New Bitter C₂₇ and C₃₀ Terpenoids from the Fungus *Ganoderma lucidum* (Reishi)

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Four new bitter terpenoids, lucidenic acids A (1), B (2), C (3) and ganoderic acid C (5), were isolated from the fruiting bodies of *Ganoderma lucidum*, together with the known bitter ganoderic acid B (4). On the basis of spectroscopic data and chemical conversion, their structures were determined to be 7 β -hydroxy-4,4,14 α -trimethyl-3,11,15-trioxo-5 α -chol-8-en-24-oic acid, 7 β ,12 β -dihydroxy-4,4,14 α -trimethyl-3,11,15-trioxo-5 α -chol-8-en-24-oic acid, 3 β ,7 β ,12 β -trihydroxy-4,4,14 α -trimethyl-11,15-dioxo-5 α -chol-8-en-24-oic acid and 7 β -hydroxy-3,11,15,23-tetraoxo-5 α -lanost-8-en-26-oic acid, respectively.

Much attention has been paid to the fungus *Ganoderma lucidum* (Japanese name: Reishi or Mannen-take, Polyporaceae) regarding some physiological effects when used as a home remedy.^{1~3)} In a previous paper,⁴⁾ we have reported some bitter terpenoids which have the C₂₇ and C₃₀ skeleton from the title fungus. This is a full report on the isolation and structural determination of four new bitter terpenoids, lucidenic acids A (1), B (2), C (3) and ganoderic acid C (5), with the identification of the known bitter triterpene, ganoderic acid B (4).⁵⁾

Dried chipped fruiting bodies of *G. lucidum* were extracted with ethanol, the extract being partitioned between chloroform and water. The chloroform layer was concentrated and separated into its acidic and neutral fractions. The acidic fraction was acidified (pH 3~4) with 6 N HCl, and the resulting precipitate was applied to silica gel column chromatography using a solvent system of chloroform-methanol. The eluate was rechromatographed on the silica gel column to give two strongly bitter compounds (1 and 5) and three slightly bitter compounds (2, 3 and 4).

Lucidenic acid C (3) was obtained as pale yellow needles (mp 199~200°C, $[\alpha]_D^{24} +140^\circ$). The molecular formula of 3 was determined to be C₂₇H₄₀O₇ (M⁺ 476.2753, calcd. for C₂₇H₄₀O₇: 476.2775). The IR spectrum indicated the presence of hydroxy groups ($\nu_{\text{max}}^{\text{KBr}}$ 3350 cm⁻¹), carbonyl groups (1720 and 1675 cm⁻¹) and a carboxyl group (3200~2400 cm⁻¹). The presence of three secondary hydroxy groups was revealed by the formation of a triacetate (3a), C₃₃H₄₆O₁₀ (M⁺ 602.3069, calcd. for C₃₃H₄₆O₁₀: 602.3092), on treating 3 with acetic anhydride/pyridine, and by giving the signals of three methine groups bearing the acetoxy group at δ 5.89 (1H, dd, *J*=8.4 and

TABLE I. ^{13}C -NMR DATA OF LUCIDENIC
ACID A (1), LUCIDENIC ACID
B (2) AND TRI-*O*-ACETYL
LUCIDENIC ACID C (3a)

Position	δ , ppm (number of bonded H)		
	1	2*	3a*
1	30.8 (2)	35.1 (2)	33.8 (2)
2	34.3 (2)	34.3 (2)	23.8 (2)
3	216.7 (0) [‡]	215.7 (0) [‡]	79.0 (1)
4	46.8 (0)	46.9 (0)	37.7 (0) [‡]
5	49.0 (1)	49.4 (1)	49.1 (1)
6	27.7 (2)	27.7 (2)	25.0 (2)
7	66.4 (1)	65.8 (1)	68.8 (1)
8	157.8 (0)	158.1 (0)	154.4 (0)
9	141.3 (0)	140.1 (0)	146.0 (0)
10	38.3 (0)	37.8 (0)	38.2 (0) [‡]
11	197.8 (0)	199.6 (0)	192.0 (0)
12	50.2 (2)	78.3 (1)	80.2 (1)
13	45.0 (0)	51.6 (0)	50.2 (0)
14	59.4 (0)	60.2 (0)	58.2 (0)
15	217.9 (0) [‡]	217.1 (0) [‡]	210.5 (0)
16	41.1 (2)	37.6 (2)	37.9 (2)
17	46.4 (1)	46.6 (1)	46.4 (1)
18	17.7 (3)	12.1 (3)	13.4 (3)
19	18.2 (3)	18.3 (3)	18.2 (3)
20	35.2 (1)	31.5 (1)	31.8 (1)
21	18.0 (3)	20.5 (3)	20.3 (3)
22	30.5 (2)	29.5 (2)	29.6 (2)
23	35.7 (2)	31.8 (2)	31.7 (2)
24	178.4 (0)	178.7 (0)	178.3 (0)
25	27.0 (3)	26.3 (3)	28.1 (3)
26	20.8 (3)	21.2 (3)	16.5 (3)
27	24.7 (3)	23.3 (3)	25.5 (3)

* Assignments were confirmed by measuring the ^1H - ^{13}C shift correlated spectra (not presented).

[‡] Assignments may be reversed.

8.4 Hz), 5.68 (1H, s) and 4.48 (1H, dd $J=11.4$ and 5.1 Hz) in the ^1H -NMR spectrum of **3a**, and δ 80.2, 79.0 and 68.8 in the ^{13}C -NMR spectrum of **3a**. The ^{13}C -NMR spectrum of **3a** was very similar to those of ganoderic acids A and B,⁵⁾ but it showed the presence of 27 C atoms excluding the acetoxy groups (Table I). The assignments are based on the data of ganoderic acids A and B,⁵⁾ methyl 3 β -acetoxy-(24*E*)-lanosta-8,24-dien-26-oate, and methyl 15 α -acetoxy-7 α -hydroxy-3-oxo-(24*E*)-lanosta-8,24-dien-26-oate,⁶⁾ 3 β -hydroxy-4,4,14 α -trimethyl-5 α -pregna-7,9(11)-diene-20*S*-carboxylic acid and its 12 β -hydroxy deriva-

tive,⁷⁾ and the 4,4,10 β -trimethyldecalsins.⁸⁾ The signals of three acetoxy groups were shown at δ 170.9, 170.3, 170.0, 21.2, 20.9 and 20.9. The presence of six methyl groups, six methylene groups, six methine groups and four fully substituted C atoms was evident. The signal at δ 210.5 indicated the presence of a carbonyl group, and the signals at δ 192.0, 154.4 and 146.0 indicated the presence of an α,β -unsaturated carbonyl group, which was supported by giving an absorption maximum at 254 nm ($\epsilon=5960$) in the UV spectrum of **3**. The signals at δ 178.3 indicated the presence of a carboxyl group, and this was confirmed by formation of the monomethyl ester (**3b**), $\text{C}_{28}\text{H}_{42}\text{O}_7$ (M^+ 490.2919, calcd. for $\text{C}_{28}\text{H}_{42}\text{O}_7$: 490.2932), on treating **3** with 3% methanolic hydrogen chloride. The ^1H -NMR spectrum of **3b** showed the signals of methyl groups at δ 1.44 (3H, s), 1.31 (3H, s), 1.13 (3H, d, $J=6.8$ Hz), 1.04 (3H, s), 0.87 (3H, s), 0.80 (3H, s) and 3.67 (3H, s, COOMe), methine groups bearing the hydroxy group at δ 4.78 (1H, ddd, $J=8.7$, 8.7 and 4.3 Hz), 4.36 (1H, d, $J=2.1$ Hz) and 3.21 (1H, dd, $J=11.1$ and 5.4 Hz), and two of the three hydroxy groups at δ 4.44 (1H, d, $J=4.3$ Hz) and 3.99 (1H, d, $J=2.1$ Hz). From this ^1H -NMR spectral data of **3b**, the presence of the following groups (I~III) of **3b** were evident. Furthermore, from the analysis of the ^1H -NMR spin-spin coupling patterns of **3b**, using double resonance experiments, the partial structures (IV~VI) of **3b** were ob-

tained. On the basis of these partial structures of **3b** and the ^{13}C -NMR spectral data of **3a** already mentioned the structure of **3** was derived, except for the configuration of the hydroxy groups. In the ^1H -NMR spectrum of **3b**, the coupling constants between $\text{H}-\text{C}(3)$ at $\delta 3.21$ and $2\text{H}-\text{C}(2)$ were 11.1 and 5.4 Hz, respectively, which indicated that the configuration of the hydroxy group at $\text{C}(3)$ was β (equatorial). The coupling constants between $\text{H}-\text{C}(7)$ at $\delta 4.78$ and $2\text{H}-\text{C}(6)$ were 8.7 and 8.7 Hz, respectively, which indicated that the configuration of the hydroxy group at $\text{C}(7)$ was β ; this agrees with those of methyl ganoderate **B**⁵⁾ and is supported by the fact that the coupling constant between $\text{H}_\alpha-\text{C}(6)$ and $\text{H}_\beta-\text{C}(7)$ of the compound 'Syl-A' is 2.0 Hz.⁹⁾ The configuration of the hydroxy group at $\text{C}(12)$ was indicated to be β by the results of the NOE experiments of **3a**. A 9.4% NOE enhancement was observed between $\text{H}-\text{C}(12)$ at $\delta 5.68$ and $\text{H}_3\text{C}(27)$ at $\delta 1.42$. Thus, the structure of lucidenic acid **C** (**3**) was determined to be $3\beta, 7\beta, 12\beta$ -trihydroxy-4,4,14 α -trimethyl-11,15-dioxo-5 α -chol-8-en-24-oic acid.

Lucidenic acid **B** (**2**) was obtained as colorless needles (mp $179\sim 181^\circ\text{C}$, $[\alpha]_{\text{D}}^{24} +169^\circ$). The molecular formula of **2** was assigned as $\text{C}_{27}\text{H}_{38}\text{O}_7$ (M^+ 474.2597, calcd. for $\text{C}_{27}\text{H}_{38}\text{O}_7$: 474.2618). The ^1H -NMR and ^{13}C -NMR data of **2** were very similar to those of **3b** and **3a**, respectively. The ^1H -NMR spectrum of **2** showed the signals of two methine groups bearing the hydroxy group at $\delta 4.83$ (1H, dd, $J=8.7$ and 8.7 Hz) and 4.38 (1H, s), but did not show any signal around $\delta 3.21$ ($\text{H}-\text{C}(3)$ of **3b**). The ^{13}C -NMR spectrum of **2** (Table I) showed the signals of three carbonyl groups at $\delta 217.1$, 215.7 and 199.6 , and two methine groups bearing the hydroxy group at $\delta 78.3$ and 65.8 . These observations indicated the presence of a carbonyl group at $\text{C}(3)$ in **2** instead of the hydroxy group in **3**. The configuration of the hydroxy group at $\text{C}(7)$ was determined to be β , since the ^1H -NMR coupling constants of the signal at $\delta 4.83$ were 8.7 and 8.7 Hz. In the NOE difference ex-

periment, when the signal of $\text{H}_3\text{C}(27)$ at $\delta 1.44$ was irradiated, a small NOE was observed for the signal of $\text{H}-\text{C}(7)$ at $\delta 4.83$ and a large NOE was observed for the signal of $\text{H}-\text{C}(12)$ at $\delta 4.38$. The former supported that the configuration of the hydroxy group at $\text{C}(7)$ was β , and the latter indicated that the configuration of the hydroxy group at $\text{C}(12)$ was β . No NOE was observed for both the signals, when the signal of $\text{H}_3\text{C}(18)$ at $\delta 0.83$ was irradiated. Furthermore, in the ^{13}C -NMR spectrum, the signal of $\text{C}(18)$ of **2** was observed in a higher field than that of **1** (Table I). This observation also indicated a β -configuration of the hydroxy group at $\text{C}(12)$ by analogy with the spectra of 3β -hydroxy-4,4,14 α -trimethyl-5 α -pregna-7,9(11)-diene-20S-carboxylic acid and its 12β -hydroxy derivative.⁷⁾ From these observations, the structure of lucidenic acid **B** (**2**) was determined to be $7\beta, 12\beta$ -dihydroxy-4,4,14 α -trimethyl-3,11,15-trioxo-5 α -chol-8-en-24-oic acid.

Lucidenic acid **A** (**1**) was obtained as colorless needles (mp $194\sim 195^\circ\text{C}$, $[\alpha]_{\text{D}}^{24} +173^\circ$). The molecular formula of **1** was determined to be $\text{C}_{27}\text{H}_{38}\text{O}_6$ (M^+ 458.2698, calcd. for $\text{C}_{27}\text{H}_{38}\text{O}_6$: 458.2669). The ^{13}C - and ^1H -NMR data of **1** were very similar to those of lucidenic acid **B** (**2**). But in the ^{13}C -NMR spectrum, **1** showed only one signal of a methine group bearing the hydroxy group at $\delta 66.4$ and gave a new signal of a methylene group at $\delta 50.2$ (see Table I). In the ^1H -NMR, **1** also showed only one signal of a methine group bearing the hydroxy group at $\delta 4.86$ (1H, dd, $J=9.5$ and 7.7 Hz). From these observations, it was indicated that **1** possessed a hydroxy group only at $\text{C}(7)$. The signals of the methylene protons at $\text{C}(12)$ showed distinct A/B double patterns at $\delta 2.75$ and 2.78 ($J=17.2$ Hz). Thus, the structure of lucidenic acid **A** (**1**) was established to be 7β -hydroxy-4,4,14 α -trimethyl-3,11,15-trioxo-5 α -chol-8-en-24-oic acid.

Similar to ganoderic acids **A** and **B**,⁵⁾ lucidenic acids **A** (**1**) and **B** (**2**), in which a carbonyl group exists at $\text{C}(3)$, have a boat-shaped ring **A**, while lucidenic acid **C** (**3**), which possesses a hydroxy group at $\text{C}(3)$, has a

chair-shaped ring A. This was deduced from the vicinal coupling constants between H_α -C(1) and 2H-C(2), and between H_β -C(1) and 2H-C(2) in the ^1H -NMR spectra. Lucidenic acid A (**1**) showed the signals due to H_α -C(1) and H_β -C(1) at δ 1.48 (ddd, $J=13.6$, 8.3 and 8.3 Hz) and δ 2.94 (ddd, $J=13.6$, 7.7 and 5.5 Hz), respectively. The coupling constants J (H_α -C(1) and 2H-C(2)) (8.3 and 8.3 Hz, resp.) and J (H_β -C(1) and 2H-C(2)) (7.7 and 5.5 Hz, resp.) indicated that the dihedral angles between H_α -C(1) and H_α -C(2) and between H_β -C(1) and H_β -C(2) were approximately zero. This suggested that **1** has a boat-shaped ring A. Lucidenic acid B (**2**) showed the signals of H_α -C(1) and H_β -C(1) at δ 1.35 (ddd, $J=13.7$, 11.0 and 6.6 Hz) and δ 2.79 (ddd, $J=13.7$, 7.0 and 4.2 Hz), respectively. Although the coupling constants of these signals are a little different from those of **1**, this also indicated that **2** has a boat-shaped ring A. The conformation might be distorted by the effect of 12 β -OH. On the other hand, methyl lucidenate C (**3b**) showed the signals of H_α -C(1) and H_β -C(1) at δ 0.92 (ddd, $J=13.4$, 13.1 and 4.6 Hz) and δ 2.61 (ddd, $J=13.4$, 3.4 and 3.4 Hz), respectively. The coupling constants of these signals indicated that **3b** has a chair-shaped ring A, and this conclusion must be applied to the conformation at ring A of lucidenic acid C (**3**).

Ganoderic acid B (**4**) was obtained as pale yellow needles (mp 212~213°C, $[\alpha]_D^{24} +138^\circ$). The molecular formula of **4** was assigned as $\text{C}_{30}\text{H}_{44}\text{O}_7$ (M^+ 516.3110, calcd. for $\text{C}_{30}\text{H}_{44}\text{O}_7$: 516.3088). Methylation of **4** with 3% methanolic hydrogen chloride gave a monomethyl ester (**4a**), $\text{C}_{31}\text{H}_{46}\text{O}_7$ (M^+ 530.3291, calcd. for $\text{C}_{31}\text{H}_{46}\text{O}_7$: 530.3245), and its ^1H - and ^{13}C -NMR data entirely agreed with those of methyl ganoderate B.⁵⁾ Thus **4** was identified as ganoderic acid B (3 β ,7 β -dihydroxy-11,15,23-trioxo-5 α -lanost-8-en-26-oic acid).

Ganoderic acid C (**5**) was obtained as colorless needles (mp 184.5~185.5°C, $[\alpha]_D^{24} +185^\circ$). It was formulated as $\text{C}_{30}\text{H}_{42}\text{O}_7$ (M^+ 514.2931, calcd. for $\text{C}_{30}\text{H}_{42}\text{O}_7$: 514.2932). The ^1H - and

^{13}C -NMR data of **5** were very similar to those of ganoderic acid B (**4**). The ^1H -NMR spectrum of **5** showed the signal of a methine group bearing the hydroxy group at δ 4.85 (1H, dd, $J=9.3$ and 7.8 Hz), but no signal around δ 3.19 (H-C(3) of **4**). The ^{13}C -NMR spectrum of **5** also did not give any signal around δ 78.2 due to C(3) of **4**, but showed a carbonyl signal at δ 216.6. These observations indicated the presence of a carbonyl group at C(3) in **5** instead of the hydroxy group in **4**. Thus, the structure of ganoderic acid C (**5**) was established to be 7 β -hydroxy-3,11,15,23-tetraoxo-5 α -lanost-8-en-26-oic acid. Since **5** had a carbonyl group at C(3) and in the ^1H -NMR showed signals due to H_α -C(1) and H_β -C(1) at δ 1.49 (ddd, $J=13.7$, 8.4 and 8.4 Hz) and δ 2.93 (ddd, $J=13.7$, 7.6 and 5.5 Hz), respectively, it was deduced that **5** has a boat conformation at ring A.

In both ganoderic acids B (**4**) and C (**5**), the configuration at C(25) has not yet been determined.

EXPERIMENTAL

General. Melting points were measured with a Yanaco micro-melting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-4 instrument, and CD spectra were measured on a JASCO J-20 instrument. Mass spectra were obtained with JEOL JMS-D300 equipment. IR and UV spectra were recorded on a Hitachi 285 spectrometer and Hitachi EPS-3T spectrophotometer, respectively. ^1H -NMR spectra were recorded on a JEOL FX-500 spectrometer and NOE analyses were determined on a Bruker AM-500 spectrometer. ^{13}C -NMR spectra were recorded on JEOL FX-100 and FX-200 spectrometers.

Isolation of lucidenic acids A (1), B (2), C (3) and ganoderic acids B (4), C (5). Dried chipped fruiting bodies of *G. lucidum* (a mixture of the mushroom form and antlered form, 6 kg) were extracted with EtOH (242 liters). The extract was concentrated and partitioned between CHCl_3 and water. The CHCl_3 layer (15 liters) was concentrated to about one tenth of its original volume, and then extracted with sat. aq. NaHCO_3 . The extract was acidified to pH 3~4 with 6N HCl at 0°C. The resulting precipitates in the water were dissolved in CHCl_3 (4 liters) and then evaporated *in vacuo* to yield a residue (68 g), which was chromatographed on silica gel (Fr. 1~11, CHCl_3 -MeOH=98:2; Fr. 12, CHCl_3 -MeOH=9:1; Fr. 13, MeOH). Compounds (**1**), (**2**) and (**5**) were obtained by

further chromatographic separations of the mixture of Fr. 2 and Fr. 3, and compounds (3) and (4) were from Fr. 6.

Lucidenic acid C ($3\beta,7\beta,12\beta$ -trihydroxy-4,4,14 α -trimethyl-11,15-dioxo-5 α -chol-8-en-24-oic acid; **3**). Compound **3** was crystallized from CHCl_3 -hexane as pale yellow needles (317.9 mg), mp 199~200°C. $[\alpha]_D^{24} +140^\circ$ ($c=0.2$, MeOH). MS m/z : 476.2753 (M^+ , $\text{C}_{27}\text{H}_{40}\text{O}_7$, 2%), 458 (2), 307 (14), 306 (100), 55 (17), 44 (12), 43 (16). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3350, 3200~2400 (br), 2950, 2850, 1720, 1675, 1260, 1090, 1040, 1020. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 254 (5960). CD λ^{MeOH} nm ($\Delta\epsilon$): 290 (−5.8), 276 (0), 248 (+15.4), 224 (0), 207 (−7.8).

Tri-O-acetyl lucidenic acid C ($3\beta,7\beta,12\beta$ -triacetoxo-4,4,14 α -trimethyl-11,15-dioxo-5 α -chol-8-en-24-oic acid; **3a**). Compound **3** (40 mg) was acetylated with acetic anhydride/pyridine to give **3a** as a pale yellow syrup (55.3 mg). MS m/z : 602.3069 (M^+ , $\text{C}_{33}\text{H}_{46}\text{O}_{10}$, 0.2%), 587 (0.7), 559 (9), 390 (100), 69 (13), 57 (28), 55 (28), 43 (46). $^1\text{H-NMR}$ $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 5.89 (1H, dd, $J=8.4$ and 8.4 Hz, 7 α -H), 5.68 (1H, s, 12 α -H), 4.48 (1H, dd, $J=11.4$ and 5.1 Hz, 3 α -H), 2.76 (1H, ddd, $J=13.7$, 3.5 and 3.5 Hz, 1 β -H), 2.56 (1H, dd, $J=18.9$ and 8.0 Hz, 16 α -H), 2.53 (1H, 6 α -H), 2.46 (1H, m, 23-H), 2.33 (1H, dd, $J=18.9$ and 8.2 Hz, 16 β -H), 2.33 (1H, m, 17-H), 2.22 (1H, 23-H), 1.88 (1H, m, 22-H), 1.77 (1H, m, 20-H), 1.6~1.7 (2H, m, 2-H), 1.43 (1H, ddd, $J=13.4$, 13.4 and 8.4 Hz, 6 β -H), 1.42 (3H, s, 27-H), 1.25 (1H, m, 22-H), 1.24 (3H, s, 19-H), 1.05 (1H, ddd, $J=13.7$, 13.0 and 4.3 Hz, 1 α -H), 1.03 (1H, dd, $J=13.4$ and 1.7 Hz, 5 α -H), 1.01 (3H, s, 18-H), 0.99 (3H, d, $J=7.0$ Hz, 21-H), 0.92 (3H, s, 25-H), 0.89 (3H, s, 26-H), 2.21 (3H, s, OAc), 2.05 (3H, s, OAc), 1.96 (3H, s, OAc).

Methyl lucidenate C (methyl $3\beta,7\beta,12\beta$ -trihydroxy-4,4,14 α -trimethyl-11,15-dioxo-5 α -chol-8-en-24-oate; **3b**). Compound **3** (24 mg) was methylated with 3% methanolic hydrogen chloride to give **3b**, which was crystallized from EtOAc as colorless needles (18.3 mg), mp 233~234.5°C. MS m/z : 490.2919 (M^+ , $\text{C}_{28}\text{H}_{42}\text{O}_7$, 4%), 472 (1), 307 (11), 306 (100), 69 (2), 55 (3), 44 (4), 43 (3). $^1\text{H-NMR}$ $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 4.78 (1H, ddd, $J=8.7$, 8.7 and 4.3 Hz, 7 α -H), 4.44 (1H, d, $J=4.3$ Hz, 7 β -OH), 4.36 (1H, d, $J=2.1$ Hz, 12 α -H), 3.99 (1H, d, $J=2.1$ Hz, 12 β -OH), 3.21 (1H, dd, $J=11.1$ and 5.4 Hz, 3 α -H), 2.66 (1H, dd, $J=19.7$ and 8.7 Hz, 16 α -H), 2.61 (1H, ddd, $J=13.1$, 3.4 and 3.4 Hz, 1 β -H), 2.45 (1H, ddd, $J=9.9$, 8.7 and 5.5 Hz, 17-H), 2.40 (1H, 23-H), 2.32 (1H, 23-H), 2.29 (1H, dd, $J=19.7$ and 5.5 Hz, 16 β -H), 2.24 (1H, ddd, $J=13.6$, 8.7 and 1.8 Hz, 6 α -H), 1.93 (1H, m, 20-H), 1.85 (1H, m, 22-H), 1.65 (2H, 2-H), 1.65 (1H, 6 β -H), 1.44 (3H, s, 27-H), 1.31 (3H, s, 19-H), 1.28 (1H, m, 22-H), 1.13 (3H, d, $J=6.8$ Hz, 21-H), 1.04 (3H, s, 26-H), 0.92 (1H, ddd, $J=13.1$, 13.1 and 4.6 Hz, 1 α -H), 0.88 (1H, dd, $J=13.1$ and 1.8 Hz, 5 α -H), 0.87 (3H, s, 25-H), 0.80 (3H, s, 18-H), 3.67 (3H, s, COOCH_3).

Lucidenic acid B ($7\beta,12\beta$ -dihydroxy-4,4,14 α -trimethyl-

$3,11,15$ -trioxo-5 α -chol-8-en-24-oic acid; **2**). Compound **2** was crystallized from EtOAc as colorless needles (130.3 mg), mp 179~181°C. $[\alpha]_D^{24} +169^\circ$ ($c=0.22$, MeOH). MS m/z : 474.2597 (M^+ , $\text{C}_{27}\text{H}_{38}\text{O}_7$, 4%), 456 (3), 304 (100), 55 (9), 44 (96), 43 (10), 40 (14). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3380, 3200~2400 (br), 2950, 2925, 2860, 1730, 1700, 1660, 1380, 1270, 1160, 1050. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 252 (6010). CD λ^{MeOH} nm ($\Delta\epsilon$): 290 (−7.0), 277 (0), 248 (+25.6), 224 (0), 208 (−12.1). $^1\text{H-NMR}$ $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 4.83 (1H, dd, $J=8.7$ and 8.7 Hz, 7 α -H), 4.38 (1H, s, 12 α -H), 2.79 (1H, ddd, $J=13.7$, 7.0 and 4.2 Hz, 1 β -H), 2.68 (1H, dd, $J=19.5$ and 8.5 Hz, 16 α -H), 2.64 (1H, ddd, $J=15.6$, 11.0 and 7.0 Hz, 2 β -H), 2.45 (2H, 17-H and 23-H), 2.40 (1H, 23-H), 2.40 (1H, ddd, $J=15.6$, 6.6 and 4.2 Hz, 2 α -H), 2.32 (1H, dd, $J=19.5$ and 10.2 Hz, 16 β -H), 2.18 (1H, ddd, $J=13.7$, 8.7 and 1.8 Hz, 6 α -H), 1.96 (1H, m, 20-H), 1.86 (1H, m, 22-H), 1.79 (1H, ddd, $J=13.7$, 13.7 and 8.7 Hz, 6 β -H), 1.48 (1H, dd, $J=13.7$ and 1.8 Hz, 5 α -H), 1.44 (3H, s, 27-H), 1.43 (3H, s, 19-H), 1.35 (1H, ddd, $J=13.7$, 11.0 and 6.6 Hz, 1 α -H), 1.30 (1H, m, 22-H), 1.15 (3H, d, $J=6.7$ Hz, 21-H), 1.13 (3H, s, 25-H), 1.13 (3H, s, 26-H), 0.83 (3H, s, 18-H).

Lucidenic acid A (7β -hydroxy-4,4,14 α -trimethyl-3,11,15-trioxo-5 α -chol-8-en-24-oic acid; **1**). Compound **1** was crystallized from EtOAc as colorless needles (1160.0 mg), mp 194~195°C. $[\alpha]_D^{24} +173^\circ$ ($c=0.2$, CHCl_3). MS m/z : 458.2698 (M^+ , $\text{C}_{27}\text{H}_{38}\text{O}_6$, 4%), 430 (2), 329 (10), 320 (5), 55 (36), 44 (100), 43 (36), 40 (71). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3440, 3300~2500 (br), 2975, 2875, 1720, 1700, 1680, 1380, 1270, 1170, 1060, 750. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 254 (7680). CD λ^{MeOH} nm ($\Delta\epsilon$): 295 (−1.9), 282 (0), 255 (+15.0), 227 (0), 212 (−7.2). $^1\text{H-NMR}$ $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 4.86 (1H, dd, $J=9.5$ and 7.7 Hz, 7 α -H), 2.94 (1H, ddd, $J=13.6$, 7.7 and 5.5 Hz, 1 β -H), 2.81 (1H, dd, $J=19.6$ and 8.2 Hz, 16 α -H), 2.78 (1H, d, $J=17.2$ Hz, 12 α -H), 2.75 (1H, d, $J=17.2$ Hz, 12 β -H), 2.52 (1H, 2-H), 2.45 (2H, 2-H and 23-H), 2.34 (1H, ddd, $J=16.4$, 8.2 and 8.2 Hz, 23-H), 2.17 (1H, dd, $J=19.6$ and 9.9 Hz, 16 β -H), 2.12 (1H, ddd, $J=13.0$, 7.7 and 1.2 Hz, 6 α -H), 2.01 (1H, ddd, $J=9.9$, 9.0 and 8.2 Hz, 17-H), 1.80 (1H, m, 22-H), 1.68 (1H, ddd, $J=13.0$, 13.0 and 9.5 Hz, 6 β -H), 1.60 (1H, m, 20-H), 1.58 (1H, dd, $J=13.0$ and 1.2 Hz, 5 α -H), 1.48 (1H, ddd, $J=13.6$, 8.3 and 8.3 Hz, 1 α -H), 1.37 (1H, 22-H), 1.35 (3H, s, 27-H), 1.26 (3H, s, 19-H), 1.14 (3H, s, 25-H), 1.11 (3H, s, 26-H), 1.01 (3H, s, 18-H), 0.99 (3H, d, $J=6.6$ Hz, 21-H).

Identification of ganoderic acid B (**4**). Compound **4** was crystallized from EtOAc-benzene as pale yellow needles (796.0 mg), mp 212~213°C. $[\alpha]_D^{24} +138^\circ$ ($c=0.2$, MeOH). MS m/z : 516.3110 (M^+ , $\text{C}_{30}\text{H}_{44}\text{O}_7$, 18%), 498 (4), 488 (19), 376 (11), 358 (32), 331 (27), 149 (15), 139 (19), 105 (27), 69 (36), 43 (100). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3420, 3200~2400 (br), 2950, 2875, 1720, 1640, 1450, 1360, 1240, 1160, 1025. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 254 (10740). CD λ^{EtOH} nm ($\Delta\epsilon$): 293 (−3.8), 279 (0), 254 (+17.5), 228 (0), 212 (−8.6). $^1\text{H-NMR}$ $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 4.80 (1H, dd, $J=8.9$ and 8.9 Hz), 3.19 (1H, dd, $J=10.8$ and 5.4 Hz), 2.78 (1H, d, $J=16.8$ Hz), 2.69 (1H, d, $J=$

16.8 Hz), 1.34 (3H, s), 1.22 (3H, d, $J=5.5$ Hz), 1.21 (3H, s), 1.03 (3H, s), 1.00 (3H, s), 0.99 (3H, d, $J=5.8$ Hz), 0.85 (3H, s). $^{13}\text{C-NMR}$ $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 217.3 (s), 207.5 (s), 197.7 (s), 180.2 (s), 156.7 (s), 142.6 (s), 78.2 (d), 66.8 (d), 28.1 (q), 24.3 (q), 19.5 (q), 18.3 (q), 17.3 (q), 16.9 (q), 15.4 (q). Compound **4** (100 mg) was methylated with 3% methanolic hydrogen chloride to give a monomethyl ester (**4a**), which was crystallized from EtOAc as pale yellow prisms (70.7 mg), mp 214~215°C. MS m/z : 530 (M^+ , $\text{C}_{31}\text{H}_{46}\text{O}_7$, 64%), 390 (20), 358 (38), 331 (20), 171 (10), 139 (29), 129 (42), 69 (57), 59 (100). $^1\text{H-NMR}$ $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 4.79 (1H, ddd, $J=8.7$, 8.7 and 4.7 Hz), 4.04 (1H, d, $J=4.7$ Hz), 3.20 (1H, dd, $J=10.6$ and 5.6 Hz), 2.77 (1H, d, $J=16.7$ Hz), 2.69 (1H, d, $J=16.7$ Hz), 1.34 (3H, s), 1.22 (3H, s), 1.19 (3H, d, $J=7.0$ Hz), 1.03 (3H, s), 1.00 (3H, s), 0.97 (3H, d, $J=5.9$ Hz), 0.85 (3H, s). $^{13}\text{C-NMR}$ $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 217.3 (s), 207.6 (s), 197.7 (s), 176.0 (s), 156.8 (s), 142.5 (s), 78.2 (d), 66.8 (d), 28.1 (q), 24.4 (q), 19.6 (q), 18.4 (q), 17.4 (q), 17.0 (q), 15.4 (q). All the analytical data for **4a**, except for its melting point, were in good agreement with those of methyl ganoderate B.

Ganoderic acid C (7 β -hydroxy-3,11,15,23-tetraoxo-5 α -lanost-8-en-26-oic acid; 5). Compound **5** was crystallized from EtOAc-cyclohexane as colorless needles (66.0 mg), mp 184.5~185.5°C. $[\alpha]_{\text{D}}^{24} +185^\circ$ ($c=0.21$, MeOH). MS m/z : 514 (M^+ , $\text{C}_{30}\text{H}_{42}\text{O}_7$, 18%), 376 (18), 356 (37), 329 (50), 167 (19), 139 (50), 69 (50), 55 (31), 43 (100). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3450, 3300~2500 (br), 2960, 2875, 1730, 1700, 1660, 1380, 1270, 1170, 1060. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (ϵ): 255 (7100). CD $\lambda_{\text{max}}^{\text{MeOH}}$ nm ($\Delta\epsilon$): 293 (−2.2), 282 (0), 254 (+19.5), 228 (0), 213 (−8.2). $^1\text{H-NMR}$ $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 4.85 (1H, dd, $J=9.3$ and 7.8 Hz, 7 α -H), 2.97 (1H, m, 25-H), 2.93 (1H, ddd, $J=13.7$, 7.6 and 5.5 Hz, 1 β -H), 2.83 (1H, dd, $J=17.7$ and 8.6 Hz, 24-H), 2.78 (1H, d, $J=17.4$ Hz, 12 α -H), 2.72 (1H, d, $J=17.4$ Hz, 12 β -H), 2.67 (1H, dd, $J=16.8$ and 4.9 Hz, 16 α -H), 2.55 (1H, 2-H), 2.50 (1H, 2-H), 2.45 (1H, 24-H), 2.38 (2H, br d, $J=4.3$ Hz, 22-2H), 2.15 (2H, m, 17-H and 20-H), 2.10 (1H, 6 α -H), 2.05 (1H, 16 β -H), 1.68 (1H, ddd, $J=13.4$, 12.5 and 9.3 Hz, 6 β -H), 1.57 (1H, dd, $J=12.5$ and 1.0 Hz, 5 α -H), 1.49 (1H, ddd, $J=13.7$, 8.4 and 8.4 Hz, 1 α -H), 1.34 (3H, s, 30-H), 1.26 (3H, s, 19-H), 1.23 (3H, d, $J=7.0$ Hz, 27-H), 1.12 (3H, s, 28-H), 1.11 (3H, s, 29-H), 1.03 (3H, s,

18-H), 1.00 (3H, d, $J=5.8$ Hz, 21-H). $^{13}\text{C-NMR}$ $\delta_{\text{TMS}}^{\text{CDCl}_3}$ (number of bonded H, position of carbon): 217.5 (0, 3-C or 15-C), 216.6 (0, 3-C or 15-C), 207.5 (0, 23-C), 197.6 (0, 11-C), 180.6 (0, 26-C), 157.8 (0, 8-C), 141.2 (0, 9-C), 66.3 (1, 7-C), 59.4 (0, 14-C), 50.1 (2, 12-C), 48.9 (1, 5-C), 48.9 (2, 22-C), 46.8 (0, 4-C), 46.5 (2, 24-C), 45.7 (1, 17-C), 45.0 (0, 13-C), 41.0 (2, 16-C), 38.3 (0, 10-C), 35.7 (2, 1-C), 34.5 (1, 25-C), 34.3 (2, 2-C), 32.0 (1, 20-C), 27.7 (2, 6-C), 27.0 (3, 28-C), 24.7 (3, 30-C), 20.8 (3, 27-C), 19.6 (3, 19-C), 18.2 (3, 21-C), 17.7 (3, 18-C), 16.9 (3, 29-C).

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