5.9)		
16	2.38 *ddd* (15, 9.8, 9.3)		2.20 *dd* (18.3, 9.5)	2.32 *ddd* (14.6, 9.5, 7.8)		
17	2.57 *dd* (10.3, 9.3)	2.49 *dd* (8.8, 8.8)	2.42 *dd* (9.5, 8.8)	2.51 *dd* (10.3, 5.2)	2.96 *dd* (9.3, 9.3)	2.55 *dd* (10.5, 10.5)
Me-18	0.45 *s*	0.49 *s*	0.54 *s*	0.46 *s*	0.55 *s*	0.55 *s*
Me-19	0.96 *s*	0.99 *s*	1.02 *s*	1.09 *s*	0.97 *s*	1.04 *s*
Me-21	2.01 *s*	1.92 *s*	1.91 *s*	1.99 *s*	—	1.28 *s*
21	—	—	—	—	6.90 *s*	—
22	5.86 *s*	5.64 *s*	5.61 *s*	5.86 *s*	5.77 *s*	2.42 *d* (13.4)
22	—	—	—	—	—	2.64 *d* (13.4)
24	2.2		2.12 *dd* (17.6, 4.9)	2.19 *dd* (17.4, 5.9)	2.63 *dd* (14.5, 7.1)	2.69 *dd* (18.1, 4.9)
24	2.78 *dd* (17.3, 8.1)	2.69 *dd* (17.6, 8.3)	2.78 *dd* (17.6, 8.3)	2.82 *dd* (17.4, 8.1)	2.77 *dd* (14.5, 6.8)	2.94 *dd* (18.1, 8.8)
25	3.03 *m*	3.01 *m*	3.03 *m*	3.05 *dd q* (8.1, 5.9, 7.3)		3.08 *m*
Me-27	1.13 *d* (7.3)	1.10 *d* (7.3)	1.10 *d* (7.3)	1.11 *d* (7.3)	1.07 *d* (7.3)	1.10 *d* (7.3)
Me-28	0.84 *s*	0.83 *s*	0.79 *s*	0.79 *s*	0.82 *s*	0.76 *s*
Me-29	0.76 *s*	0.78 *s*	0.63 *s*	0.65 *s*	0.74 *s*	0.74 *s*
Me-30	1.14 *s*	1.35 *s*	1.20 *s*	1.05 *s*	1.17 *s*	1.04 *s*
COOMe	—	—	3.40 *s*	3.37 *s*	—	3.38 *s*
OH-15α	—	—	—	4.77 *d* (2.0)	—	4.67 *d* (2.0)

*Values in parentheses are coupling constants in Hz.

ganoderenic acid F was defined as 3,7,11,15,23-pentaoxo-5α-lanosta-8,20*E*-dien-26-oic acid (**2**).

Compound **3**, methy ganoderenate H, $C_{31}H_{42}O_7$, showed similar ^{1}H NMR data (Table 1) to that of **2** in spite of the presence of the ester methyl signal (δ3.40). However, the measurement of its ^{1}H NMR spectrum in $CDCl_3$ gave the signal of a methine proton bearing a hydroxyl group at δ3.29 (*dd*, J = 10.5, 5.0), which revealed the presence of a β-hydroxyl group at C-3. Therefore, methyl ganoderenate H was defined as methyl 3β-hydroxy-7,11,15,23-tetraoxo-5α-lanosta-8,20*E*-dien-26-oate (**3**).

The molecular formula of methyl ganoderenate I (**4**) was determined to be $C_{31}H_{44}O_7$ by HRMS. Its ^{1}H NMR (Table 1) and ^{13}C NMR (Table 2) data were closely similar to those of **1**. However, its ^{1}H NMR spectrum in $CDCl_3$ revealed the presence of a β-hydroxyl group at C-3 [δ3.29 (*dd*, J = 10.5, 5.0)], which was supported by the ^{13}C NMR signal at δ 77.0. From these data, the structure of methyl ganoderenate I was shown to be 3β,15α-dihydroxy-7,11,23-trioxo-5α-lanosta-8,20*E*-dien-26-oate (**4**).

The ^{1}H NMR and ^{13}C NMR (Table 2) data of compound **5**, $C_{30}H_{42}O_7$, resembled those of **1**–**4**, but the signals at δ69.0 (^{13}C NMR) and δ4.70 (^{1}H NMR) indicated the presence of a β-hydroxyl group at C-7. Since these data entirely agreed with those of ganoderenic acid A, **5** was identified as ganoderenic acid A [16].

Compound **6**, furanoganoderic acid, gave a molecular ion peak at m/z 510 and was formulated to be $C_{30}H_{38}O_7$. Its ^{1}H NMR spectrum (Table 1) resembled that of **1**, but did not show any signal due to Me-21 around δ 2.1. Two olefinic protons were observed at δ 6.90 (1H, *s*) and 5.77 (1H, *s*), and it was revealed by measuring its ^{1}H COSY spectrum that both the signals were connected with each other in a long range coupling. Its ^{13}C NMR (Table 2) also resembled that of **1**. It showed the signals of two olefinic methine carbons (δ 107.7 and 138.4) and four olefinic tertiary carbons (δ 153.2, 153.6, 150.9 and 124.4), however, it lacked the signals due to the methyl carbon (δ 21.1; Me-21) and the conjugated carbonyl carbon (δ 197.3; C-23) which were observed in **1**. The ^{13}C NMR signals due to the skeleton were in complete agreement with each other. From these spectral data, the presence of a 2,4-substituted furan ring was indicated in the side chain of **6**. Taking into account the biogenesis of the triterpenoid, structure **6** was proposed for furanoganoderic acid (21,23-epoxy-15α-hydroxy-3,7,11-trioxo-5α-lanosta-8,20(21),22-trien-26-oic acid).

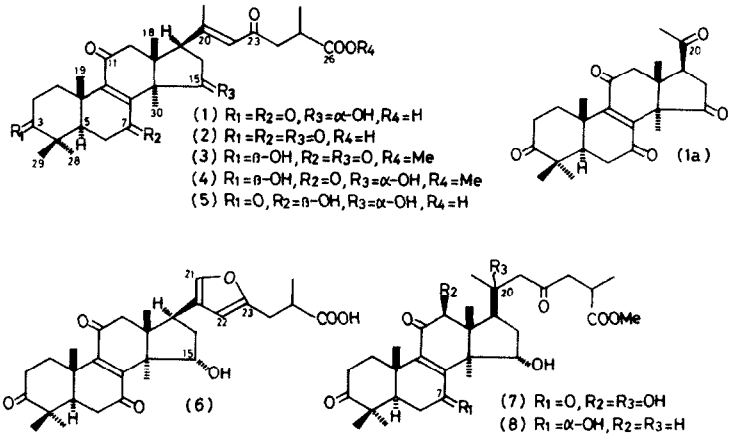
Compound **7**, methyl ganoderate AP, gave a molecular ion peak at m/z 560 in FDMS, and a dehydrated ion peak

Table 2. ^{13}C NMR spectral data of compounds **1**, **2** and **4**–**7** [67.8 MHz, C_6D_6 (**1**, **2**, **4**, **7**) or $CDCl_3$ (**5**, **6**), TMS as int. standard]

C	1	2	4	5	6	7
1	35.2 (2)*	34.9 (2)	34.5 (2)	35.5 (2)	35.2 (2)	34.5 (2)
2	33.9 (2)	34.7 (2)	27.9 (2)	34.2 (2)	34.0 (2)	33.9 (2)
3	213.0 (0)	213.3 (0)	77.0 (1)	217.1 (0)	214.9 (0)[a]	208.9 (0)
4	46.3 (0)	46.8 (0)	40.4 (0)	46.6 (0)	46.6 (0)	46.2 (0)
5	49.0 (1)	48.5 (1)	50.1 (1)	48.8 (1)	49.3 (1)	49.1 (1)
6	36.8 (2)	36.1 (2)	36.5 (2)	29.0 (2)	36.9 (2)	36.8 (2)
7	204.5 (0)	198.4 (0)[a]	205.0 (0)	69.0 (1)	204.5 (0)	203.5 (0)
8	150.3 (0)	146.9 (0)	149.6 (0)	158.8 (0)	150.9 (0)	151.1 (0)
9	152.6 (0)	149.5 (0)	154.6 (0)	140.4 (0)	153.2 (0)[b]	152.6 (0)
10	39.2 (0)	39.5 (0)	38.8 (0)	38.1 (0)	39.4 (0)	38.9 (0)
11	199.8 (0)	198.1 (0)[a]	200.1 (0)	198.9 (0)	200.9 (0)	200.9 (0)
12	50.5 (2)	47.8 (2)	51.0 (2)	50.5 (2)	49.6 (2)	78.5 (1)
13	48.6 (0)	44.8 (0)	49.2 (0)	48.1 (0)	48.2 (0)	54.4 (0)
14	52.4 (0)	56.8 (0)	52.5 (0)	53.4 (0)	51.8 (0)	55.0 (0)
15	72.9 (1)	204.9 (0)	72.9 (1)	72.7 (1)	72.9 (1)	72.1 (1)
16	32.3 (2)	37.1 (2)	32.5 (2)	31.9 (2)	31.7 (2)	33.3 (2)
17	52.0 (1)	50.8 (1)	52.1 (1)	52.2 (1)	39.2 (1)[c]	55.3 (1)
18	16.7 (3)	17.5 (3)	15.5 (3)	19.0 (3)	16.6 (3)	13.1 (3)
19	17.4 (3)	18.4 (3)	17.3 (3)	19.9 (3)	17.6 (3)	17.3 (3)
20	155.6 (0)	153.6 (0)	155.7 (0)	157.1 (0)	124.4 (0)	72.9 (0)
21	21.1 (3)	21.5 (3)	21.1 (3)	21.3 (3)	138.4 (1)	26.4 (3)
22	124.5 (1)	124.6 (1)	124.6 (1)	124.2 (1)	107.7 (1)	51.2 (2)
23	197.4 (0)	197.2 (0)	197.3 (0)	198.6 (0)	153.6 (0)[b]	208.9 (0)
24	47.6 (2)	47.6 (2)	47.9 (2)	47.5 (2)	34.3 (2)[a]	48.3 (2)
25	35.2 (1)	35.1 (1)	35.2 (1)	35.1 (1)	38.5 (1)[c]	35.0 (1)
26	181.2 (0)	181.2 (0)	175.9 (0)	180.2 (0)	180.0 (0)	176.3 (0)
27	17.0 (3)	17.0 (3)	17.3 (3)	17.1 (3)	18.9 (3)	17.2 (3)
28	27.0 (3)	27.2 (3)	27.7 (3)	27.4 (3)	27.3 (3)	27.9 (3)
29	20.3 (3)	20.3 (3)	18.7 (3)	20.7 (3)	20.4 (3)	19.6 (3)
30	20.7 (3)	20.9 (3)	20.7 (3)	19.4 (3)	20.5 (3)	20.7 (3)
COOMe	—	—	51.4 (3)	—		51.4 (3)

[a,b,c] Assignments may be reversed.

* Number of bonded H in parenthesis.



$[M^+ - H_2O, C_{31}H_{42}O_8]$ in EIMS. Its ^1H NMR spectrum (Table 1) was similar to that of **1**. However, the methyl signal due to Me-21 was shifted to up field to δ1.28 (δ 1.48 in $CDCl_3$), and the signals due to methylene protons at C-22 were observed at δ 2.42 and 2.64 as AB doublets ($J = 13.4$). Therefore, the presence of a tertiary hydroxyl group at C-20 was indicated in analogy with ganoderic acid N and O [12]. The signal at δ 4.14 (*s*), which was observed at δ 4.57 in $CDCl_3$, indicated the presence of a hydroxyl group at C-12 and its configuration was assigned to be β because the ^{13}C NMR signal due to Me-18 was shifted up field to δ 13.1 by the γ-gauche effect [6, 12]. From these observations and ^{13}C NMR data (Table 2), the structure of methyl ganoderate AP was established to be methyl 12β,15α,20-trihydroxy-3,7,11,23-tetraoxo-5α-lanost-8-en-26-oate (**7**).

Compound **8** was obtained as a methyl ester and its formula was assigned to be $C_{31}H_{46}O_7$. Its ^1H NMR data showed the presence of a 7α-hydroxyl group [7β-H; δ 4.59 (*dd*, $J = 4.4, 1.5$)] and a 15α-hydroxyl group [15β-H; δ 4.61 (*dd*, $J = 9.3, 6.4$)], and entirely agreed with that of the methyl ester of compound B8 isolated by Kikuchi *et al.* from *G. lucidum* [19]. Thus, **8** was identified as the methyl ester of compound B8.

Among the triterpenoid components obtained here, **1**, **5** and **6** showed an intense bitterness and their taste threshold values were determined to be 1×10^{-6} M, 1×10^{-5} M and 1×10^{-6} M, respectively, when the organoleptic test was carried out by an ascending series of concentrations in a 10% ethanol solution [31].

EXPERIMENTAL

Extraction and isolation. Dried chipped fruiting bodies of *G. applanatum* (272 g) were extracted with EtOH. The extract was concd and partitioned between $CHCl_3$ and H_2O. The $CHCl_3$ layer (5.5 g) was chromatographed on a silica gel column ($CHCl_3$–MeOH) to give five fractions (Frs I–V). Fr.II was dissolved in EtOAc–MeOH and insoluble ergosterol was removed by filtration. The soluble part (1.2 g) was rechromatographed several times on a silica gel column and a Lobar column (RP-18) to yield compounds **1** (317.1 mg), **2** (49.7 mg) and **6** (8.5 mg). Fr.III was separated into five fractions (Frs.IIIa–IIIe) on a silica gel column. Fr.IIIb (224 mg) was treated with ethereal CH_2N_2 and subjected to silica gel CC and Lobar CC (RP-18) to yield compounds **3** (3.4 mg), **4** (19.3 mg) and **7** (9.0 mg). Fr.IIIc was also methylated with CH_2N_2 and then purified on a silica gel column and a Lobar column (RP-18) to give compounds **5** (3.6 mg) and **8** (4.4 mg).

Ganoderenic acid G (**1**). $[\alpha]_D^{23}$ +189° (EtOH; *c* 0.2). EIMS *m/z* (rel. int.): 512.2728 $[M]^+$ ($C_{30}H_{40}O_7$, calc. 512.2775) (5), 494 (57), 476 (11), 433 (11), 397 (10), 380 (27), 315 (13), 179 (100); IR ν_{max}^{film} cm^{-1}: 3480, 2970, 1660, 1600; UV λ_{max}^{EtOH} nm (ε): 246 (8900), 277 (sh, 4040); ^1H NMR $\delta_{TMS}^{CDCl_3}$: 6.09 (1H, *s*), 4.41 (1H, *dd*, $J = 9.8, 5.9$), 2.12 (3H, *s*), 1.28 (3H, *s*), 1.27 (3H, *s*), 1.23 (3H, *d*, $J = 6.9$), 1.15 (3H, *s*), 1.13 (3H, *s*), 0.74 (3H, *s*).

Ozonolysis and PDC oxidation of **1**. Compound **1** (26 mg) was dissolved in EtOAc (1 ml) and then O_3 was bubbled through the soln for 1 hr at −70°. After addition of dimethylsulphide (10 eq.), the reaction mixture was allowed to stand for 2 hr at room temp. The soln was concd, and the product (7.1 mg) was dissolved in DMF (0.3 mg) and added with PDC (30 mg). After stirring for 3 hr at room temp., the reaction mixture was diluted with H_2O and then extracted with Et_2O. The organic layer was washed with satd aq. NaCl and dried on Na_2SO_4. Concn and purification on a silica gel column gave the product **1a** ($C_{24}H_{30}O_5$, 0.5 mg), which was also prepared from lucidone B by PDC oxidation as described in ref. [12]. The ^1H NMR and EIMS data of **1a** entirely agree with the literature values [12]. The CD spectra of the two products (**1a**), which were prepared from **1** and lucidone B, also completely agreed with each other. CD λ^{MeOH} nm ($\Delta\varepsilon$): 330 (0), 308 (−1.7), 293 (0), 276 (+5.3), 251 (0), 246 (−0.5), 241 (0), 224 (+7.5), 213 (0).

Ganoderenic acid F (**2**). $[\alpha]_D^{23}$ +93° (EtOH; *c* 0.2). EIMS *m/z* (rel. int.): 510.2582 $[M]^+$ ($C_{30}H_{38}O_7$, calc. 510.2618) (15), 492 (16), 300 (51), 192 (30), 115 (74), 69 (54), 43 (100); IR ν_{max}^{film} cm^{-1}: 2970, 1680, 1600; UV λ_{max}^{EtOH} nm (ε): 244 (19500); ^1H NMR $\delta_{TMS}^{CDCl_3}$: 6.06 (1H, *s*), 3.21 (1H, *t*, $J = 9.3$; 17-H), 2.16 (3H, *s*), 1.69 (3H, *s*), 1.27 (3H, *s*), 1.24 (3H, *d*, $J = 6.8$), 1.15 (3H, *s*), 1.12 (3H, *s*), 0.74 (3H, *s*).

Methyl ganoderenate H (**3**). $[\alpha]_D^{23}$ +61° (EtOH; *c* 0.2). EIMS *m/z* (rel. int.): 526.2969 $[M]^+$ ($C_{31}H_{42}O_7$, calc. 526.2932) (8), 397 (8), 302 (5), 206 (8), 129 (100); IR ν_{max}^{film} cm^{-1}: 3480, 2900, 1720, 1670, 1600; UV λ_{max}^{EtOH} nm (ε): 244 (13900), 268 (sh, 6200); ^1H NMR $\delta_{TMS}^{CDCl_3}$: 3.70 (3H, *s*), 3.28 (1H, *dd*, $J = 10.5, 5.0$; 3α-H), 3.15 (1H, *t*, $J = 7.0$; 17-H), 2.14 (3H, *s*), 1.55 (3H, *s*), 1.25 (3H, *s*), 1.20 (3H, *d*, $J = 7.0$), 1.04 (3H, *s*), 0.89 (3H, *s*), 0.71 (3H, *s*).

Methyl ganoderenate I (**4**). $[\alpha]_D^{23}$ +96° (EtOH; *c* 0.2). EIMS *m/z* (rel. int.): 528.3092 $[M]^+$ ($C_{31}H_{44}O_7$, calc. 528.3088) (13), 381 (9), 327 (15), 314 (19), 197 (19), 165 (27), 129 (100); IR ν_{max}^{film} cm^{-1}: 3550, 3000, 1760, 1700, 1640; UV λ_{max}^{EtOH} nm (ε): 248 (17340), 280 (sh, 8010); ^1H NMR $\delta_{TMS}^{CDCl_3}$: 4.47 (1H, *dd*, $J = 7.0, 5.0$), 3.69 (3H, *s*), 3.29 (1H, *dd*, $J = 10.5, 5.0$; 3α-H), 2.12 (3H, *s*), 1.29 (3H, *s*), 1.22 (3H, *s*), 1.19 (3H, *d*, $J = 7.0$), 1.04 (3H, *s*), 0.90 (3H, *s*), 0.72 (3H, *s*).

Ganoderenic acid A (**5**). $[\alpha]_D^{23}$ +122° (EtOH; *c* 0.2). EIMS *m/z* (rel. int.): 514.2960 $[M]^+$ ($C_{30}H_{42}O_7$, calc. 514.2932) (2), 496 (21), 382 (33), 229 (21), 179 (27), 139 (28), 69 (48), 43 (100); IR ν_{max}^{film} cm^{-1}: 3350, 2960, 1660, 1600; UV λ_{max}^{EtOH} nm (ε): 248 (18450); ^1H NMR $\delta_{TMS}^{CDCl_3}$: 6.11 (1H, *s*), 4.90 (1H, *dd*, *J* = 9.8, 7.3), 4.66 (1H, *ddd*, *J* = 9.9, 9.8, 2.5), 2.84 (1H, *ddd*, *J* = 13.7, 7.8, 5.9; 1β-H), 2.80 (1H, *d*, *J* = 15.6; 12α-H), 2.37 (1H, *d*, *J* = 15.6; 12β-H), 2.11 (3H, *s*), 1.49 (1H, *ddd*, *J* = 13.7, 8.8, 8.8; 1α-H), 1.34 (3H, *s*), 1.26 (3H, *s*), 1.23 (3H, *d*, *J* = 6.9), 1.13 (3H, *s*), 1.10 (3H, *s*), 0.78 (3H, *s*).

Furanoganoderic acid (**6**). $[\alpha]_D^{23}$ +70° (EtOH; *c* 0.2). EIMS *m/z* (rel. int.): 510.2599 $[M]^+$ ($C_{30}H_{38}O_7$, calc. 510.2618) (5), 466 (3), 437 (2), 312 (100), 301 (9), 210 (8), 180 (25), 135 (7), 107 (26); IR ν_{max}^{film} cm^{-1}: 3480, 2910, 1680, 1160. UV λ_{max}^{EtOH} nm (ε): 216 (7870), 267 (5850); ^1H NMR $\delta_{TMS}^{CDCl_3}$: 7.10 (1H, *s*, 21-H), 5.89 (1H, *s*, 22-H), 4.46 (1H, *dd*, *J* = 10, 5), 3.22 (1H, *t*, *J* = 7), 1.29 (3H, *s*), 1.27 (3H, *s*), 1.19 (3H, *d*, *J* = 7.0), 1.15 (3H, *s*), 1.12 (3H, *s*), 0.66 (3H, *s*).

Methyl ganoderate AP (**7**). $[\alpha]_D^{23}$ +71° (EtOH; *c* 0.2). FDMS *m/z*: 560 $[M]^+$; EIMS *m/z* (rel. int.): 542.2849 $[M-H_2O]^+$ ($C_{31}H_{42}O_8$, calc. 542.2881) (7), 197 (6), 165 (11), 129 (100). IR ν_{max}^{film} cm^{-1}: 3400, 2960, 1700; UV λ_{max}^{EtOH} nm (ε): 261 (6690); ^1H NMR $\delta_{TMS}^{CDCl_3}$: 4.57 (1H, *s*), 4.36 (1H, *dd*, *J* = 10, 5), 3.68 (3H, *s*), 1.48 (3H, *s*), 1.27 (3H, *s*), 1.20 (3H, *s*), 1.18 (3H, *d*, *J* = 7), 1.15 (3H, *s*), 0.84 (3H, *s*).

*Methyl ester of compound B*8 (**8**). $[\alpha]_D^{23}$ +104° (EtOH; *c* 0.2). EIMS *m/z* (rel. int.): 530.3225 $[M]^+$ ($C_{31}H_{46}O_7$, calc. 530.3245) (13), 402 (13), 234 (18), 171 (20), 129 (67), 107 (20), 69 (60), 59 (100); IR ν_{max}^{film} cm^{-1}: 3350, 1700, 1650. UV λ_{max}^{EtOH} nm (ε): 254 (5360); ^1H NMR $\delta_{TMS}^{CDCl_3}$: 4.61 (1H, *dd*, *J* = 9.3, 6.4), 4.59 (1H, *dd*, *J* = 4.4, 1.5), 3.68 (3H, *s*), 2.84 (1H, *dd*, *J* = 17.6, 8.3), 2.76 (1H, *dd*, *J* = 18.6), 2.61 (1H, *ddd*, *J* = 15.6, 9.8, 5.9), 2.42 (1H, *d*, *J* = 18.6), 2.38 (1H, *dd*, *J* = 16.6, 3.9), 2.27 (1H, *dd*, *J* = 16.6, 9.1), 2.09 (1H, *dd*, *J* = 12.7, 2.7), 1.30 (3H, *s*), 1.17 (3H, *d*, *J* = 8), 1.16 (3H, *s*), 1.08 (3H, *s*), 1.03 (3H, *s*), 0.89 (3H, *s*), 0.84 (3H, *s*).

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