Chem. Pharm. Bull. 34(10)4030—4036(1986)

Constituents of the Fungus *Ganoderma lucidum* (FR.) KARST. III.[1] Structures of Ganolucidic Acids A and B, New Lanostane-Type Triterpenoids[2]

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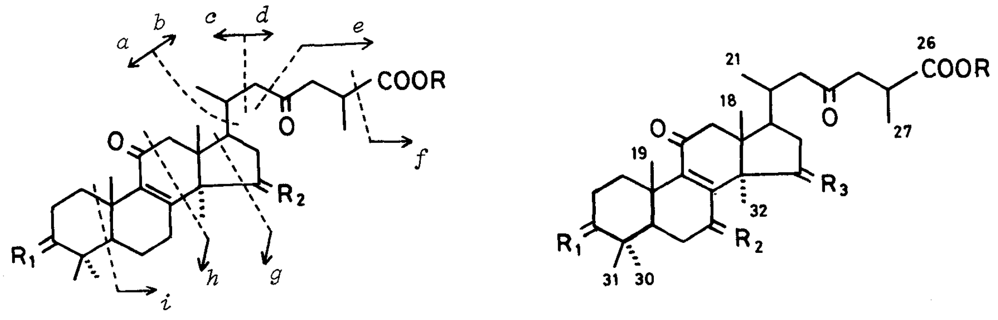
(Received March 25, 1986)

The structures of ganolucidic acids A and B, new lanostane-type triterpenoids isolated from the surface part of the gills of *Ganoderma lucidum* (Polypolaceae), were determined to be **1a** and **2a**, respectively. Detailed analyses of 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 NMR techniques.

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

In previous papers,[1,3] the structures of fourteen new triterpenoids: ganoderic acids C2, E—I, and K, lucidenic acids D2, E2, and F, and compounds B8, B9, C5′, and C6, isolated from the surface part of the gills of *Ganoderma lucidum* (FR.) KARST. (Polypolaceae), were reported. This paper deals with the structures of two new triterpenoids named ganolucidic acids A (**1a**) and B (**2a**), both of which are minor components of the fungus and were isolated as the methyl esters (**1b** and **2b**, respectively).

Methyl ganolucidate A (**1b**), mp 192—194 °C, $[\alpha]_D$ +188° (CHCl$_3$), showed the molecular ion peak at m/z 514 in the mass spectrum (MS) and its molecular formula was determined to be $C_{31}H_{46}O_6$ by high-resolution MS measurement. It exhibited a ultraviolet (UV) absorption at 256.5 nm (log ε: 4.00), characteristic of an α,β-unsaturated carbonyl



1: $R_1=O$, $R_2=\mathord{<}^{H}_{OH}$

2: $R_1=\mathord{<}^{OH}_{H}$, $R_2=\mathord{<}^{H}_{OH}$

3: $R_1=O$, $R_2=O$

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

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

6: $R_1=O$, $R_2=O$, $R_3=O$

a: R=H, **b**: $R=CH_3$

Chart 1

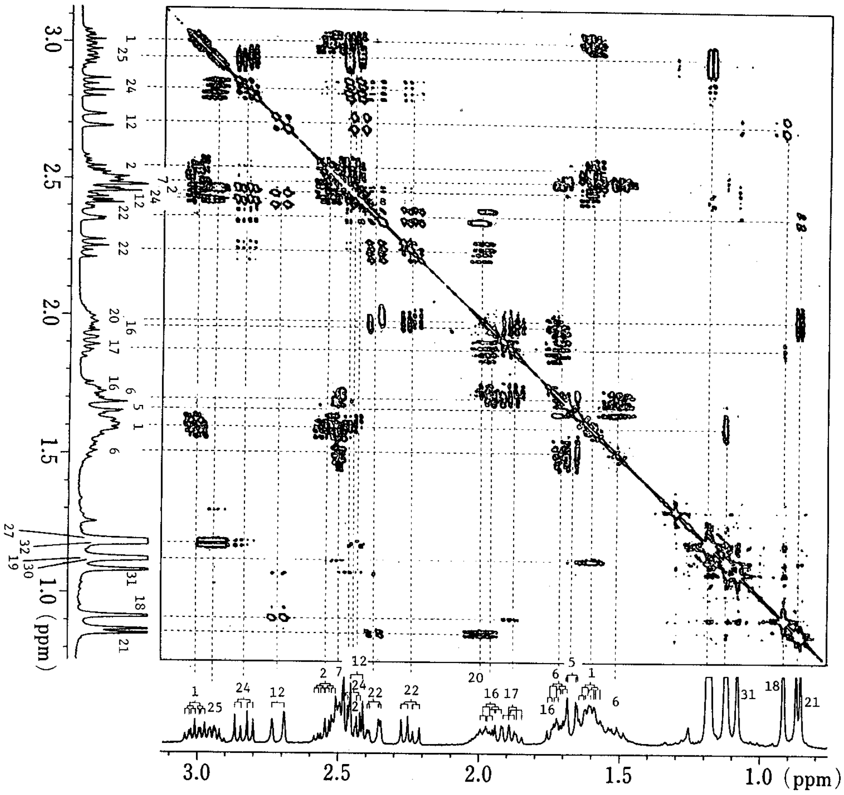


Fig. 1. Contour Map of the Highly Resolved ^1H–^1H Shift Correlated Spectrum of Methyl Ganolucidate A (**1b**) in the Upfield Region

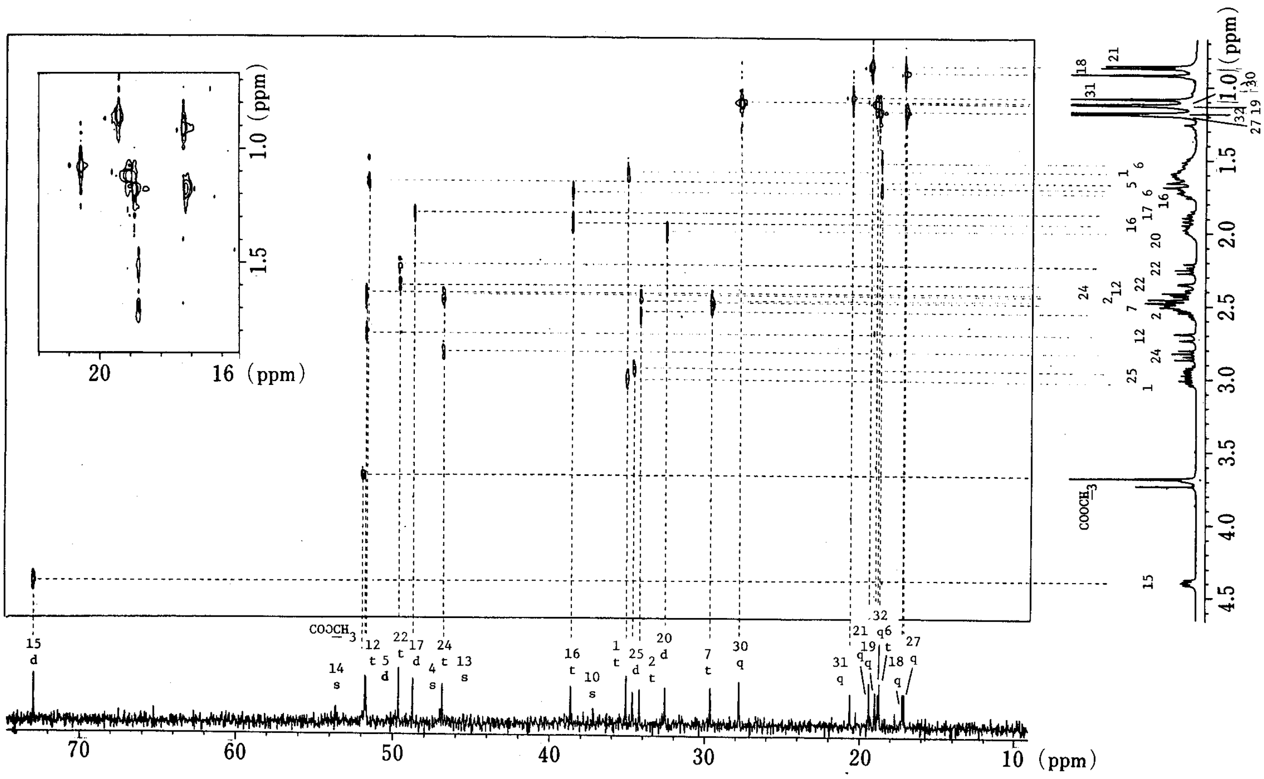


Fig. 2. Contour Map of the ^1H–^{13}C Shift Correlated Spectrum of Methyl Ganolucidate A (**1b**) in the Upfield Region

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.

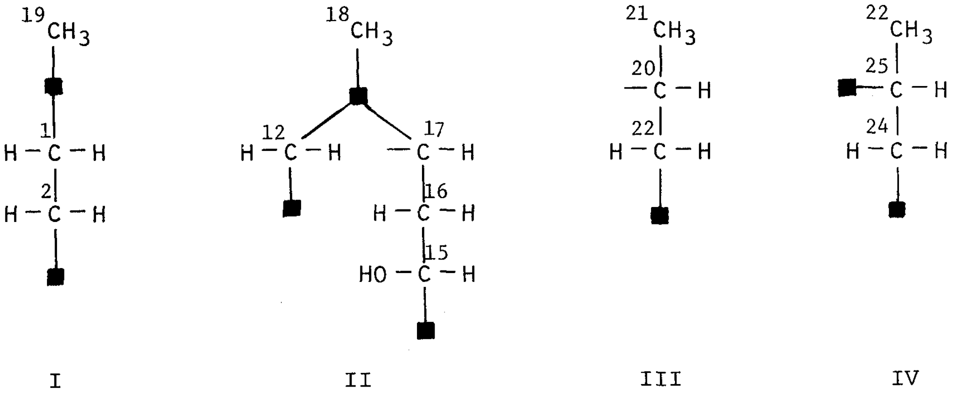


Fig. 3

grouping, and infrared (IR) absorption bands at 3450 (hydroxyl), 1730, 1710, and 1650 cm^{-1} (carbonyl). The proton nuclear magnetic resonance (^1H-NMR) spectrum of **1b** exhibited a double doublet at δ 4.39 ($J=9$, 5.5 Hz) due to a carbinol methine proton along with two *sec*-methyl and five *tert*-methyl signals. Its spectral pattern resembled that of methyl ganoderate A (**4b**),[4] but it was characterized by the appearance of complicatedly overlapped signals corresponding to six protons around δ 2.50, and the absence of one of the two signals due to the carbinol methine protons in **4b**. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **1b** also resembled that of **4b**, but it showed a signal due to only one carbinol methine carbon (δ 72.9) instead of two in **4b**, along with signals due to four carbonyl carbons (δ 217.7, 208.3, 198.1, and 176.2).

Then, in order to analyze the proton and carbon sequences in **1b** in detail, we measured the ^1H–^1H and ^1H–^{13}C shift correlation NMR spectra (Figs. 1 and 2) and nuclear Overhauser effect's (NOE's); the results are given in Tables I and II. From a consideration of the ^1H splitting pattern and coupling constants and the presence of long-range couplings between 12α-H and 18-methyl, 17-H and 18-methyl, 1α-H and 19-methyl, and 22-H and 21-methyl, partial structures I, II, III, and IV (Fig. 3) could be deduced in **1b**. Furthermore, comparison of its ^{13}C-NMR data with those of **4b** indicated that the chemical shifts of carbons in rings A, C, and D and in the side chain were practically the same as those of the corresponding carbons in **4b**. Further, there were signals due to a methine and two methylene carbons at δ 51.7, 18.7, and 29.6, respectively, which were clearly assignable to the carbons in ring B (C-5, C-6, and C-7) (Table II). Therefore, **1b** was supposed to be the 7-deoxy derivative of **4b**. In accordance with this, the MS of **1b** showed significant fragment peaks at m/z 417 (i+H), 371 (c), 343 (a), 287 (g+H), 217 (h−H), 171 (b), 144 (d+H), 139 (b−MeOH), and 129 (e) (Table III), which could be analyzed as shown in Chart 1.[3,4]

Oxidation of **1b** with chromium trioxide in acetic acid afforded the tetraoxo ester (**3b**), $C_{31}H_{44}O_6$, which showed the molecular ion peak at m/z 512 together with fragment ion peaks at m/z 415 (i+H), 368 (c−H), 350 (c−H-H_2O), 341 (a), 287 (g+H), 171 (b), 139 (b−MeOH), and 129 (e). The ^1H- and ^{13}C-NMR spectra of **3b** compared with those of methyl ganoderate E (**6b**)[3] indicated the apparent absence of an oxygenic functional group at the C-7 position (Tables I and II). On the basis of these findings, methyl ganolucidate A was determined to be methyl 15α-hydroxy-3,11,23-trioxo-5α-lanost-8-en-26-oate (**1b**).

Methyl ganolucidate B (**2b**), mp 167—169 °C, $[\alpha]_D$ +114° ($CHCl_3$), has the molecular formula $C_{31}H_{48}O_6$ as confirmed by the high-resolution MS data. It showed UV and IR spectra very similar to those of methyl ganolucidate A (**1b**). Its ^1H-NMR spectrum was also similar to that of **1b**, but it showed a new double doublet at δ 3.24 ($J=11.5$, 5 Hz) and a marked upfield shift of a *tert*-methyl signal to δ 0.83 (31-CH_3). This spectral behavior resembled that of methyl ganoderate C2 (**5b**),[3,6] whose 3-methine and 31-methyl protons

Table I. ^{1}H-NMR Spectral Data for Triterpene Methyl Esters from *Ganoderma lucidum*

Compd. Proton	**1b**[a]	**2b**[a]	**3b**[a]	**4b**[a]	**5b**[a]	**6b**[a]
1-H (α)	1.61[b] ddd (14, 9, 7.2)	1.07[b] td (13, 4.5)	1.60[b] ddd (12, 11, *ca.* 7)	1.46[b] dt (14, 8)	*ca.* 0.93[b]	1.74[b] ddd (14, 9.5, 6)
1-H (β)	3.01 ddd (14, 8, 5.5)	3.00 dt (13.5, 3.5)	2.98 dt (13.5, 7)	2.85 dt (14, 7)	2.74 dt (13.5, 4)	2.87 ddd (14, 8, 5.5)
2-H (α)	2.46 ddd (15, 8, 7)	1.62 td-like (12, 3.5)	2.46 ddd (15.5, 8.5, 7.5)	2.45 dd (8, 7)	*ca.* 1.60	2.47 ddd (15, 8, 6.5)
2-H (β)	2.55 ddd (15, 9, 5.5)	1.69 dq-like	2.54 ddd (15, 10, 6)		*ca.* 1.66	2.61 ddd (15, 9.7, 6)
3-H (α)		3.24 dd (11.5, 5)			3.20 dd (10.8, 5.8)	
5-H (α)	1.67 dd (12, 1.8)	0.91 dd (12.5, 1.2)	1.66 dd (12.5, 2)	*ca.* 1.67	0.92 dd (13, 1)	2.32 dd (14.8, 2.8)
6-H (α)	1.72 ddd (13, 5, 2)	1.77 ddt (13, 6.5, 1.5)	1.73 dddd (12, 7.5, 2, 1)	*ca.* 1.69	2.14 ddd (12.5, 7.5, 1)	2.47 dd (13.4, 2.8)
6-H (β)	1.50 tdd (12.5, 10, 8)	1.46 tdd (12.5, 11, 6.5)	1.45 qd (12, 5)	*ca.* 2.06	1.59 td (12.5, 10.5)	2.69 dd (15, 13.4)
7-H (α)	2.50 dd-like	2.42 ddd (19, 11, 6.5)	2.60 ddd (20, 12.5, 7)	4.62 dd (10, 6.2)	4.54 dd (10.3, 7.5)	
7-H (β)		2.49 ddd (19, 6, 1)	3.02 ddd (20, 5, 1)			
12-H (α)	2.71[c] d (17)	2.72[c] d (16.5)	2.73[c] d (17)	2.75[c] br d (16)	2.76[c] br d (15.5)	2.87[c] br d (16.2)
12-H (β)	2.43 d (17)	2.41 d (16.5)	2.65 d (17)	2.50 d (16)	2.46 d (15.5)	2.75 d (16.2)
15-H (β)	4.39 dd (9, 5.5)	4.37 dd (9, 5.5)		4.80 br t (8)	4.74 br t (7.5)	
16-H (α)	1.96 ddd (13, 9.5, 8)	1.94 ddd (13.5, 9.5, 8.2)	2.57 dd (18, 7)	*ca.* 1.82	*ca.* 1.78	2.74 dd (18.2, 9.1)
16-H (β)	1.72 ddd (13, 9.5, 5.5)	1.70 ddd (13.5, 9, 6)	1.98 dd (18, 9.5)			1.86 dd (18.2, 8.4)
17-H (α)	1.88[c] dt (10.5, 8)	1.86[c] dt (10.5, 9)	2.06 td (10, 7)	*ca.* 1.83[c] m	*ca.* 1.80[c] m	2.24 dt (10, 8.5)
20-H	1.99 m	1.98 m	2.13 m	*ca.* 2.03 m	2.02 m	2.10 m
22-H	2.24 dd (16.5, 9.5)	2.23 dd (16.5, 9.2)	2.354 d (7.3)	2.26 dd (16.5, 9.2)	2.24 dd (16.5, 9.5)	2.359 d (6.7)
22-H	2.37[d] dd (16.5, 3)	2.36[d] dd (16.5, 3)	2.357[d] d (4.9)	2.40[d] dd (16.5, 2.8)	2.40[d] dd (16.5, 3)	2.361[d] d (4.9)
24-H	2.45 dd (17.5, 5.5)	2.45 dd (17.5, 5)	2.43 dd (17.5, 5)	2.46 dd (17.5, 5.5)	2.46 dd (17.8, 5)	2.43 dd (17.7, 5.2)
24-H	2.83 dd (17.5, 8.5)	2.83 dd (17.5, 8.5)	2.85 dd (17.5, 8.5)	2.83 dd (17.5, 8.5)	2.83 dd (17.8, 9)	2.83 dd (17.7, 9)
25-H	2.95 dqd (8.5, 7, 5)	2.94 dqd (8.5, 7, 5)	2.95 m	2.95 dqd (8.5, 7, 5.5)	2.94 dqd (9, 7, 5)	2.96 dqd (9, 7, 5)
18-H_3	0.92	0.90	0.95	0.99	0.96	0.89
19-H_3	1.123	1.12	1.11	1.28	1.25	1.28
21-H_3	0.86 d (6)	0.85 d (6)	0.98 d (6.4)	0.89 d (6)	0.88 d (6.5)	0.98 d (6.4)
27-H_3	1.18 d (7)	1.18 d (7)	1.19 d (7)	1.18 d (7)	1.18 d (7.5)	1.19 d (7)
30-H_3	1.118[e]	1.02[e]	1.12	1.12[e]	1.02[e]	1.14[e]
31-H_3	1.08	0.83	1.08	1.10	0.84	1.12
32-H_3	1.18	1.16	1.30	1.26	1.24	1.64
$COOCH_3$	3.68	3.68	3.68	3.68	3.68	3.68

δ values in $CDCl_3$ and coupling constants in Hz. Previous assignments of some signals were revised (ref. 2). *a*) ^{1}H–^{1}H Shift correlation spectra were measured. *b*—*d*) Long-range coupling was observed with 19-Me, 18-Me, and 21-Me, respectively. *e*) Assignments were confirmed by NOE experiments.

Table II. ^{13}C-NMR Spectral Data for Triterpene Methyl Esters from *Ganoderma lucidum*

Compd. ^{13}C	**1b**a)	**2b**a)	**3b**	**4b**a)	**5b**a)	**6b**a)
1	35.1 t	34.4 t	35.1 t	35.5 t	34.6 t	34.6 t
2	34.2 t	28.0 t	34.1 t	34.3 t	27.8 t	33.8 t
3	217.7 s	78.7 d	217.8 s	217.4 s	78.2 d	215.2 s
4	47.0b) s	39.0 s	47.0 s	46.8b) s	38.6b) s	47.0b) s
5	51.7 d	51.8 d	51.4 d	48.7 d	49.1 d	50.9 d
6	18.7 t	17.4 t	18.6 t	29.0 t	28.2 t	37.3 t
7	29.6 t	30.4 t	29.2 t	68.9 d	69.5 d	199.3 s
8	163.2 s	162.9 s	160.3 s	159.3 s	158.1 s	149.7 s
9	138.6 s	140.0 s	139.3 s	140.1 s	141.9 s	146.8 s
10	37.1 s	37.8 s	37.5 s	38.0 s	38.5b) s	39.4 s
11	198.1 s	198.3 s	197.0 s	199.6 s	199.9 s	199.3 s
12	51.7 t	52.1 t	49.8b) t	51.7 t	51.9 t	48.9 t
13	46.8b) s	47.2 s	44.8 s	46.6b) s	47.1 s	43.9b) s
14	53.6 s	53.5 s	57.9 s	54.0 s	54.0 s	57.2 s
15	72.9 d	73.0 d	212.4 s	72.4 d	72.5 d	206.8 s
16	38.6 t	38.7 t	40.8 t	36.2 t	36.1 t	39.8 t
17	48.7 d	48.7 d	45.0 d	48.1 d	48.1 d	44.5 d
18	17.2 q	17.1 q	17.0 q	17.3 q	17.1 q	16.1 q
19	19.0 q	19.0 q	18.9 q	19.4 q	19.6 q	18.6 q
20	32.6 d	32.5 d	32.0 d	32.7 d	32.7 d	32.0 d
21	19.4 q	19.4 q	19.6 q	19.6 q	19.6 q	19.8 q
22	49.6 t	49.7 t	49.3b) t	49.7 t	49.7 t	49.1 t
23	208.3 s	208.3 s	207.8 s	208.7 s	208.7 s	207.6 s
24	46.8 t	46.8 t	46.8 t	46.8 t	46.7 t	46.7 t
25	34.7 d	34.6 d	34.7 d	34.6 d	34.6 d	34.7 d
26	176.2 s	176.1 s	176.1 s	176.3 s	176.3 s	176.1 s
27	17.1 q	17.1 q	17.1 q	17.1 q	17.1 q	17.1 q
30	27.8 q	28.3 q	27.8 q	27.4 q	28.2 q	27.6 q
31	20.6 q	15.7 q	20.6 q	20.7 q	15.7 q	20.3 q
32	18.8 q	18.8 q	23.2 q	19.5 q	19.4 q	20.9 q
OCH_3	51.9 q	51.8 q	51.9 q	52.0 q	51.9 q	51.9 q

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 Shift correlation spectra were measured. *b*) Assignments may be interchanged for each compound.

resonated at δ 3.20 (dd, $J=10.8$, 5.8 Hz) and δ 0.84, respectively (Table I).

In turn, the ^{13}C-NMR spectrum of **2b**, which was fully analyzed by a combination of ^{1}H–^{1}H and ^{1}H–^{13}C shift correlation techniques, was found to be quite parallel with that of **1b** except for remarkable upfield shifts of a few signals due to ring A carbons (C-2, C-3, and C-4) (Table II). Furthermore, its ^{13}C spectral pattern was also similar to that of **5b**, except for a few signals assignable to some of the ring B carbons (C-5, C-6, and C-7) (Table II). This suggested that **2b** might be the 7-deoxy derivative of **5b**. Support for this was provided by inspection of the MS of **2b**, in which significant fragment peaks were observed at 373 (c), 309 ($a-H_2O$), 289 (g+H), 219 (h−H), 201 ($h-H-H_2O$), 171 (b), 144 (d+H), and 129 (e). Finally, oxidation of **2b** with chromium trioxide in acetic acid gave the tetraoxo compound (**3b**), which was identical with the sample prepared by the oxidation of **1b**. Thus the structure of methyl ganolucidate B was assigned as **2b**.7)

We have isolated more than twenty triterpenoids from the surface part of gills of fruit bodies of *Ganoderma lucidum*. Constituents of the other parts of the fungus are now under investigation.

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

	1b	**2b**	**3b**
M^+	514 (27)	516 (88)	512 (83)
M^+-CH_3	499 (2)	501 (10)	497 (5)
M^+-nH_2O	496 (3)	498 (59) 480 (42)	494 (41)
M^+-CO	486 (28)		484 (7)
M^+-OCH_3	483 (7)		481 (22)
$M^+-CH_3-nH_2O$		483 (59) 465 (51)	
$M^+-HCOOCH_3$			452 (7)
a	343 (2)		341 (18)
$a-nH_2O$	325 (4)	309 (15)	323 (44)
b	171 (15)	171 (27)	171 (38)
$b-CH_3OH$	139 (32)	139 (32)	139 (32)
c	371 (12)	373 (7)	
$c-H$	370 (2)		368 (10)
$c-H-nH_2O$	352 (6)	354 (7) 336 (27)	350 (100)
$c-H-CH_3-nH_2O$	337 (4)	321 (24)	335 (12)
$d+H$	144 (24)	144 (15)	
e	129 (32)	129 (62)	129 (72)
f	59 (61)	59 (100)	59 (100)
$g+H$	287 (24)	289 (15)	287 (51)
$h-H$	217 (9)	219 (11)	
$h-H-H_2O$		201 (62)	
$i+H$	417 (100)		415 (51)

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 °C. UV spectra were taken with a Shimadzu 202 UV spectrometer in EtOH solutions and IR spectra with a JASCO IRA-2 spectrometer in $CHCl_3$. MS and high-resolution MS were obtained with a JEOL D-300 spectrometer (ionization voltage, 70 eV; accelerating voltage, 3 kV) using a direct inlet system. ^1H- 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 (2-D) ^1H–^1H and ^1H–^{13}C shift correlation spectra were measured under the same conditions as described in a previous paper.[3)] Preparative thin layer chromatography (TLC) was carried out on Merck Kieselgel GF_{254} plates; developed 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*.

Isolation and Properties of Triterpenoids from *Ganoderma lucidum* (FR.) KARST.——Extraction and isolation of triterpenoids 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[3)]; *i.e.*, after methylation of the acidic fraction of the ether extract, the crude product was separated by a combination of silica gel column chromatography and preparative TLC to give methyl ganolucidate A (**1b**) (10 mg) and methyl ganolucidate B (**2b**) (15 mg) together with other triterpenoids.

Methyl Ganolucidate A (**1b**): Colorless needles (from ether), mp 192—194 °C, $[\alpha]_D$ +188 ° (c=0.5). UV λ_{max} nm (log ε): 256.5 (4.00). IR ν_{max} cm^{-1}: 3450, 1730, 1710, 1650. ^1H- and ^{13}C-NMR: Tables I and II. MS data: Table III. High-resolution MS m/z: Found 514.3300, Calcd for $C_{31}H_{46}O_6$ (M^+) 514.3294; Found 486.3364, Calcd for $C_{30}H_{46}O_5$ 486.3346; Found 417.2634, Calcd for $C_{25}H_{37}O_5$ 417.2640; Found 371.2585, Calcd for $C_{24}H_{35}O_3$ 371.2586; Found 287.2031, Calcd for $C_{19}H_{27}O_2$ 287.2011; Found 217.1214, Calcd for $C_{14}H_{17}O_2$ 217.1228; Found 171.0992, Calcd for $C_9H_{15}O_3$ 171.1021; Found 144.0769, Calcd for $C_7H_{12}O_3$ 144.0787; Found 139.0768, Calcd for $C_8H_{11}O_2$ 139.0758; Found 129.0543, Calcd for $C_6H_9O_3$ 129.0552.

Methyl Ganolucidate B (**2b**): Colorless needles (from ether), mp 167—169 °C, $[\alpha]_D$ +114 ° (c=0.5). UV λ_{max} nm (log ε): 257.5 (3.73). IR ν_{max} cm^{-1}: 3450, 1730, 1715, 1650. ^1H- and ^{13}C-NMR: Tables I and II. MS data: Table III.

High-resolution MS m/z: Found 516.3486, Calcd for $C_{31}H_{48}O_6$ (M^+) 516.3451; Found 501.3255, Calcd for $C_{30}H_{45}O_6$ 501.3216; Found 498.3345, Calcd for $C_{31}H_{46}O_5$ 498.3345; Found 373.2775, Calcd for $C_{24}H_{37}O_3$ 373.2743; Found 321.2177, Calcd for $C_{23}H_{29}O$ 321.2218; Found 289.2204, Calcd for $C_{19}H_{29}O_2$ 289.2168; Found 201.1278, Calcd for $C_{14}H_{17}O$ 201.1279; Found 171.0980, Calcd for $C_9H_{15}O_3$ 171.1021; Found 144.0793, Calcd for $C_7H_{12}O_3$ 144.0787; Found 139.0758, Calcd for $C_8H_{11}O_2$ 139.0758; Found 129.0551, Calcd for $C_6H_9O_3$ 129.0552.

Oxidation of Methyl Ganolucidate A (1b)——A solution of CrO_3 (10 mg) in AcOH (0.8 ml) containing water (0.2 ml) was added under vigorous stirring to a solution of **1b** (3 mg) in AcOH (0.8 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 over anhydrous $MgSO_4$, and concentrated. The residue was purified by preparative TLC with acetone–$CHCl_3$ (15 : 85) to give the tetraoxo compound (**3b**) (3 mg), amorphous powder, $[\alpha]_D$ $+178°$ ($c=0.25$). UV λ_{max} nm ($\log\varepsilon$): 254 (3.59). IR ν_{max} cm^{-1}: 1740, 1715, 1700 (sh), 1650. ^1H- and ^{13}C-NMR: Tables I and II. MS data: Table III. High-resolution MS m/z: Found 512.3167, Calcd for $C_{31}H_{44}O_6$ (M^+) 512.3138; Found 415.2471, Calcd for $C_{25}H_{35}O_5$ 415.2484; Found 350.2294, Calcd for $C_{24}H_{30}O_2$ 350.2304; Found 335.2101, Calcd for $C_{23}H_{27}O_2$ 335.2070; Found 341.2060, Calcd for $C_{22}H_{29}O_3$ 341.2116; Found 323.1973, Calcd for $C_{22}H_{27}O_2$ 323.2010; Found 287.2041, Calcd for $C_{19}H_{27}O_2$ 287.2011; Found 171.0994, Calcd for $O_9H_{15}O_3$ 171.1021; Found 139.0777, Calcd for $C_8H_{11}O_2$ 139.0758; Found 129.0587, Calcd for $C_6H_9O_3$ 129.0552.

Oxidation of Methyl Ganolucidate B (2b)——Compound **2b** (5 mg) was reacted with CrO_3 (10 mg) in AcOH in the same manner as above and the product was purified by preparative TLC to yield **3b** (4.5 mg) as an amorphous material. Its identity was confirmed by spectral comparisons.

References and Notes

1) Part II: T. Kikuchi, S. Kanomi, Y. Murai, S. Kadota, K. Tsubono, and Z. Ogita, *Chem. Pharm. Bull.*, **34**, 4018 (1986).
2) A part of this work was reported in our preliminary communication: T. Kikuchi, S. Matsuda, Y. Murai, and Z. Ogita, *Chem. Pharm. Bull.*, **33**, 2628 (1985).
3) Part I: T. Kikuchi, S. Kanomi, S. Kadota, Y. Murai, K. Tsubono, and Z. Ogita, *Chem. Pharm. Bull.*, **34**, 3695 (1986).
4) T. Kubota, Y. Asaka, I. Miura, and H. Mori, *Helv. Chim. Acta*, **65**, 611 (1982).
5) A. Bax, "Two-Dimensional NMR in Liquids," D. Reidel Publishing Co., Dordrecht, Holland, 1982; R. Benn and H. Gunther, *Angew. Chem. Int. Ed. Engl.*, **22**, 350 (1983).
6) In our preliminary communication, compound **5a** was designated as ganoderic acid D. Independently, Yamasaki and Komoda *et al.* have isolated the same compound and named it ganoderic acid C. After discussion with Prof. Yamasaki and Prof. Komoda, the name ganoderic acid C2 was proposed for **5a**. See H. Kohda, W. Tokumoto, K. Sakamoto, M. Fujii, Y. Hirai, K. Yamasaki, Y. Komoda, H. Nakamura, S. Ishihara, and M. Uchida, *Chem. Pharm. Bull.*, **33**, 1367 (1985); T. Kikuchi, S. Matsuda, S. Kadota, Y. Murai, and Z. Ogita, *ibid.*, **33**, 2624 (1985).
7) The stereochemistry at the 25-position in **1b** and **2b** is believed to be R in view of the close similarity of their ^1H- and ^{13}C-NMR spectra with those of **4b** having the established stereochemistry (see ref. 4).