[Chem. Pharm. Bull. 34(10)4018—4029(1986)]

Constituents of the Fungus *Ganoderma lucidum* (FR.) KARST. II.[1] Structures of Ganoderic Acids F, G, and H, Lucidenic Acids D2 and E2, and Related Compounds[2]

TOHRU KIKUCHI,* SATOKO KANOMI (née MATSUDA), YOSHIHIRO MURAI,
SHIGETOSHI KADOTA, KOJI TSUBONO, and ZEN-ICHI OGITA

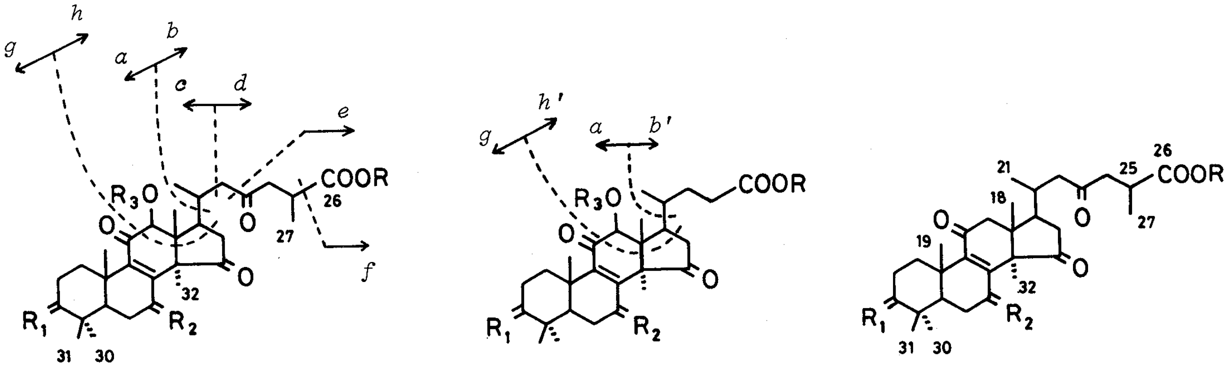
Research Institute for Wakan-Yaku (Oriental Medicines), Toyama Medical and Pharmaceutical University, 2630 Sugitani, Toyama 930–01, Japan

(Received March 22, 1986)

Seven new triterpenes, ganoderic acids F, G, and H, lucidenic acids D2 and E2, compound C5′, and compound C6, were isolated from the surface part of gills of *Ganoderma lucidum*. The structures **3a**, **1a**, **4a**, **6a**, **7a**, **2b**, and **5b** were proposed for these compounds, respectively. Detailed analyses of the proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra were performed by using two-dimensional (2-D) ^{1}H–^{1}H and ^{1}H–^{13}C shift correlation techniques.

Keywords——*Ganoderma lucidum*; Polypolaceae; triterpene acid; ganoderic acid; lucidenic acid; 2-D NMR; ^{1}H–^{1}H shift correlation NMR; ^{1}H–^{13}C shift correlation NMR; MS

In the preceding paper,[1] we reported the isolation of sixteen new triterpene acids together with five known compounds from the surface part of gills of *Ganoderma lucidum* (FR.) KARST. (Polypolaceae), which is widely used as a home remedy (Reishi). Structure elucidation of seven components, ganoderic acids C2, E, I, and K, lucidenic acid F, compound B8, and compound B9, was also reported. This paper describes in detail the



1: $R_1 = <^{\text{OH}}_{\text{H}}$, $R_2 = <^{\text{OH}}_{\text{H}}$, $R_3 = \text{H}$

2: $R_1 = \text{O}$, $R_2 = <^{\text{OH}}_{\text{H}}$, $R_3 = \text{H}$

3: $R_1 = \text{O}$, $R_2 = \text{O}$, $R_3 = \text{Ac}$

4: $R_1 = <^{\text{OH}}_{\text{H}}$, $R_2 = \text{O}$, $R_3 = \text{Ac}$

5: $R_1 = <^{\text{OH}}_{\text{H}}$, $R_2 = \text{O}$, $R_3 = \text{H}$

11: $R_1 = <^{\text{OAc}}_{\text{H}}$, $R_2 = <^{\text{OAc}}_{\text{H}}$, $R_3 = \text{Ac}$

6: $R_1 = \text{O}$, $R_2 = \text{O}$, $R_3 = \text{Ac}$

7: $R_1 = <^{\text{OH}}_{\text{H}}$, $R_2 = \text{O}$, $R_3 = \text{Ac}$

12: $R_1 = <^{\text{OH}}_{\text{H}}$, $R_2 = <^{\text{OH}}_{\text{H}}$, $R_3 = \text{H}$

8: $R_1 = <^{\text{OH}}_{\text{H}}$, $R_2 = <^{\text{OH}}_{\text{H}}$

9: $R_1 = \text{O}$, $R_2 = <^{\text{OH}}_{\text{H}}$

10: $R_1 = \text{O}$, $R_2 = \text{O}$

a: $R = \text{H}$, **b**: $R = \text{CH}_3$

Chart 1

structure elucidation of five new compounds named ganoderic acids F (**3a**), G (**1a**), and H (**4a**),[3] lucidenic acids D2 (**6a**) and E2 (**7a**),[4] and two related compounds tentatively named compound C5′ (**2b**) and compound C6 (**5b**), all of which were isolated as the methyl esters. These compounds are minor components of the fungus, and their structure analyses were done with the aid of two-dimensional nuclear magnetic resonance (2-D NMR) spectral measurements.

Methyl ganoderate G (**1b**) showed mp 134—135 °C and $[\alpha]_D$ +64° ($CHCl_3$), and its molecular formula was determined to be $C_{31}H_{46}O_8$ from the mass spectrum (MS) (M^+: *m/z* 546) and high-resolution MS measurements. It showed an absorption band at 252.5 nm (log ε: 4.01) due to an α,β-unsaturated carbonyl grouping in the ultraviolet (UV) absorption spectrum and characteristic absorptions at 3450 (hydroxyl), 1735 (sh) (five-membered ketone), 1730 (ester), 1720 (ketone), 1660 cm^{-1} (α,β-unsaturated ketone) in the infrared (IR) absorption spectrum.

The ^1H-NMR spectrum of **1b** exhibited signals due to three carbinol methine protons (δ 3.20, 4.35, and 4.77) and two *sec*- and five *tert*-methyl groups along with other signals, which were fully analyzed by the application of ^1H–^1H shift correlation spectroscopy (Fig. 1 and Table I). The whole spectral pattern of **1b** closely resembled that of methyl ganoderate B (**8b**)[5] except for the appearance of a new doublet (δ 4.35, $J=2.5$ Hz; changes to a singlet on addition of deuterium oxide) due to one of the carbinol methine protons instead of a pair of doublets arising from the 12-methylene protons in the latter (**8b**) and the appreciable upfield and downfield shifts of the 18- and 19-methyl signals, respectively, suggesting that **1b** may be the 12-hydroxy derivative of **8b**. This was substantiated by the ^{13}C-NMR spectrum of **1b**, which was also analyzed by means of ^1H–^{13}C shift correlation spectroscopy (Fig. 2). As shown in Table II, the signals assignable to C-12 and C-13 were markedly shifted downfield (27.6 and 6.6 ppm, respectively), while the signal due to C-18 was shifted upfield by 5.4 ppm,

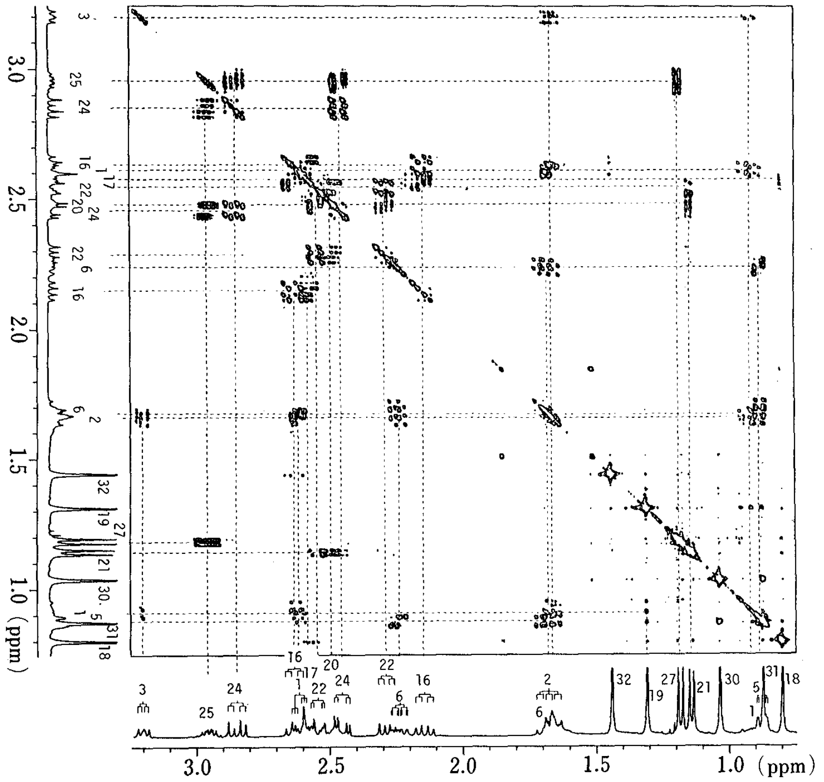


Fig. 1. Contour Map of the Highly Resolved ^1H–^1H Shift Correlated Spectrum of Methyl Ganoderate G (**1b**) in the Upfield Region

TABLE I. ^{1}H-NMR Spectral Data for Lanostane-

Compd. Proton	**1b**[a]	**2b**[a]	**5b**[a]	**3b**[a]	**4b**[a]
1-H (α)	0.92[b] ddd (13, 10, 5)	1.34[b] ddd (13.2, 11, 7)	1.14[b] td (13, 4.5)	1.72[b] ddd (14, 9, 6)	1.18[b] td (13, 5)
1-H (β)	2.61 dt (13, 4.0)	2.79 ddd (13, 7, 4.5)	2.76 dt (13.5, 4)	2.76 ddd (14, 8, 5)	2.73 dt (13.5, 4)
2-H (α)	1.65 m	2.40 ddd (15.8, 6.5, 4.5)	*ca.* 1.75	2.47 ddd (15.5, 8.5, 6)	1.67 tt-like
2-H (β)		2.64 ddd (15.8, 11.5, 7)		2.61 ddd (15.5, 9.5, 6)	1.74 m
3-H	3.20 dd (10, 7)		3.27 dd (11, 5.5)		3.26 dd (11, 5)
5-H	0.89 dd (13.5, 1.8)	1.47 dd (14, 2.3)	1.56 dd (14.5, 2.7)	2.31 dd (15, 2.5)	1.56 dd (14.5, 2.5)
6-H (α)	2.24 ddd (13.5, 8.5, 1.5)	2.18 ddd (13.5, 8, 2)	2.58 dd (14.5, 2.6)	2.49 dd (14, 2.5)	2.58 dd (14, 2.5)
6-H (β)	1.68 td (13.5, 9)	1.78 td (14, 9)	2.69 t (14.5)	2.72 dd (15, 14)	2.68 t (14)
7-H (α)	4.77 td (9, 4.5)	4.84 td (8.5, 4.5)			
12-H (α)	4.35[c] d (2.5)	4.36[c] d (2)	4.51 d (3)	5.67 s	5.62[c] s
12-H (β)					
16-H (α)	2.63 dd (18, 8.2)	2.65 dd (18.8, 8.5)	2.71 dd (16.5, 9.8)	2.79 dd (18, 10)	2.77 dd (18, 9.8)
16-H (β)	2.15 dd (18, 8.5)	2.17 dd (18.7, 9.2)	1.90 dd (16.5, 6.5)	1.91 dd (18, 8)	1.91 dd (18, 8)
17-H	2.57 m	*ca.* 2.57	*ca.* 2.66	2.57 ddd (10, 8, 5.5)	2.53 ddd (9.5, 8, 6)
20-H	2.49	2.48	2.31 m	2.30 m	2.31 m
22-H	2.29 dd (15.8, 8.5)	2.30 dd (15.5, 8)	2.29 dd (19, 8.5)	2.31 d-like (13.5)	2.31 d-like
22-H	2.54[d] dd (15.8, 3.5)	2.55[d] dd (15.5, 4)	2.46[d] dd (19.8, 7.5)	2.42 d-like (14)	2.42 m
23-H					
23-H					
24-H	2.45 dd (17.5, 5)	2.46 dd (17.5, 5)	2.45 dd (17.5, 5)	2.42 dd (17.5, 5)	2.42 dd (17.5, 5)
24-H	2.85 dd (17.5, 9)	2.86 dd (17.5, 8.5)	2.84 dd (17.5, 8.5)	2.83 dd (17.5, 8.8)	2.82 dd (17.5, 8.5)
25-H	2.96 dqd (8.8, 7, 5)	2.96 dqd (8.5, 7, 5)	2.95 dqd (8.5, 7, 5)	2.95 dqd (8.5, 7, 5)	2.95 dqd (8.5, 7, 5)
18-H_3	0.80	0.84	0.65	0.85	0.82
19-H_3	1.32	1.43	1.37	1.33	1.33
21-H_3	1.14 d (6)	1.15 d (6.4)	1.12 d (6)	0.99 d (6)	0.99 d (6)
27-H_3	1.19 d (7)	1.19 d (7)	1.18 d (7)	1.18 d (7)	1.18 d (7)
30-H_3	1.04	1.13	1.03	1.14	1.03
31-H_3	0.88		0.90	1.12	0.88
32-H_3	1.44	1.44	1.70	1.80	1.73
COOC$\underline{H}_3$	3.68	3.68	3.68	3.68	3.67
O$\underline{H}$	4.37 d (4.5) 4.01 d (2.5)	4.46 d (4.5) 3.95 d (2)	3.90 d (3)		
C$\underline{H}_3$COO				2.25	2.24

δ values in $CDCl_3$ and coupling constants in Hz. Previous assignments of some signals were revised (ref. 2). *a*) ^{1}H–^{1}H
e) Assignments were confirmed by NOE experiments.

Type Triterpenes from *Ganoderma lucidum*

8b[a]	**9b**[a]	**10b**[a]	**6b**[a]	**7b**[a]	**12b**[a]
0.98[b] td	1.47[b] dt	1.74[b] ddd	1.73[b] ddd	1.18[b] td	0.92[b] td
(14, 5.5)	(13.5, 8.5)	(14, 9.5, 6)	(14.5, 10, 6.5)	(13, 4.5)	(13, 6)
2.83 dt	2.95 ddd	2.87 ddd	2.77 ddd	2.73 dt	2.62 dt
(13.5, 3.5)	(13.5, 7.5, 5.5)	(14, 8, 5.5)	(14, 8.5, 6)	(13.5, 3.5)	(13, 3.5)
ca. 1.60	2.46 ddd	2.47 ddd	2.425 ddd	1.72 m	*ca.* 1.66
	(16, 8, 5.5)	(15, 8, 6.5)	(15.5, 8, 5.5)		
ca. 1.66	2.54 ddd	2.61 ddd	2.61 ddd		
	(16, 8.5, 7.5)	(15, 9.7, 6)	(15.5, 9.5, 6)		
3.20 dd				3.26 dd	3.21 dd
(10.5, 5.5)				(11, 5)	(9, 7)
0.87 dd	1.56 dd	2.32 dd	2.31 dd	1.56 dd	0.88 dd
(13, 1.5)	(13, 1.5)	(14.8, 2.8)	(15, 2.5)	(14.2, 2.5)	(13, 2)
2.18 ddd	2.11 ddd	2.47 dd	2.49 dd	2.58 dd	2.24 ddd
(13, 8, 1.5)	(13, 8, 1.5)	(13.4, 2.8)	(15, 2.5)	(14, 2.5)	(13.5, 8.5, 2)
1.61 td	1.67 td	2.69 dd	2.73 dd	2.67 t	1.68 td
(13, 9.5)	(13, 9.2)	(15, 13.4)	(14.8, 14)	(14)	(13, 8.8)
4.79 ddd	4.87 ddd				4.78 td
(9.5, 8, 4.5)	(9.2, 8, 4.5)				(8.5, 4.5)
2.77[c] br d	2.77[c] br d	2.87[c] br d	5.67 s	5.62[c] s	4.36 d
(17)	(17.5)	(16.2)			(2.5)
2.69 d	2.72 d	2.75 d			
(17)	(17.5)	(16.2)			
2.67 m	2.68	2.74 dd	2.83 dd	2.79 dd	2.66 dd
		(18.2, 9.1)	(18.5, 10)	(18.2, 9.5)	(19.5, 8.5)
2.05 m	2.07	1.86 dd	2.08 dd	2.08 dd	2.29 dd
		(18.2, 8.4)	(18.5, 8)	(18.2, 8.1)	(19.5, 10)
2.12 m	2.13 m	2.24 dt	2.48 dt	2.46 dt	2.46 ddd
		(10, 8.5)	(10, 8)	(9, 8)	(10, 8.5, 5.5)
ca. 2.14 m	*ca.* 2.16 m	2.10 m	1.64 m	1.66 m	1.93 m
2.36 d		2.359 d	1.30 dtd	1.29 dtd	1.28 dtd
(6.4)	2.37 d	(6.7)	(13.5, 8.5, 5)	(14, 8.5, 5)	(13.5, 9, 5)
2.362[d] d	(5)	2.361[d] d	1.84[d] dtd	1.84[d] dtd	1.85[d] dddd
(4.6)		(4.9)	(13.5, 8.5, 2.5)	(13.5, 8, 2.5)	(13, 10, 6.5, 2.5)
			2.28 dt	2.27 dt	2.30 ddd
			(16, 8.5)	(16, 8)	(16, 9, 6.5)
			2.41 ddd	2.40 ddd	2.42 ddd
			(16, 8.5, 5.5)	(16, 8.8, 5.5)	(15, 9.5, 5.5)
2.43 dd	2.44 dd	2.43 dd			
(17.5, 5)	(17.5, 5)	(17.7, 5.2)			
2.85 dd	2.85 dd	2.83 dd			
(17.5, 8.5)	(17.5, 8.8)	(17.7, 9)			
2.96 dqd	2.96 dqd	2.96 dqd			
(8.8, 7, 5)	(9, 7, 5)	(9, 7, 5)			
1.00	1.03	0.89	0.86	0.83	0.80
1.22	1.26	1.28	1.33	1.33	1.31
0.99 d (6)	1.00 d (6)	0.98 d (6.4)	1.00 d (6.8)	1.00 d (6.8)	1.13 d (6.7)
1.19 d (7)	1.19 d (7)	1.19 d (7)			
1.03	1.13	1.14[e]	1.14[e]	1.03[e]	1.04
0.85	1.11	1.12	1.12	0.89	0.87
1.34	1.34	1.64	1.81	1.73	1.44
3.68	3.69	3.68	3.68	3.67	3.67
4.03 d (4.5)	4.055 d (4.5)				3.98 d (2.5)
					4.42 d (4.5)
				2.22	

Correlation spectra were measured. *b—d*) Long-range coupling was observed with 19-Me, 18-Me, and 21-Me, respectively.

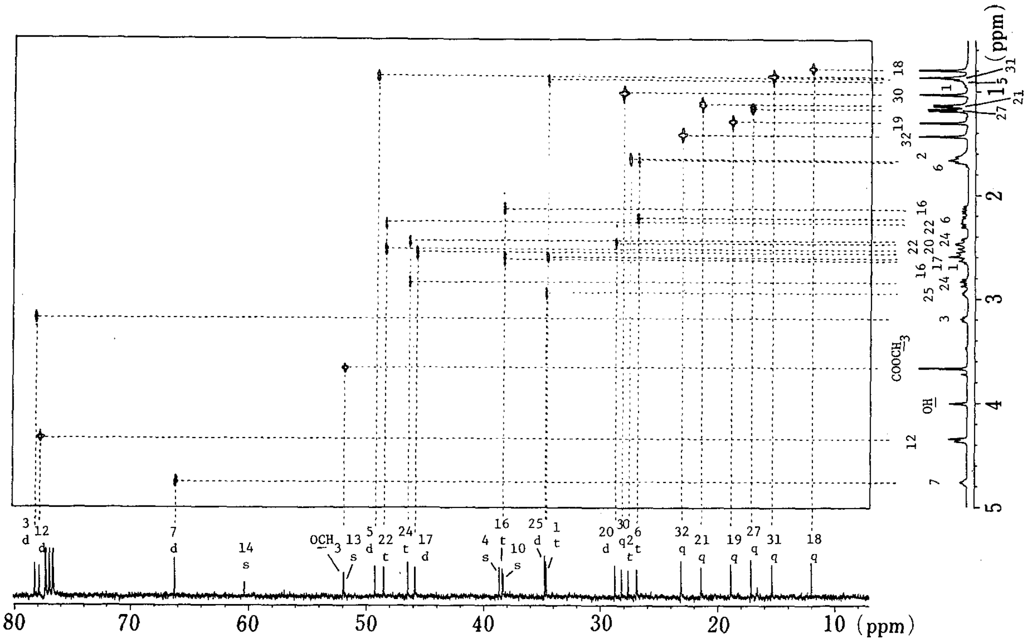


Fig. 2. Contour Map of the ^1H–^{13}C Shift Correlated Spectrum of Methyl Ganoderate G (**1b**) in the Upfield Region

The ^1H shifts are shown on the ordinate and the ^{13}C shifts on the abscissa. The multiplicities of carbon signals were determined by means of off-resonance, and are indicated as s, d, t, and q.

compared with the corresponding signals in **8b**.

In accordance with the above assumption, the MS of **1b** exhibited fragment peaks at *m/z* 403 (*c*), 384 ($c-H-H_2O$), 375 (*a*), 357 ($a-H_2O$), 306 ($g+H$, base peak), 287 ($g-H_2O$), 241 (*h*), and 191 ($h-H_2O-MeOH$), which could be reasonably explained by the fragmentations depicted in Chart 1. The characteristic peaks arising from the side chain were also observed at *m/z* 171 (*b*), 139 ($b-MeOH$), 129 (*e*), and 59 (*f*).[5] Furthermore, acetylation of **1b** yielded the triacetate (**11b**), which showed the ^1H-NMR signal due to the 12-methine proton at δ 5.69 as a singlet. This signal showed about 10% nuclear Overhauser effect (NOE) increase upon irradiation of the 32-methyl protons (δ 1.42), indicating that the 12-acetoxyl group is in β-configuration. Based on these findings, the structure of methyl ganoderate G was assigned as **1b**.

Compound C5′ (**2b**), mp 118.5—121.5 °, $[\alpha]_D$ +101 ° ($CHCl_3$), showed an absorption band (251 nm) due to a conjugated carbonyl group in the UV spectrum and a hydroxyl band (3400 cm^{-1}) and strong carbonyl bands (1740—1650 cm^{-1}) in the IR spectrum. The MS of **2b** exhibited the molecular ion peak at *m/z* 544 and its molecular formula, $C_{31}H_{44}O_8$, was confirmed by high-resolution MS measurement. In the ^1H-NMR spectrum, **2b** showed signals due to two carbinol methine protons (δ 4.36 and 4.84) along with two *sec*- and five *tert*-methyl signals (Table I). The whole spectral pattern was similar to those of methyl ganoderate C1 (**9b**)[6] and methyl ganoderate G (**1b**), as can be seen in Table I, suggesting that **2b** may be the 12-hydroxy derivative of **9b** or the 3-oxo derivative of **1b**. This was supported by the analysis of its ^{13}C-NMR spectrum, compared with those of **9b** and **1b**; the signal assignable to C-12 appeared at δ 78.1 (Table II). Furthermore, the fragmentation pattern in the MS of **2b** was parallel with that of **1b**, as shown in Table III. Eventually, compound C5′ was found to be identical with methyl ganoderate D (**2b**), reported by Sakamura *et al.*,[7] by spectral comparisons.

Methyl ganoderate F (**3b**), amorphous powder, $[\alpha]_D$ +111 ° ($CHCl_3$), has the molecular

TABLE II. ^{13}C-NMR Spectral Data for Lanostane-Type Triterpenes from *Ganoderma lucidum*

Compd. ^{13}C	1b$^{a)}$	2b	5b	3b	4b$^{a)}$	8b$^{a)}$	9b$^{a)}$	10b$^{a)}$	6b	7b$^{a)}$	12b$^{d)}$
1	34.6 t	35.2 t	33.4 t	34.1 t	33.2 t	34.9 t	35.5 t	34.6 t	34.0 t	33.3 t	34.6
2	27.6 t	34.3 t	27.4 t	33.7 t	27.3 t	27.7 t	34.1 t	33.8 t	33.8 t	27.4 t	27.6
3	78.3 d	216.8 s	77.5 d	214.8 s	77.3 d	78.3 d	217.3 s	215.2 s	214.8 s	77.5 d	78.3
4	38.6$^{b)}$ s	47.0 s	40.3 s	46.9 s	40.4 s	38.9$^{b)}$ s	46.6 s	47.0$^{b)}$ s	46.9 s	40.5 s	38.6$^{b)}$
5	49.2 d	49.5 d	51.5 d	51.0 d	51.4 d	49.2 d	48.7 d	50.9 d	51.0 d	51.4 d	49.2
6	26.9 t	27.8 t	36.8 t	37.5 t	36.6 t	26.7 t	27.6 t	37.3 t	37.4 t	36.7 t	26.9
7	66.2 d	65.8 d	198.8$^{b)}$ s	198.7$^{b)}$ s	198.5$^{b)}$ s	66.9 d	66.1 d	199.3 s	198.5$^{b)}$ s	198.8$^{b)}$ s	66.3
8	157.4 s	158.3 s	150.5 s	149.9 s	151.6 s	156.9 s	157.7 s	149.7 s	149.7 s	151.6 s	157.6
9	141.9 s	140.5 s	147.1 s	146.1 s	145.7 s	142.7 s	141.0 s	146.8 s	146.2 s	146.0 s	141.9
10	38.4$^{b)}$ s	37.9 s	39.2 s	39.3 s	39.1 s	38.7$^{b)}$ s	38.1 s	39.4 s	39.3 s	39.2 s	38.3$^{b)}$
11	199.3 s	199.5 s	201.6$^{b)}$ s	194.1$^{b)}$ s	193.9$^{b)}$ s	197.8 s	197.4 s	199.3 s	194.1$^{b)}$ s	194.1$^{b)}$ s	199.5
12	77.9 d	78.1 d	77.5 d	79.0 d	79.1 d	50.3 t	50.0 t	48.9 t	79.1 d	79.4 d	78.2
13	51.9 s	51.7 s	49.8 s	47.7 s	47.9 s	45.3 s	44.8 s	43.9$^{b)}$ s	47.6 s	48.0 s	51.9
14	60.3 s	60.4 s	57.9 s	58.6 s	58.4 s	59.4 s	59.2 s	57.2 s	58.6 s	58.5 s	60.2
15	216.8 s	215.5 s	206.0 s	205.4 s	205.5 s	217.4 s	216.3 s	206.8 s	205.8 s	206.0 s	217.2
16	38.4 t	38.5 t	37.9 t	37.8 t	37.8 t	40.9 t	40.8 t	39.8 t	37.4 t	37.6 t	37.7
17	45.8 d	45.8 d	45.3 d	44.5 d	44.7 d	45.6 d	45.6 d	44.5 d	45.2 d	45.5 d	46.7
18	12.0 q	12.1 q	10.9 q	12.1 q	12.1 q	17.4 q	17.5 q	16.1 q	12.0 q	12.1 q	12.0
19	18.8 q	18.3 q	18.1 q	18.7 q	17.9 q	18.5 q	18.0 q	18.6 q	18.6 q	18.0 q	18.8
20	28.7 d	28.7 d	29.5 d	29.4 d	29.3 d	32.0 d	31.8 d	32.0 d	33.0 d	33.0 d	31.7
21	21.4 q	21.4$^{b)}$ q	21.3$^{c)}$ q	21.6 q	21.7 q	19.7 q	19.5 q	19.8 q	20.1 q	20.2 q	20.6
22	48.4 t	48.5 t	48.9 t	48.5 t	48.4 t	49.1 t	48.9 t	49.1 t	30.1 t	30.2 t	29.8
23	208.1 s	208.1 s	208.1 s	207.4 s	207.4 s	207.7 s	207.6 s	207.6 s	31.6 t	31.8 t	32.0
24	46.4 t	46.4 t	46.6 t	46.7 t	46.6 t	46.8 t	46.6 t	46.7 t	173.6 s	173.7 s	174.0
25	34.7 d	34.7 d	34.7 d	34.7 d	34.6 d	34.7 d	34.4 d	34.7 d			
26	176.1 s	176.1 s	176.1 s	176.0 s	176.0 s	176.1 s	175.9 s	176.1 s			
27	17.1 q	17.1 q	17.1 q	17.1 q	17.0 q	17.1 q	16.9 q	17.1 q			
30	28.1 q	26.3 q	28.0 q	27.6 q	27.9 q	28.2 q	26.8 q	27.6 q	27.6 q	27.9 q	28.1
31	15.4 q	21.3$^{b)}$ q	15.6 q	20.4 q	15.5 q	15.5 q	20.6 q	20.3 q	20.4 q	15.6 q	15.4
32	23.1 q	23.3 q	20.3$^{c)}$ q	20.8 q	21.2 q	24.4 q	24.5 q	20.9 q	20.8 q	21.4 q	23.2
O$\underline{C}$H$_3$	51.9 q	51.9 q	51.9 q	51.9 q	51.8 q	51.9 q	51.7 q	51.9 q	51.6 q	51.6 q	51.6
OCO$\underline{C}$H$_3$				20.9 q	20.8 q				20.8 q	20.9 q	
O$\underline{C}$OCH$_3$				170.2 s	170.1 s				170.0 s	170.1 s	

δ values in CDCl$_3$. The multiplicities of carbon signals are indicated as s, d, t, and q. Previous assignments of some signals were revised (ref. 2). *a*) ^{1}H–^{13}C Correlation spectra were measured. *b*) Assignments may be interchanged for each compound. *c*) Assignments were confirmed by the selective decoupling method. *d*) Only the complete decoupling spectrum was measured.

Table III. MS Data of Triterpene Methyl Esters from *Ganoderma lucidum* (Relative Intensity in Parenthesis)

	1b	**2b**	**5b**	**3b**	**4b**		**6b**	**7b**
M^+	546 (23)	544 (4)	544 (62)	584 (3)	586 (10)		528 (14)	530 (5)
$\mathrm{M}^+-\mathrm{CH_2CO}$				542 (13)	544 (21)		486 (22)	488 (2)
$\mathrm{M}^+-n\mathrm{H_2O}$ (AcOH)	528 (20) 510 (6)	526 (8)	526 (10)	524 (12)	568, (5) 508 (7)	526 (18)	468 (27)	470 (10)
$\mathrm{M}^+-\mathrm{MeOH}$			512 (9)					
$\mathrm{M}^+-\mathrm{CH_2CO}$–MeOH				510 (10)	512 (10)			
a	375 (18)	373 (6)	373 (24)	413 (7)	415 (18)		413 (5)	415 (2)
$a-\mathrm{CH_2CO}$				371 (8)	373 (13)		371 (11)	373 (5)
$a-\mathrm{H_2O}$ (AcOH)	357 (10)	355 (5)	355 (66)	353 (8)	355 (14)		353 (8)	355 (2)
b (*b′*)	171 (14)	171 (10)	171 (20)	171 (14)	171 (11)		115 (9)	115 (3)
$b-\mathrm{MeOH}$	139 (37)	139 (30)	139 (83)	139 (29)	139 (33)			
$b'-\mathrm{HCOOMe}$							55 (49)	55 (10)
c	403 (5)			441 (9)	443 (6)			
$c-\mathrm{H}$–$\mathrm{H_2O}$ (AcOH)	384 (10)		382 (25)	380 (12)	382 (15)			
$d+\mathrm{H}$		144 (9)						
e	129 (49)	129 (40)	129 (89)	129 (100)	129 (100)			
f	59 (65)	59 (44)	59 (100)	59 (58)	59 (62)			
$g+\mathrm{H}$	306 (100)	304 (100)	304 (90)	302 (20)	304 (81)		302 (100)	304 (100)
$g-\mathrm{H_2O}$	287 (33)							
h (*h′*)	241 (11)	241 (9)	241 (16)	283 (12)	283 (40)		227 (30)	227 (10)
$h\,(h')-\mathrm{CH_2CO}$				241 (23)	241 (48)		185 (84)	185 (23)
$h-\mathrm{H_2O}$ (AcOH)		223 (6)		223 (20)	223 (36)			
$h-\mathrm{MeOH}$		209 (8)	209 (11)					
$h\,(h')-\mathrm{CH_2CO}$–MeOH				209 (22)	209 (33)		153 (32)	153 (10)
$h-\mathrm{H_2O}$ (AcOH)–MeOH	191 (10)	191 (9)	191 (12)	191 (39)	191 (73)			
$h'-\mathrm{HCOOMe}$							167 (95)	167 (30)
$h'-\mathrm{HCOOMe}$–MeOH							135 (22)	135 (8)

formula $C_{33}H_{44}O_9$ and showed a characteristic UV absorption band at 252 nm and strong IR absorptions at 1745—1680 cm^{-1}. The ^{1}H-NMR spectrum of **3b** exhibited a signal due to an acetoxyl methyl group (δ 2.25) along with two *sec*- and five *tert*-methyl signals. The spectral pattern was closely similar to that of methyl ganoderate E (**10b**),[1] but it was characterized by the appearance of a singlet at δ 5.67 assignable to the acetoxyl-bearing methine proton instead of a pair of doublets (δ 2.87 and 2.75) due to the 12-methylene protons in the latter compound (**10b**) (Table I). Inspection of the ^{13}C-NMR spectrum compared with that of **10b** revealed a marked downfield shift of the C-12 signal (δ 79.0), suggesting the presence of an acetoxyl group at the 12-position (Table II). This was supported by the upfield shift of the C-18 signal (δ 12.1), which may be ascribed to the γ-effect of the acetoxyl group. Furthermore, irradiation of the 32-methyl protons at δ 1.80 induced a 15% NOE increase of the methine signal at δ 5.67, indicating the β-orientation of the acetoxyl group. Thus, methyl ganoderate F should be 12β-acetoxy-3,7,11,15,23-pentaoxo-5α-lanost-8-en-26-oate (**3b**). In accordance with this structure, the MS of **3b** showed the molecular ion peak at *m*/*z* 584 and significant fragment peaks at *m*/*z* 441 (*c*), 413 (*a*), 380 (*c*$-$H–AcOH), 371 (*a*$-CH_2CO$), 353 (*a*$-$AcOH), 302 (*g*$+$H), 283 (*h*), 241 (*h*$-CH_2CO$), and 223 (*h*$-$AcOH) together with other fragment ion peaks (Table III).

Methyl ganoderate H (**4b**), mp 155—156 °C, $[\alpha]_D$ $+55°$ ($CHCl_3$), was analyzed as $C_{33}H_{46}O_9$ and the molecular formula was confirmed by high-resolution MS measurement. It showed an absorption at 256 nm, characteristic of a conjugated carbonyl grouping, in the UV spectrum, and strong absorption bands at 1745—1695 cm^{-1} in the IR spectrum which resembled that of methyl ganoderate F (**3b**) except for an additional hydroxyl band at 3400 cm^{-1}. The ^{1}H-NMR spectrum also resembled that of **3b**, but it showed a new signal due to a carbinol methine proton at δ 3.26 (dd, $J=11$, 5 Hz) accompanied with the upfield shift of two *tert*-methyl signals (δ 1.03 and 0.88) assignable to the 30- and 31-methyl groups, and moreover, considerable changes were observed in the signal pattern of the 1- and 2-methylene

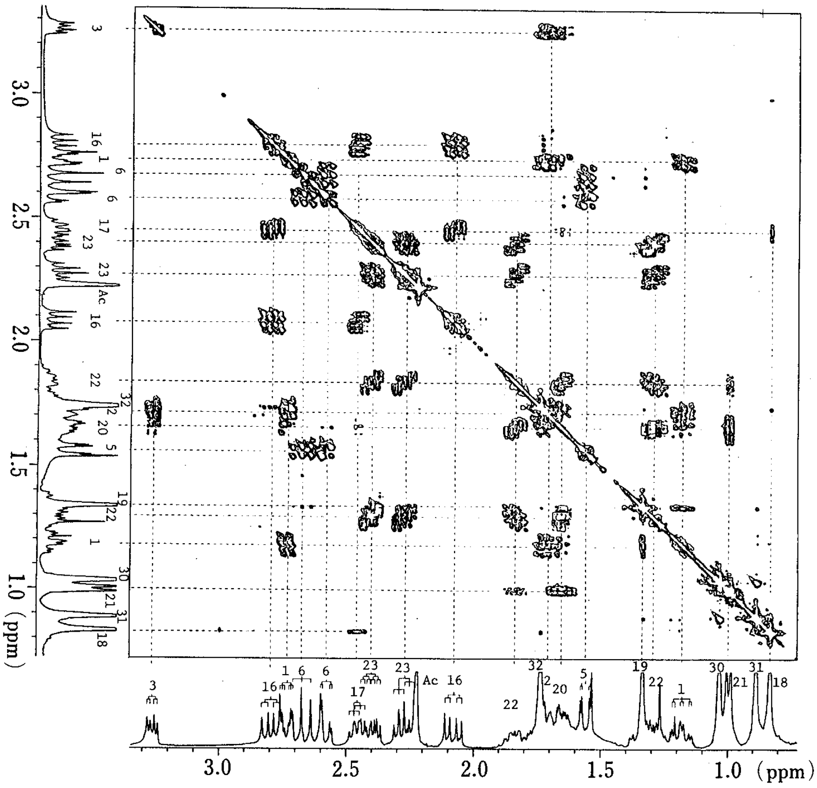


Fig. 3. Contour Map of the Highly Resolved ^{1}H–^{1}H Shift Correlated Spectrum of Methyl Lucidenate E2 (**7b**) in the Upfield Region

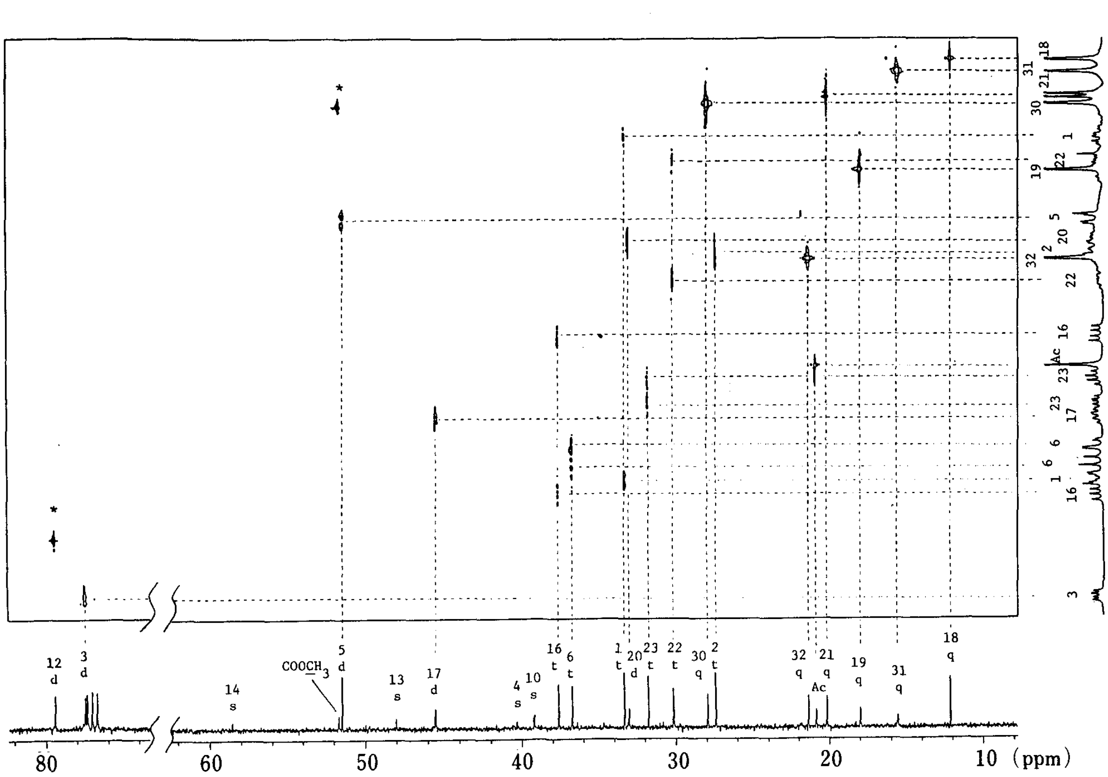


Fig. 4. Contour Map of the ^{1}H–^{13}C Shift Correlated Spectrum of Methyl Lucidenate E2 (**7b**) in the Upfield Region

The ^{1}H shifts are shown on the ordinate and the ^{13}C shifts on the abscissa. The multiplicities of carbon signals were determined by means of off-resonance, and are indicated as s, d, t, and q.

* Folded cross-peaks of the ester methyl and 12-methine protons.

protons (Table I). This suggested that **4b** might have a 3β-hydroxyl group instead of the 3-oxo group in **3b**. This was supported by its ^{13}C-NMR spectrum compared with that of **3b** (Table II). As expected, the chemical shifts of most of the carbon signals of **4b** were practically the same as those of the corresponding signals of **3b**, but the signals ascribable to C-2, C-3, and C-4 (δ 27.3, 77.3, and 40.4, respectively) markedly shifted upfield, reflecting the structural change in ring A. Further, the MS pattern of **4b** was quite parallel with that of **3b**, with several fragment peaks shifted by 2 mass units (Table III). Finally, oxidation of **4b** with chromium trioxide in acetic acid yielded the pentaoxo compound, identified as methyl ganoderate F (**3b**). From these findings, methyl ganoderate H was determined to be methyl 12β-acetoxy-3β-hydroxy-7,11,15,23-tetraoxo-5α-lanost-8-en-26-oate (**4b**).

Compound C6 (**5b**), mp 146—148 °C, is one of the very minor components of the fungus, and its molecular formula was determined to be $C_{31}H_{44}O_8$ by MS and high-resolution MS measurements. The UV and IR spectra of **5b** were similar to those of methyl ganoderate H (**4b**), but no IR bands due to an acetoxyl were observed. Also the ^{1}H- and ^{13}C-NMR spectra of **5b** closely resembled those of **4b**, except for the lack of ^{1}H- and ^{13}C-signals due to the acetyl group in **4b** and the upfield shifts of both the 12-proton and C-12 signals (Tables I and II). Based on these data, the structure of compound C6 was assigned as **5b**.[8] A support was provided by its MS, which was parallel with that of **4b** except that the M$^+$ peak and fragment peaks *a* and *h* were shifted by 42 mass units as shown in Table III.

Methyl lucidenate D2 (**6b**), amorphous, $[\alpha]_D$ +136 ° (CHCl$_3$), and methyl lucidenate E2 (**7b**), mp 141—144 °C, $[\alpha]_D$ +86 ° (CHCl$_3$), have the molecular formulae $C_{30}H_{40}O_8$ and $C_{30}H_{42}O_8$, respectively, as determined by microanalyses and high-resolution MS measurements. The UV and IR spectra of **6b** and **7b** resembled those of methyl ganoderates F (**3b**) and H (**4b**), respectively. The ^{1}H- and ^{13}C-NMR spectra of **6b** and **7b** also closely resembled those of **3b** and **4b**, respectively, but the ^{1}H-NMR spectra of **6b** and **7b** were both characterized by the disappearance of a doublet due to the 27-methyl protons (δ 1.18) (Table I and Fig. 3). Instead, the ^{13}C-NMR spectra of both **6b** and **7b** showed signals due to only six carbons that were assignable to the side chain carbons, indicating the presence of a γ-substituted methyl pentanoate grouping (Table II and Fig. 4). This was verified by comparison of their ^{1}H- and ^{13}C-NMR spectra with those of methyl lucidenate C (**12b**);[6] the chemical shifts and signal patterns arising from the side chains were practically identical with each other (Tables I and II).

In the MS, **6b** exhibited the most prominent peak at m/z 302 (this could be ascribed to the fragment $g+H$ produced by cleavage at the C, D-rings in the same manner as in the case of **3b**) and its counterpart (h') at m/z 227 accompanied with the fragment ions a (m/z 413) and b' (m/z 115) and related ions. The MS of **7b** was quite parallel with that of **6b** except for the 2 mass unit shifts of the fragments $g+H$ and a (Table III). In view of these data, the structures of methyl lucidenates D2 and E2 were assigned as **6b** and **7b**, respectively.

The biological activities of the above compounds are currently under investigation.

Experimental

Melting points were determined on a Kofler-type apparatus and are uncorrected. Optical rotations were measured in $CHCl_3$ solutions on a JASCO DIP-4 automatic polarimeter at 20—22 °C. UV spectra were taken with a Shimadzu 202 UV spectrometer in EtOH solutions and IR spectra with a JASCO IRA-2 spectrometer in $CHCl_3$ unless otherwise specified. MS and high-resolution MS were obtained with a JEOL JMS D-300 spectrometer (ionization voltage, 70 eV; accelerating voltage, 3 kV) using a direct inlet system. ^{1}H- and ^{13}C-NMR spectra were taken on a JEOL JNM-GX 400 spectrometer in $CDCl_3$ solutions with tetramethylsilane as an internal standard, and chemical shifts are recorded in δ values. Two-dimensional ^{1}H–^{1}H and ^{1}H–^{13}C shift correlation spectra were measured under the same conditions as described in the preceding paper.[1] Preparative thin layer chromatography (TLC) was carried out on Merck Kieselgel GF_{254} plates and plates were examined under UV light. Extraction of substances from the silica gel was done with MeOH–CH_2Cl_2 (5 : 95) and solutions were concentrated *in vacuo*. For drying organic solutions, anhydrous $MgSO_4$ was employed.

Isolation and Properties of Triterpene Acids from *Ganoderma lucidum* (Fr.) Karst.——Extraction and isolation of triterpene acids from the surface part (12.8 g) of the gills of dried fruit bodies of *Ganoderma lucidum* (2.56 kg) were described in our previous paper[1]; *i.e.*, after methylation, the crude product was separated by a combination of silica gel column chromatography and preparative TLC to give methyl lucidenate D2 (**6b**) (32 mg), methyl ganoderate F (**3b**) (56 mg), compound C5′ (**2b**) (31 mg), methyl lucidenate E2 (**7b**) (32 mg), methyl ganoderate H (**4b**) (120 mg), methyl ganoderate G (**1b**) (36 mg), and compound C6 (**5b**) (4 mg) in the order of polarity.

Methyl Ganoderate G (**1b**): Colorless prisms (from ether), mp 134—135 °C, $[\alpha]_D$ +64° (c=1.0). UV λ_{max} nm (log ε): 252.5 (4.01). IR ν_{max} cm^{-1}: 3450, 1735 (sh), 1730, 1720, 1660. ^{1}H- and ^{13}C-NMR: Tables I and II. MS data: Table III. High-resolution MS m/z: Found 546.3191, Calcd for $C_{31}H_{46}O_8$ (M^+) 546.3192; Found 528.3119, Calcd for $C_{31}H_{44}O_7$ 528.3086; Found 375.2173, Calcd for $C_{22}H_{31}O_5$ 375.2172; Found 306.1821, Calcd for $C_{18}H_{26}O_4$ 306.1831; Found 191.1098, Calcd for $C_{12}H_{15}O_2$ 191.1072; Found 171.1056, Calcd for $C_9H_{15}O_3$ 171.1021; Found 139.0767, Calcd for $C_8H_{11}O_2$ 139.0758; Found 129.0567, Calcd for $C_6H_9O_3$ 129.0552.

Compound C5′ (Methyl Ganoderate D) (**2b**): Colorless needles (from ether), mp 118.5—121.5 °C, $[\alpha]_D$ +101° (c=0.5). UV λ_{max} nm (log ε): 251 (3.38). IR ν_{max}^{KBr} cm^{-1}: 3400, 1740 (sh), 1730 (sh), 1720, 1710, 1650. ^{1}H- and ^{13}C-NMR: Tables I and II. MS data: Table III. High-resolution MS m/z: Found 544.3040, Calcd for $C_{31}H_{44}O_8$ (M^+) 544.3036; Found 526.2897, Calcd for $C_{31}H_{42}O_7$ 526.2929; Found 373.2015, Calcd for $C_{22}H_{29}O_5$ 373.2015; Found 355.1937, Calcd for $C_{22}H_{27}O_4$ 355.1909; Found 304.1718, Calcd for $C_{18}H_{24}O_4$ 304.1675; Found 241.1432, Calcd for $C_{13}H_{21}O_4$ 241.1439; Found 223.1316, Calcd for $C_{13}H_{19}O_3$ 223.1334; Found 209.1168, Calcd for $C_{12}H_{17}O_3$ 209.1177; Found 191.1069, Calcd for $C_{12}H_{15}O_2$ 191.1072; Found 171.1009, Calcd for $C_9H_{15}O_3$ 171.1021; Found 144.0809, Calcd for $C_7H_{12}O_3$ 144.0787; Found 139.0756, Calcd for $C_8H_{11}O_2$ 139.0758; Found 129.0550, Calcd for $C_6H_9O_3$ 129.0552.

Methyl Ganoderate F (**3b**): Yellowish amorphous powder, $[\alpha]_D$ +111° (c=1.0). UV λ_{max} nm (log ε): 251.5 (3.91). IR ν_{max} cm^{-1}: 1745, 1735 (sh), 1710, 1700, 1680 (sh), 1220. ^{1}H- and ^{13}C-NMR: Tables I and II. MS data: Table III. *Anal.* Calcd for $C_{33}H_{44}O_9 \cdot 1/2H_2O$: C, 66.78; H, 7.64. Found: C, 67.13; H, 7.63. High-resolution MS m/z: Found 584.3000, Calcd for $C_{33}H_{44}O_9$ (M^+) 584.2986; Found 542.2867, Calcd for $C_{31}H_{42}O_8$ 542.2879; Found 524.2793, Calcd for $C_{31}H_{40}O_7$ 524.2774; Found 441.2297, Calcd for $C_{26}H_{33}O_6$ 441.2278; Found 413.1961, Calcd for $C_{24}H_{29}O_6$ 413.1963; Found 380.2008, Calcd for $C_{24}H_{28}O_4$ 380.1988; Found 371.1823, Calcd for $C_{22}H_{27}O_5$ 371.1858; Found 353.1738, Calcd for $C_{22}H_{25}O_4$ 353.1752; Found 302.1506, Calcd for $C_{18}H_{22}O_4$ 302.1507; Found 283.1536, Calcd for $C_{15}H_{23}O_5$ 283.1545; Found 241.1425, Calcd for $C_{13}H_{21}O_4$ 241.1439; Found 223.1335, Calcd for $C_{13}H_{19}O_3$ 223.1334; Found 209.1166, Calcd for $C_{12}H_{17}O_3$ 209.1177; Found 191.1074, Calcd for $C_{12}H_{15}O_2$ 191.1072; Found 171.1008, Calcd for $C_9H_{15}O_3$ 171.1021; Found 139.0762, Calcd for $C_8H_{11}O_2$ 139.0758; Found 129.0553, Calcd for $C_6H_9O_3$ 129.0552.

Methyl Ganoderate H (**4b**): Yellow needles (from EtOH), mp 155—156 °C, $[\alpha]_D$ +55° (c=0.5). UV λ_{max} nm (log ε): 256 (3.87). IR ν_{max} cm^{-1}: 3400, 1745, 1735 (sh), 1720, 1695, 1680 (sh), 1220. ^{1}H- and ^{13}C-NMR: Tables I and II. MS data: Table III. *Anal.* Calcd for $C_{33}H_{46}O_9$: C, 67.55; H, 7.90. Found: C, 67.57; H, 8.01. High-resolution MS m/z: Found 586.3148, Calcd for $C_{33}H_{46}O_9$ (M^+) 586.3142; Found 544.3033, Calcd for $C_{31}H_{44}O_8$ 544.3035; Found 526.2927, Calcd for $C_{31}H_{42}O_7$ 526.2929; Found 512.2818, Calcd for $C_{30}H_{40}O_7$ 512.2774; Found 443.2418, Calcd for $C_{26}H_{35}O_6$ 443.2423; Found 415.2108, Calcd for $C_{24}H_{31}O_6$ 415.2120; Found 382.2131, Calcd for $C_{24}H_{30}O_4$ 382.2145; Found 373.1994, Calcd for $C_{22}H_{29}O_5$ 373.2014; Found 304.1675, Calcd for $C_{18}H_{24}O_4$ 304.1675; Found 283.1547, Calcd for $C_{15}H_{23}O_5$ 283.1545; Found 241.1429, Calcd for $C_{13}H_{21}O_4$ 241.1439; Found 223.1332, Calcd for $C_{13}H_{19}O_3$ 223.1334; Found 209.1174, Calcd for $C_{12}H_{17}O_3$ 209.1177; Found 191.1066, Calcd for $C_{12}H_{15}O_2$ 191.1072; Found 171.1010, Calcd for $C_9H_{15}O_3$ 171.1021; Found 139.0760, Calcd for $C_8H_{11}O_2$ 139.0758; Found 129.0563, Calcd for $C_6H_9O_3$ 129.0552.

Compound C6 (**5b**): Pale yellow prisms (from ether), mp 146—148 °C. UV λ_{max} nm (log ε): 253.5 (3.43). IR ν_{max}^{KBr} cm^{-1}: 3500, 3430, 1745, 1735 (sh), 1720, 1700, 1690, 1675 (sh). ^{1}H- and ^{13}C-NMR: Tables I and II. MS data: Table III. High-resolution MS m/z: Found 544.3006, Calcd for $C_{31}H_{44}O_8$ (M^+) 544.3036; Found 526.2918, Calcd for $C_{31}H_{42}O_7$ 526.2930; Found 512.2786, Calcd for $C_{30}H_{40}O_7$ 512.2774; Found 382.2149, Calcd for $C_{24}H_{30}O_4$ 382.2145; Found 373.2015, Calcd for $C_{22}H_{29}O_5$ 373.2015; Found 355.1908, Calcd for $C_{22}H_{27}O_4$ 355.1909; Found 304.1667, Calcd for $C_{18}H_{24}O_4$ 304.1675; Found 241.1426, Calcd for $C_{13}H_{21}O_4$ 241.1439; Found 209.1173, Calcd for $C_{12}H_{17}O_3$ 209.1177; Found 191.1099, Calcd for $C_{12}H_{15}O_2$ 191.1072; Found 171.1021, Calcd for $C_9H_{15}O_2$ 171.1021; Found 139.0746, Calcd for $C_8H_{11}O_2$ 139.0758; Found 129.0546, Calcd for $C_6H_9O_3$ 129.0552.

Methyl Lucidenate D2 (**6b**): Yellowish amorphous powder, $[\alpha]_D$ +136° (c=1.0). UV λ_{max} nm (log ε): 252.5 (3.96). IR ν_{max} cm^{-1}: 1745, 1735 (sh), 1700, 1680 (sh), 1220. ^{1}H- and ^{13}C-NMR: Tables I and II. MS data: Table III. *Anal.* Calcd for $C_{30}H_{40}O_8 \cdot 1/2H_2O$: C, 67.03; H, 7.68. Found: C, 67.20; H, 7.47. High-resolution MS m/z: Found 528.2722, Calcd for $C_{30}H_{40}O_8$ (M^+) 528.2722; Found 486.2622, Calcd for $C_{28}H_{38}O_7$ 486.2617; Found 468.2520, Calcd for $C_{28}H_{36}O_6$ 468.2512; Found 413.1957, Calcd for $C_{24}H_{29}O_6$ 413.1963; Found 371.1827, Calcd for $C_{22}H_{27}O_5$ 371.1858; Found 302.1482, Calcd for $C_{18}H_{22}O_4$ 302.1507; Found 227.1265, Calcd for $C_{12}H_{19}O_4$ 227.1283; Found 185.1157, Calcd for $C_{10}H_{17}O_3$ 185.1177; Found 167.1056, Calcd for $C_{10}H_{15}O_2$ 167.1072; Found 153.0880, Calcd for $C_9H_{13}O_2$ 153.0915; Found 135.0812, Calcd for $C_9H_{11}O$ 135.0710; Found 115.0744, Calcd for $C_6H_{11}O_2$ 115.0758.

Methyl Lucidenate E2 (**7b**): Yellow needles (from ether), mp 141—144 °C, $[\alpha]_D$ +86° (c=0.5). UV λ_{max} nm (log ε): 256 (3.75). IR ν_{max} cm^{-1}: 3400, 1745, 1735 (sh), 1720 (sh), 1690, 1680 (sh), 1220. ^{1}H- and ^{13}C-NMR: Tables I and II. MS data: Table III. *Anal.* Calcd for $C_{30}H_{42}O_8 \cdot 1/2H_2O$: C, 66.78; H, 8.03. Found: C, 66.98; H, 7.94. High-resolution MS m/z: Found 530.2879, Calcd for $C_{30}H_{42}O_8$ (M^+) 530.2879; Found 488.2767, Calcd for $C_{28}H_{40}O_7$ 488.2773; Found 470.2626, Calcd for $C_{28}H_{38}O_6$ 470.2668; Found 415.2085, Calcd for $C_{24}H_{31}O_6$ 415.2120; Found 373.2034, Calcd for $C_{22}H_{29}O_5$ 373.2014; Found 304.1680, Calcd for $C_{18}H_{29}O_4$ 304.1675; Found 227.1270, Calcd for $C_{12}H_{19}O_4$ 227.1283; Found 185.1153, Calcd for $C_{10}H_{17}O_3$ 185.1177; Found 167.1062, Calcd for $C_{10}H_{15}O_2$ 167.1071; Found 153.0878, Calcd for $C_9H_{13}O_2$ 153.0915; Found 135.0814, Calcd for $C_9H_{11}O_1$ 135.0710.

Acetylation of Methyl Ganoderate G (1b)——A mixture of **1b** (5 mg), acetic anhydride (3 drops), and pyridine (3 drops) was allowed to stand overnight at room temperature. Then, water was added to the reaction mixture and the precipitate was collected by filtration. This was purified by preparative TLC with acetone–$CHCl_3$ (15:85) as the eluent to give the triacetate (**11b**) (5 mg), amorphous powder. IR ν_{max} cm^{-1}: 1740 (sh), 1730, 1720 (sh), 1670, 1220. ^{1}H-NMR δ: 5.90 (1H, t, J=8.5 Hz, 7α-H), 5.69 (1H, s, 12α-H), 4.49 (1H, dd, J=10, 6 Hz, 3α-H), 2.26, 2.05, 1.96 (each 3H, s, OAc), 1.42 (3H, s, 32-Me), 1.24 (3H, s, 19-Me), 1.17 (3H, d, J=7 Hz, 27-Me), 1.00 (3H, s, 30-Me), 0.96 (3H, d, J=5.5 Hz, 21-Me), 0.92 (3H, s, 31-Me), 0.89 (3H, s, 18-Me). MS m/z (%): 672 (M^+) (7), 630 (12), 612 (5), 501 (20), 441 (6), 390 (100), 283 (27), 251 (6), 241 (31), 223 (22), 209 (19), 191 (41), 171 (12), 139 (41), 129 (73), 59 (66).

Oxidation of Methyl Ganoderate H (4b)——A solution of CrO_3 (10 mg) in AcOH (0.5 ml) containing water (0.2 ml) was added under vigorous stirring to a solution of **4b** (5 mg) in AcOH (0.5 ml) at room temperature. Stirring was continued for 2 h, then the mixture was diluted with water and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried, and concentrated. The residue was purified by preparative TLC with acetone–$CHCl_3$ (15:85) to give the pentaoxo compound (**3b**) (4.3 mg), an amorphous material, which was identified as methyl ganoderate F (**3b**) by TLC, IR, and ^{1}H-NMR comparisons.

References and Notes

1) Part I: T. Kikuchi, S. Kanomi, S. Kadota, Y. Murai, K. Tsubono, and Z. Ogita, *Chem. Pharm. Bull.*, **34**, 3695

(1986).

2) A part of this work was reported in our preliminary communications: *a*) T. Kikuchi, S. Matsuda, S. Kadota, Y. Murai, and Z. Ogita, *Chem. Pharm. Bull.*, **33**, 2624 (1985); *b*) T. Kikuchi, S. Matsuda, Y. Murai, and Z. Ogita, *ibid.*, **33**, 2628 (1985). A part of this work was presented at the 2nd Annual Meeting of the Medical and Pharmaceutical Society for Wakan-Yaku, Kyoto, September 1985, Abstr., p. 114.

3) Furuya *et al.* have isolated **4a** independently from the same fungus and designated it as ganoderic acid C. After discussion with Prof. Furuya, the name "ganoderic acid H" was adopted for this compound. See M. Hirotani, T. Furuya, and M. Shiro, *Phytochemistry*, **24**, 2055 (1985).

4) In our preliminary communication, **6a** and **7a** were designated as lucidenic acids D and E, respectively (ref. 2*a*). Sakamura *et al.* have also reported the isolation of new C_{27} terpenoids named lucidenic acids D and E. After discussion with Prof. Sakamura, our compounds have been named lucidenic acids D2 (**6a**) and E2 (**7a**), while Sakamura's compounds have been designated as lucidenic acids D1 and E1, respectively. See ref. 7 and also see T. Nishitoba, H. Sato, and S. Sakamura, *Agric. Biol. Chem.*, **49**, 3637 (1985).

5) T. Kubota, Y. Asaka, I. Miura, and H. Mori, *Helv. Chim. Acta*, **65**, 611 (1982).

6) T. Nishitoba, H. Sato, T. Kasai, H. Kawagishi, and S. Sakamura, *Agric. Biol. Chem.*, **48**, 2905 (1984); *idem, ibid.*, **49**, 1793 (1985).

7) T. Nishitoba, H. Sato, and S. Sakamura, *Agric. Biol. Chem.*, **49**, 1547 (1985).

8) The possibility that compound C6 is an artifact produced in the separation procedure can not be excluded at present.