Novel Triterpenoids from the Fungus *Ganoderma lucidum*Tsuyoshi NISHITOBA, Kyoko ODA, Hiroji SATO
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The structures of eight novel triterpenoids, ganoderiol C (1), D (2), E (3), F (4), G (5), H (6), I (7), and ganolucidic acid E (8), isolated from the fruiting body of *Ganoderma lucidum* were determined by spectroscopic methods. In addition, the absolute configuration at C-23 of ganolucidic acid D (9) was determined from the CD spectrum of its *p*-dimethylaminobenzoate derivative.

We have already reported a series of highly oxidized lanostane triterpenoids, some of them as bitter principles, from the fungus *Ganoderma lucidum*.^{1,2)} Recently, we further isolated the novel triterpene alcohols, ganoderiol C (1), D (2), E (3), F (4), G (5), H (6) and I (7), and triterpene acid, ganolucidic acid E (8), from the fruiting body of the fungus. In this paper, we describe their structural elucidation, and also mention the absolute configuration at C-23 of ganolucidic acid D (9) that was previously reported.³⁾

Ganoderiol C (1) was purified as its diacetate (1a), which gave a molecular ion peak at m/z 602 and was formulated to be $C_{36}H_{58}O_7$ by HR-EI-MS. The IR spectrum of 1a showed the presence of a hydroxyl group (3460 cm^{-1}) and carbonyl groups ($1735, 1705\text{ cm}^{-1}$). The $^1\text{H-NMR}$ signals at δ 4.90 (1H, dd), 4.14 (1H, d), 3.91 (1H, d) and 1.21 (3H, s) indicated that 1a had the same side chain with that of

ganodermanontriol (**10**),⁵⁾ although 24- and 26-hydroxyl groups were acetylated in **1a**. The attachment of an α -ethoxyl group at C-7 was suggested by the signals at δ 3.77 (1H, br. s), 3.61 (1H, dq), 3.35 (1H, dq) and 1.21 (3H, dd), in analogy with the 7 α -methoxyl groups in the mycelial ganoderic acids.²⁾ This assignment

was confirmed by converting **1a** into **10a** with H₂SO₄. The free rotation about the bond between C-7 and the attached oxygen is restricted by 1,3-diaxial-like interactions between the 7 α -ethoxyl group and 5 α -hydrogen and between the former and 14 α -methyl group. Therefore, the 7 α -ethoxyl group may be locat-

TABLE I. ¹³C-NMR DATA OF **1a**, **2**, **3a**, **4** AND **6**
(67.8 MHz in CDCl₃, except for **6** in C₅D₅N)

Carbon	δ , ppm (Number of bonded H)				
	1a	2	3a	4	6
1	35.2 (2)	35.4 (2)	34.6 (2)	36.1 (2)	35.2 (2)
2	34.4 (2)	34.4 (2)	23.7 (2)*	34.9 (2)	28.9 (2)*
3	217.6 (0)	214.6 (0)	79.6 (1)	216.8 (0)	77.1 (1)
4	46.8 (0)	47.3 (0)	37.8 (0)	47.5 (0)	40.1 (1)
5	45.0 (1)	49.1 (1)	49.0 (1)	50.8 (1)	49.6 (1)
6	24.2 (2)	37.2 (2)	35.8 (2)	23.7 (2)	37.2 (2)
7	76.4 (1)	198.1 (0)	198.6 (0)	120.0 (1)	198.7 (0)
8	135.5 (0)	139.6 (0)	139.0 (0)	142.9 (0)	138.9 (0)
9	139.2 (0)	162.8 (0)	164.6 (0)	144.6 (0)	164.9 (0)
10	37.8 (0)	39.5 (0)	39.7 (0)	37.3 (0)	39.5 (0)
11	21.1 (2)	23.9 (2)	23.9 (2)*	117.3 (1)	23.8 (2)
12	30.3 (2)	30.2 (2)	30.2 (2)	37.9 (2)	30.5 (2)
13	45.0 (0)	45.0 (0)	45.0 (0)	43.8 (0)	45.2 (2)
14	50.0 (0)	47.8 (0)	47.8 (0)	50.4 (0)	48.2 (0)
15	28.1 (2)	28.7 (2)	28.8 (2)	27.9 (2)	28.3 (2)
16	31.1 (2)	31.9 (2)	32.0 (2)	31.5 (2)	32.7 (2)
17	50.4 (1)	50.5 (1)	49.9 (1)	50.9 (1)	50.6 (1)
18	16.2 (3)*	16.0 (3)	15.8 (3)	15.8 (3)	16.1 (3)*
19	17.4 (3)	17.9 (3)	16.4 (3)	22.5 (3)	18.3 (3)
20	36.7 (1)	36.6 (1)	36.2 (1)	36.1 (1)	37.3 (1)
21	18.7 (3)	18.9 (3)	18.5 (3)*	18.4 (3)	19.3 (3)
22	32.7 (2)	33.6 (2)	36.5 (2)	36.7 (2)	34.5 (2)
23	26.0 (2)	28.8 (2)	24.7 (2)	24.4 (2)	29.1 (2)*
24	74.8 (1)	79.1 (1)	137.2 (1)	131.7 (1)	77.1 (1)
25	73.3 (0)	73.9 (0)	128.8 (0)	136.8 (0)	74.8 (0)
26	68.5 (2)	67.7 (2)	66.8 (2)	67.7 (2)	69.3 (2)
27	20.2 (3)	20.9 (3)	59.9 (2)	60.2 (2)	20.1 (3)
28	25.3 (3)	25.4 (3)	27.4 (3)	25.5 (3)*	27.9 (3)
29	21.4 (3)	21.4 (3)	21.2 (3)	22.1 (3)	16.0 (3)*
30	26.3 (3)	25.0 (3)	25.0 (3)	25.4 (3)*	25.2 (3)
7 α -OCH ₂ CH ₃	64.0 (2)	—	—	—	—
7 α -OCH ₂ CH ₃	16.0 (3)*	—	—	—	—
-OCOCH ₃	171.1 (0)	—	170.0 (0)	—	—
	170.6 (0)	—	170.8 (0)	—	—
	—	—	170.9 (0)	—	—
-OCOCH ₃	21.0 (3)	—	18.7 (3)*	—	—
	20.8 (3)	—	21.0 (3)	—	—
	—	—	20.9 (3)	—	—

* Assignments may be reversed.

ed at the outside of the skeleton. In this situations, its methylene protons would not be magnetically equivalent and would show the unique coupling pattern in the ^1H -NMR spectrum. The ^{13}C -NMR spectrum of **1a** (Table I) shows the presence of a carbonyl group at C-3 and a double bond between C-8 and C-9. On the basis of these observations, the depicted structure was concluded for **1a**, and therefore, ganoderiol C was assigned to be 7α -ethoxy-24,25,26-trihydroxy- 5α -lanost-8-en-3-one (**1**). It is not clear in this stage whether **1** was a natural product or an artifact.

Ganoderiol D (**2**) was obtained as a mixture with a small amount of ganoderiol E (**3**), which was acetylated to give the diacetate **2a** ($\text{C}_{34}\text{H}_{52}\text{O}_7$) and triacetate **3a** ($\text{C}_{36}\text{H}_{54}\text{O}_7$). The ^1H -NMR spectrum of **2a** was similar to that of **1a**, but showed no signals due to the 7α -ethoxyl group. The ^{13}C -NMR spectrum of crude **2** showed clear data as listed in Table I, and indicates the presence of an α,β -unsaturated carbonyl group (δ 198.1, 162.8 and 139.6), which was supported by the UV absorption maximum (254 nm) of **2a**. The position of the conjugated carbonyl group at C-7 was ascertained from the results of a ^1H -NMR double resonance experiment on **2a**. The signals due to the 5α , 6α and 6β -protons were observed at ABX type at δ 2.14, 2.33 and 2.54, respectively. From these data, the structure for **2a** was determined, and ganoderiol D was deduced to be 24,25,26-trihydroxy- 5α -lanost-8-en-3,7-dione (**2**).

The ^1H -NMR spectrum of **3a** indicated the presence of an acetylated 3β -hydroxyl group [δ 4.51 (1H, dd, $3\alpha\text{-H}$)] and two acetylated allylic alcohols [δ 5.77 (1H, t), 4.66 (2H, s) and 4.56 (2H, s)] in the side chain by analogy with ganoderatriol (**11**).⁴⁾ The presence of an α,β -unsaturated carbonyl group at C-7 was assumed from the ^{13}C -NMR signals (198.6, 164.6 and 139.0; Table I) and the UV absorption maximum (255 nm). This assignment was supported by the ^1H -COSY spectrum, in which the ABX-type coupling of the signals due to the 5α , 6α and 6β -protons was observed. The ^{13}C -NMR signal of C-24 was observed

in a lower field (δ 137.2) than that of C-25 (δ 128.8), in contrast with the data for ganodermanotriol (**10**)⁵⁾ and ganoderiol F (**4**). This result may have been caused by acetylation of the hydroxyl groups at C-26 and C-27 in **3a**. From these spectral evidences the represented structure was deduced for **3a**, and therefore, ganoderiol E was determined to be $3\beta,26,27$ -trihydroxy- 5α -lanosta-8,24-dien-7-one (**3**).

Ganoderiol F (**4**), $\text{C}_{30}\text{H}_{46}\text{O}_3$, showed similar ^1H - and ^{13}C -NMR (Table I) spectra to those of ganoderatriol (**11**), but the presence of a carbonyl group at C-3 in **4**, instead of the β -hydroxyl group in **11** was suggested by the ^{13}C -NMR signal (δ 216.8). In the ^{13}C -NMR spectra of **4** and **11**, some differences were observed in the side chain moiety. This discrepancy is attributable to the solvents used (CDCl_3 for **4** and $\text{C}_5\text{D}_5\text{N}$ for **11**). Consequently, the structure of ganoderiol F was defined to be 26,27-dihydroxy- 5α -lanosta-7,9(11),24-trien-3-one (**4**).

Ganoderiol G (**5**) was formulated to be $\text{C}_{31}\text{H}_{52}\text{O}_5$. Its ^1H -NMR spectrum closely resembled that of **1**, but showed that the 7α -ethoxyl group in **1** was replaced by a 7α -methoxyl group [δ 3.67 (1H, br. s; $7\beta\text{-H}$), and 3.32 (3H, s)]. Therefore, ganoderiol G was concluded to be 24,25,26-trihydroxy- 7α -methoxy- 5α -lanost-8-en-3-one (**5**).

Ganoderiol H (**6**), $\text{C}_{30}\text{H}_{50}\text{O}_5$, showed a similar ^1H -NMR spectrum to that of **2**, but the additional signal at δ 3.27 (1H, dd) indicated the presence of a 3β -hydroxyl group in **6** instead of the carbonyl group in **2**. The ^{13}C -NMR data (Table I) of **6** also support this result. From these spectral evidences, ganoderiol H was elucidated to be $3\beta,24,25,26$ -tetrahydroxy- 5α -lanost-8-en-7-one (**6**).

The ^1H -NMR spectrum of ganoderiol I (**7**), $\text{C}_{31}\text{H}_{50}\text{O}_5$, was similar to that of ganoderiol B (**12**),⁵⁾ but the signals at δ 4.06 (1H, br. s) and 3.33 (3H, s) suggested the presence of a 7α -methoxyl group. The former signal due to $7\beta\text{-H}$ was deshielded by 0.39 ppm more than that of **5**, which was caused by the effect of the 15α -hydroxyl group. From these data, the structure

FIG. 1. CD and UV Spectra of **9b** (—) and **9a** (---).

of ganoderiol I was assigned to be $15\alpha,26,27$ -trihydroxy- 5α -lanosta-8,24-dien-3-one (**7**).

Ganolucidic acid E (**8**) was purified as its methyl ester (**8a**, $C_{31}H_{46}O_5$). In the UV spectrum, **8a** showed the presence of the α,β -unsaturated carbonyl (257 nm) and carboxyl (219 nm) groups. The 1H -NMR spectrum of **8a** closely resembled that of methyl ganolucide D (**9a**),³⁾ but with the hydroxyl group absent at C-23. The olefinic proton at C-24 was observed in a lower field [δ 6.73 (1H, tq)] than that [δ 6.59 (1H, dq)] of **9a**. From these observations, the depicted structure was proposed for **8a**, and the original ganolucidic acid E was established to be 15α -hydroxy-3,11-dioxo- 5α -lanosta-8,24*E*-dien-26-oic acid (**8**).

Biogenetically, ganolucidic acid D (**9**) may be produced from ganolucidic acid E (**8**) by allylic oxidation at C-23, and be further converted to a series of ganoderic acids.¹⁾ So it is important to resolve the stereochemistry of the hydroxyl group at C-23 in **9**. **9a** was converted to its mono-*p*-dimethylaminobenzoate derivative (**9b**, $C_{40}H_{55}NO_7$). The UV and CD spectra of **9b** are presented in Fig. 1 with those of **9a**, **9b** showing a positive Cotton effect at 315 nm ($\Delta\epsilon +1.9$) caused by mutual interaction between the conjugated carboxyl group and the *p*-dimethylaminobenzoate chromophore. Taking account of this result and the 1H -NMR

coupling constant (9.2 Hz) between 23-H and 24-H in **9b**, the positive chirality between the two chromophores was designated as shown in Fig. 1.⁶⁾ Therefore, the absolute configuration at C-23 in **9b** was unequivocally defined to be *S*. Since no stereochemical inversion existed in the converting process from **9** into **9b**, the absolute configuration at C-23 in **9** was also assigned to be *S*.

EXPERIMENTAL

General. Melting points (mp) 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 with JASCO J-20 instrument. IR and UV spectra were obtained with a Hitachi 285 spectrometer and Hitachi EPS-3T spectrophotometer, respectively. 1H - and ^{13}C -NMR spectra were recorded on a JEOL FX-270 spectrometer. Column chromatography was carried out with Wakogel C-200 (Wako), Kieselgel 60 (230~400 mesh, Merck) and a Lobar column (RP-18, Merck). PTLC was performed on pre-coated Kieselgel 60 F_{254} (0.5 mm thickness, Merck) and RP-18 F_{254} s (Merck). TLC was done on pre-coated Kieselgel 60 F_{254} plates (0.2 mm thickness, Merck).

Extraction and isolation. The neutral fraction (217 g) obtained from the EtOH extract of *G. lucidum* (a mixture of two strains⁷⁾) was separated into three fractions (Fr. I, Fr. II and Fr. III) as previously reported.⁵⁾ Fr. I was further separated by silica gel and Lobar column chromatographies into several fractions (Frs. D, K, M and P). Frs. D and K were acetylated (Ac_2O /pyridine) and subjected to silica gel column chromatography to give com-

pounds **1a** (107 mg) and **2a** (50.5 mg), and **3a** (6.9 mg), respectively. Compound **4** (56 mg) was crystallized (CHCl_3 -MeOH) from Fr. K. Compound **8a** (3 mg) was obtained by PTLC of Fr. P after methylation with CH_3N_2 . On the other hand, Fr. III was rechromatographed four times on a silica gel column to give Fr. U, which was further purified by the combination of column chromatography, PTLC and crystallization to yield compounds **5** (3 mg), **6** (15 mg) and **7** (3 mg).

24,26-Di-O-acetyl ganoderiol C (1a). Colorless syrup, $[\alpha]_{\text{D}}^{23} + 54^\circ$ ($c=0.1$, EtOH). MS m/z : 602.4191 (M^+ , $\text{C}_{36}\text{H}_{58}\text{O}_7$, 2%), 587 (5), 556 ($\text{M}^+ - \text{C}_2\text{H}_5\text{OH}$, 8), 496 (8), 309 (46), 43 (100). IR ν_{max} (film) cm^{-1} : 3460, 2960, 2870, 1735, 1705. NMR δ_{H} (CDCl_3): 4.90 (1H, dd, $J=10.3$, 2.6; 24-H), 4.14 (1H, d, $J=11.4$; 26-H), 3.91 (1H, d, $J=11.4$; 26-H), 3.77 (1H, br. s; 7 β -H), 3.61 (1H, dq, $J=8.8$, 7.0; 7 α -OCH₂CH₃), 3.35 (1H, dq, $J=8.8$, 7.0; 7 α -OCH₂CH₃), 1.21 (3H, dd, $J=7.0$, 7.0; 7 α -OCH₂CH₃), 1.21 (3H, s; 27-H), 1.11 (3H, s; 28-H), 1.08 (3H, s; 29-H), 1.06 (3H, s; 19 or 30-H), 1.05 (3H, s; 19 or 30-H), 0.90 (3H, d, $J=6.6$; 21-H), 0.62 (3H, s; 18-H), 2.11 (3H, s; OCOCH₃), 2.07 (3H, s; OCOCH₃). Alkaline treatment of **1a** gave the original ganoderiol C (**1**), which was confirmed on TLC.

Acid treatment of 1a. **1a** (6.2 mg) was dissolved in acetone (2.5 ml), and to the solution 5N- H_2SO_4 was added at 0°C. The reaction mixture was stirred at room temperature for thirty minutes. After removing the acetone *in vacuo*, the solution was diluted with water and extracted with CHCl_3 . The organic layer was dried with Na_2SO_4 and then concentrated to give the product (**10a**), which was purified by PTLC (5.5 mg, yield). MS m/z : 556.3793 (M^+ , $\text{C}_{34}\text{H}_{52}\text{O}_6$, 3%), 538 (5), 496 (5), 309 (50), 269 (26), 55 (36), 43 (100). NMR δ_{H} (CDCl_3): 5.50 (1H, d, $J=6.2$; 7-H), 5.38 (1H, d, $J=5.5$; 11-H), 4.90 (1H, dd, $J=10.0$, 2.7; 24-H), 4.14 (1H, d, $J=11.4$; 26-H), 3.91 (1H, d, $J=11.4$; 26-H), 2.77 (1H, ddd, $J=14.8$, 14.8, 6.0; 2 β -H), 1.21 (3H, s; 27-H), 1.20 (3H, s; 19-H), 1.13 (3H, s; 28-H), 1.09 (3H, s; 29-H), 0.91 (3H, d, $J=6.2$; 21-H), 0.87 (3H, s; 30-H), 0.58 (3H, s; 18-H), 2.11 (3H, s; OCOCH₃), 2.08 (3H, s; OCOCH₃).

24,26-Di-O-acetyl ganoderiol D (2a). Colorless syrup, $[\alpha]_{\text{D}}^{21} + 8^\circ$ ($c=0.1$, MeOH). MS m/z : 572.3639 (M^+ , $\text{C}_{34}\text{H}_{52}\text{O}_7$, 6%), 557 (6), 339 (15), 327 (13), 69 (65), 57 (87), 43 (100). IR ν_{max} (film) cm^{-1} : 3440, 2950, 2860, 1730, 1705, 1655, 1575. UV λ_{max} (MeOH) nm (ϵ): 254 (9730). NMR δ_{H} (CDCl_3): 4.90 (1H, dd, $J=9.9$, 2.6; 24-H), 4.13 (1H, d, $J=11.4$; 26-H), 3.90 (1H, d, $J=11.4$; 26-H), 2.70 (1H, ddd, $J=15.8$, 12.1, 7.0; 2 β -H), 2.54 (1H, dd, $J=16.0$, 14.5; 6 β -H), 2.46 (1H, ddd, $J=15.8$, 5.9, 3.7; 2 α -H), 2.33 (1H, dd, $J=16.0$, 3.3; 6 α -H), 2.14 (1H, dd, $J=14.5$, 3.3; 5 α -H), 1.33 (3H, s; 30-H), 1.20 (3H, s; 27-H), 1.12 (3H, s; 28-H), 1.10 (3H, s; 29-H), 0.93 (3H, s; 19-H), 0.92 (3H, d, $J=5.9$; 21-H), 0.67 (3H, s; 18-H).

3,26,27-Tri-O-acetyl ganoderiol E (3a). Colorless syrup, $[\alpha]_{\text{D}}^{21} + 18^\circ$ ($c=0.1$, MeOH). MS m/z : 598.3836 (M^+ , $\text{C}_{36}\text{H}_{54}\text{O}_7$, 13%), 583 (11), 538 (15), 463 (28), 369 (23), 121 (42), 43 (100). IR ν_{max} (film) cm^{-1} : 3000, 2940, 2860, 1720, 1650, 1570. UV λ_{max} (MeOH) nm (ϵ): 255 (9160). NMR δ_{H} (CDCl_3): 5.77 (1H, t, $J=7.3$; 24-H), 4.66 (2H, s; 27-H), 4.56 (2H, s; 26-H), 4.51 (1H, dd, $J=11.4$, 4.4; 3-H), 2.46 (1H, dd, $J=16.0$, 12.0; 6 β -H), 2.38 (1H, dd, $J=16.0$, 5.0; 6 α -H), 1.19 (3H, s; 30-H), 0.95 (3H, s; 19-H), 0.93 (3H, d, $J=5.9$; 21-H), 0.91 (3H, s; 28-H), 0.89 (3H, s; 29-H), 0.65 (3H, s; 18-H), 2.06 (9H, s; OCOCH₃ $\times$ 3).

Ganoderiol F (4). **4** was obtained as pale yellow plates (from CHCl_3 -MeOH), mp 116~120°C, $[\alpha]_{\text{D}}^{21} + 42^\circ$ ($c=0.1$, MeOH). MS m/z : 454.3430 (M^+ , $\text{C}_{30}\text{H}_{46}\text{O}_3$, 4%), 436 (6), 309 (100), 69 (24), 55 (40), 41 (31). IR ν_{max} (film) cm^{-1} : 3350, 2900, 2850, 1690. UV λ_{max} (MeOH) nm (ϵ): 237 (16600), 245 (19200), 253 (12500). NMR δ_{H} (CDCl_3): 5.56 (1H, t, $J=7.3$; 24-H), 5.51 (1H, d, $J=6.9$; 7-H), 5.39 (1H, d, $J=5.9$; 11-H), 4.33 (2H, s; 27-H), 4.22 (2H, s; 26-H), 2.78 (1H, ddd, $J=14.7$, 14.7, 5.5; 2 β -H), 1.20 (3H, s; 19-H), 1.13 (3H, s; 28-H), 1.09 (3H, s; 29-H), 0.92 (3H, d, $J=6.6$; 21-H), 0.88 (3H, s; 30-H), 0.59 (3H, s; 18-H).

Ganoderiol G (5). Colorless syrup, $[\alpha]_{\text{D}}^{24} + 34^\circ$ ($c=0.1$, MeOH). MS m/z : 504.3860 (M^+ , $\text{C}_{31}\text{H}_{52}\text{O}_5$, 22%), 489 (43), 472 (17), 457 (19), 366 (64), 95 (55), 69 (62), 55 (78), 43 (100). IR ν_{max} (film) cm^{-1} : 3380, 2920, 2870, 1700. NMR δ_{H} (CDCl_3): 3.84 (1H, d, $J=11.4$; 26-H), 3.67 (1H, br. s; 7 β -H), 3.49 (1H, d, $J=11.0$; 26-H), 3.47 (1H, t, $J=8.0$; 24-H), 3.32 (3H, s; 7 α -OCH₃), 1.26 (3H, s; 27-H), 1.12 (3H, s; 28-H), 1.09 (3H, s; 29-H), 1.05 (3H, s; 30-H), 1.05 (3H, s; 19-H), 0.90 (3H, d, $J=8.8$; 21-H), 0.64 (3H, s; 18-H).

Ganoderiol H (6). **6** was obtained as colorless needles, mp 200~201.5°C, $[\alpha]_{\text{D}}^{24} + 22^\circ$ ($c=0.1$, MeOH). MS m/z : 490.3625 (M^+ , $\text{C}_{30}\text{H}_{50}\text{O}_5$, 30%), 475 (47), 415 (46), 381 (35), 329 (35), 121 (74), 69 (59), 55 (68), 43 (100). IR ν_{max} (film) cm^{-1} : 3380, 2950, 2860, 1640. UV λ_{max} (MeOH) nm (ϵ): 255 (9170). NMR δ_{H} (CDCl_3): 3.82 (1H, d, $J=11.4$; 26-H), 3.46 (1H, d, $J=11.4$; 26-H), 3.43 (1H, dd, $J=10.0$, 1.5; 24-H), 3.27 (1H, dd, $J=11.2$, 4.9; 3 α -H), 2.46 (1H, dd, $J=16.5$, 11.7; 6 β -H), 2.38 (1H, dd, $J=16.5$, 6.2; 6 α -H), 1.17 (3H, s; 30-H), 1.11 (3H, s; 27-H), 1.00 (3H, s; 28-H), 0.93 (3H, d, $J=7.7$; 21-H), 0.92 (3H, s; 19-H), 0.88 (3H, s; 29-H), 0.66 (3H, s; 18-H).

Ganoderiol I (7). Colorless syrup, $[\alpha]_{\text{D}}^{22} + 53^\circ$ ($c=0.1$, MeOH). MS m/z : 502.3675 (M^+ , $\text{C}_{31}\text{H}_{50}\text{O}_5$, 3%), 470 (7), 452 (2), 349 (59), 325 (45), 175 (66), 69 (60), 55 (99), 43 (100). IR ν_{max} (film) cm^{-1} : 3380, 2920, 2870, 1700. NMR δ_{H} (CDCl_3): 5.55 (1H, t, $J=7.3$; 24-H), 4.35 (1H, t, $J=8.8$; 15 β -H), 4.33 (2H, s; 27-H), 4.22 (2H, s; 26-H), 4.06 (1H, br. s; 7 β -H), 3.33 (3H, s; 7 α -OCH₃), 2.58 (1H, ddd, $J=15.9$, 10.6, 7.3; 2 β -H), 2.46 (1H, ddd, $J=15.9$, 7.3, 3.8; 2 α -

H), 1.13 (3H, s; 28-H), 1.10 (3H, s; 29 or 30-H), 1.08 (3H, s; 29 or 30-H), 1.02 (3H, s; 19-H), 0.89 (3H, d, $J=6.6$; 21-H), 0.66 (3H, s; 18-H).

Methyl ganolucidate E (8a). Colorless syrup, $[\alpha]_D^{24} + 154^\circ$ ($c=0.1$, MeOH). MS m/z : 498.3335 (M^+ , $C_{31}H_{46}O_5$, 22%), 470 (18), 401 (100), 287 (69), 95 (34), 69 (28), 55 (36), 41 (29). IR $\nu_{\max}$ (film) cm^{-1} : 3450, 2940, 2920, 2870, 1700, 1635, 1570. UV $\lambda_{\max}$ (MeOH) nm (ϵ): 219 (12100), 257 (7080). NMR δ_H ($CDCl_3$): 6.73 (1H, tq, $J=7.5$, 1.5; 24-H), 4.39 (1H, dd, $J=9.2$, 5.7; 15 β -H), 3.01 (1H, ddd, $J=13.9$, 8.2, 5.6; 1 β -H), 2.72 (1H, d, $J=17.2$; 12 α -H), 2.45 (1H, d, $J=16.9$; 12 β -H), 1.83 (3H, s; 27-H), 1.18 (3H, s; 30-H), 1.13 (3H, s; 19 or 28-H), 1.12 (3H, s; 19 or 28-H), 1.08 (3H, s; 29-H), 0.89 (3H, s; 18-H), 0.89 (3H, d, $J=6.2$; 21-H), 3.74 (3H, s; $COOCH_3$).

Preparation of compound 9b. Methyl ganolucidate D (**9a**, 2.9 mg) and *p*-dimethylaminobenzoyl chloride (5 mg) were dissolved in anhydrous pyridine (0.1 ml) and refluxed under nitrogen with stirring. Two hours later, the reaction was terminated by adding ice-cold water to the reaction mixture, which was then extracted with EtOAc. After washing with sat. aq. NH_4Cl and sat. aq. NaCl, the organic layer was dried with Na_2SO_4 and concentrated. The products were purified by PTLC to yield the 23-*O*-monobenzoate (**9b**, $C_{40}H_{55}NO_7$, 0.4 mg) and 15 α ,23-*O*-dibenzoate (**9c**, $C_{49}H_{64}N_2O_8$, 1.5 mg). The physicochemical properties for **9b** are as follows: MS m/z : 661.3966 (M^+ , 6.6%), 165 (100), 148 (40), 125 (23), 95 (16), 69 (22), 55 (28), 44 (44). UV $\lambda_{\max}$ (EtOH) nm (ϵ): 315 (17500), 258 (5780). CD λ ($c=0.01$, EtOH) nm ($\Delta\epsilon$): 328 (0), 315 (+1.9), 256 (+6.6), 227 (0). NMR δ_H ($CDCl_3$): 7.88 (2H, d, $J=9.0$), 6.64 (2H, d, $J=9.0$), 6.64 (1H, overlapped; 24-H), 5.80 (1H, m; 23-H), 4.37 (1H, m; 15 β -H), 3.75 (3H, s; $COOCH_3$), 3.04 (6H, s), 2.70 (1H, d, $J=17.4$; 12 α -H), 2.43 (1H, d, $J=17.4$; 12 β -H), 2.00 (3H, s; 27-H), 1.26 (3H, s;

30-H), 1.12 (6H, s; 19 and 29-H), 1.08 (3H, s; 28-H), 0.99 (3H, d, $J=6.6$; 21-H), 0.86 (3H, s; 18-H). NMR δ_H (C_5D_5N): 8.25 (2H, d, $J=9.2$), 7.00 (1H, dq, $J=9.2$, 1.5; 24-H), 6.74 (2H, d, $J=9.2$), 6.15 (1H, m; 23-H), 4.64 (1H, m), 3.65 (3H, s), 2.92 (1H, d, $J=17.2$), 2.80 (6H, s), 2.64 (1H, d, $J=17.2$), 2.17 (1H, d, $J=1.5$; 27-H), 1.48 (3H, s), 1.25 (3H, s), 1.12 (6H, s), 1.09 (3H, d, $J=6.6$), 0.94 (3H, s).

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