Phytochemistry, Vol. 26, No. 6, pp. 1777–1784, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00
Pergamon Journals Ltd.

TRITERPENOIDS FROM THE FUNGUS *GANODERMA LUCIDUM*

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(*Received* 26 *August* 1986)

Key Word Index—*Ganoderma lucidum*; Polyporaceae; triterpenoids; ganoderic acid; ganoderenic acid; lucidenic acid; lucidone.

Abstract—Ten novel components, ganoderic acid, ganoderenic acid and lucidenic acid derivatives, were isolated from the fruiting body of the fungus *Ganoderma lucidum*. Their structures were elucidated mainly by spectroscopic and chemical methods.

INTRODUCTION

Ganoderma lucidum is well known as a crude drug in China and Japan, and its fruiting body contains large amounts of highly oxidized triterpenoids [1–13]. In this paper, we describe the structures of the novel minor components, ganoderic acids M, N and O, ganoderenic acid E and lucidenic acids H, I, J, K, L and M, along with the identification of ganoderic acid H [8] (also reported as ganoderic acid C in ref. [10] and revised as ganoderic acid D in ref. [12]), K [13], compound B9 [13] and lucidenic acids E_2 (reported as lucidenic acid E in ref. [8]).

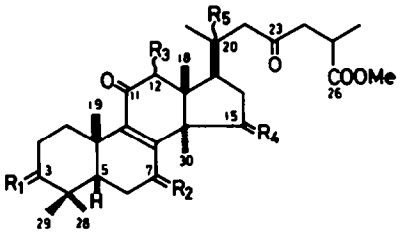
RESULTS AND DISCUSSION

The acidic part of the chloroform layer from the ethanol extract of *G. lucidum* was separated into several fractions by silica gel column chromatography and reverse-phase LC. Some of the fractions were methylated with diazomethane and subjected to silica gel column chromatography, prep. TLC, reverse-phase LC and/or HPLC to give the methyl esters of 14 triterpenoid acids (**1–14**).

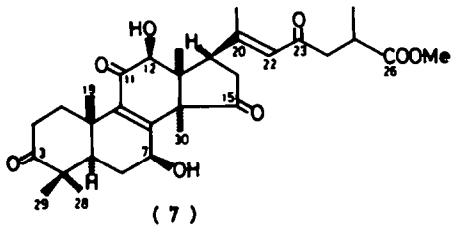
Compound **1**, methyl ganoderate M ($[M]^+$, *m/z* 544), was assigned the molecular formula $C_{31}H_{44}O_8$ by HRMS. Its ^1H NMR spectrum was very similar to that of ganoderic acid D [2] (Table 1), but the configuration of the hydroxyl group at C-12 was indicated to be α from the chemical shift of H-12 (δ 3.78, *s*) cf. ^1H NMR spectra of lucidenic acid E [2]. Thus, the structure of **1** was determined to be methyl 7β,12α-dihydroxy-3,11,15,23-tetraoxo-5α-lanost-8-en-26-oate.

Compound **2**, methyl ganoderate N, showed a molecular ion peak at *m/z* 544 by both FDMS and EIMS, although its relative intensity was very weak (0.06%) in EIMS. Its molecular formula was assigned as $C_{31}H_{44}O_8$ by HRMS. Its ^{13}C (Table 2) and ^1H NMR (Table 1) spectra resembled those of ganoderic acid C_1 [1, 3] (reported as ganoderic acid C in refs [1] and [3]). However, the signal at δ 72.9 (^{13}C NMR) and singlet methyl group at δ 1.41 (^1H NMR) suggested the presence of an additional hydroxyl group at C-20. Thus the structure of methyl ganoderate N was established to be methyl 7β,20-dihydroxy-3,11,15,23-tetraoxo-5α-lanost-8-en-26-oate (**2**). The weak intensity of the molecular ion peak in EIMS is ascribable to a McLafferty rearrangement and consequent easy cleavage between C-20 and C-22 (Fig. 1). Alkaline treatment of **2** caused a *retro*-aldol condensation and the resulting cleavage between C-20 and C-22 to yield lucidone B (**15**) [2] (Fig. 2). These observations also supported the above structure for **2**.

Compound **3**, methyl ganoderate O, gave no molecular ion peak in EIMS, but gave it at *m/z* 542 in FDMS. Its ^1H NMR spectrum (Table 1) contained six singlet methyl signals and one doublet methyl signal at high field,



(1) R_1=R_4=O, R_2=β-OH, R_3=α-OH, R_5=O
(2) R_1=R_4=O, R_2=β-OH, R_3=H, R_5=OH
(3) R_1=R_2=R_4=O, R_3=H, R_5=OH
(4) R_1=β-OH, R_2=O, R_3=R_5=H, R_4=α-OH
(5) R_1=β-OH, R_2=R_4=α-OH, R_3=R_5=H
(5a) R_1=β-OAc, R_2=α-OH, R_3=R_5=H, R_4=α-OAc
(5b) R_1=R_2=R_4=O, R_3=R_5=H
(6) R_1=β-OH, R_2=R_4=O, R_3=β-OAc, R_5=H



(7)

Table 1. ^{1}H NMR spectral data of compounds 1–7 [$CDCl_3$ or C_5D_5N(3), TMS as int. standard]

H	1*	2†	3*	4*	5*	6†	7*
1α	1.82 *ddd* (13.6, 8.7, 8.3)**	1.47 *ddd* (13.6, 8.5, 8.5)	1.79 *ddd* (14.1, 10.4, 5.9)	1.30 *m*	1.17 *ddd* (13.7. 13.2, 3.4)	1.18 *ddd* (13.6, 13.3, 5.8)	
1β	2.89 *ddd* (13.6, 7.8, 5.9)	2.95 *m*	3.0 *m*	2.84 *ddd* (12.7, 4.9, 4.9)	3.00 *ddd* (13.7, 3.4, 3.4)	2.73 *ddd* (13.6, 3.3, 3.3)	2.79 *ddd* (13.2, 7.1, 4.2)
2α	2.50 *ddd* (15.1, 8.3, 7.8)	2.50 *m*	2.46 *ddd* (15.6, 8.8, 5.9)	1.70 *m*	1.65 *m*	1.70 *m*	2.41 *ddd* (15.6, 6.6, 4.2)
2β	2.54 *ddd* (15.1, 8.7, 5.9)	2.50 *m*	2.66 *ddd* (15.6, 10.4, 5.9)	1.70 *m*	1.65 *m*	1.70 *m*	2.65 *ddd* (15.6, 11.2, 6.8)
3α	—	—	—	3.28 *dd* (11.7, 6.5)	3.31 *dd* (10.5, 5.4)	3.26 *dd* (10.3, 5.5)	—
5α	1.74 *dd* (13.7, 1.0)	1.55 *dd* (12.6, 1.1)	2.48 *dd* (14.7, 2.4)	1.54 *dd* (13.2, 4.4)	1.30 *dd* (13.2, 1.5)	1.56 *dd* (13.9, 2.9)	1.48 *dd* (13.7, 2.0)
6α	2.11 *ddd* (13.2, 7.3, 1.0)	2.12 *ddd* (12.6, 7.7, 1.1)	2.53 *dd* (13.2, 2.4)	2.55 *dd* (15.6, 4.4)	1.80 *m*	2.57 *dd* (14.3, 2.9)	2.20 *ddd* (13.7, 8.6, 2.0)
6β	1.65 *ddd* (13.7, 13.2, 9.8)	1.68 *ddd* (12.6, 12.6, 9.0)	2.76 *dd* (14.7, 13.2)	2.59 *dd* (15.6, 13.2)	1.75 *m*	2.67 *dd* (14.3, 13.9)	1.79 *ddd* (13.7, 13.7, 8.6)
7α	4.85 *dd*, (9.8, 7.3)	4.84 *dd* (9.0, 7.7)	—	—	—	—	4.84 *dd* (8.6, 8.6)
7β	—	—	—	—	4.56 *m*	—	—
12α	—	2.77 *d* (17.2)	3.25 *d* (16.6)	2.83 *d* (16.6)	2.77 *dq* (17.6, 1.0)	5.63 *s*	4.46 *s*
12β	3.78 *s*	2.85 *d* (17.2)	3.12 *d* (16.6)	2.53 *d* (16.6)	2.39 *d* (17.6)	—	—
15β	—	—	—	4.34 *dd* (7.3, 7.3)	4.58 *m*	—	—
16α	2.73 *dd* (22.5, 8.3)	2.86 *dd* (19.4, 10.3)	3.0 *m*	1.85 *m*	1.90 *m*	2.77 *dd* (18.1, 9.9)	2.72 *dd* (20.0, 8.3)
16β	2.11 *dd* (22.5, 12.7)	2.45 *m*	3.0 *m*	1.85 *m*	1.90 *m*	1.91 *dd* (18.1, 8.2)	2.56 *dd* (20.0, 10.3)
17	2.73 *m*	2.25 *dd* (10, 9)	2.92 *dd* (8.3, 8.3)	1.85 *m*	1.90 *m*		3.32 *dd* (10.3, 8.3)
Me-18	1.03 *s*	1.17 *s*	1.38 *s*	0.89 *s*	0.87 *d* (1.0)	0.89 *s*	0.80 *s*
Me-19	1.15 *s*	1.26 *s*	1.32 *s*	1.14 *s*	1.06 *s*	1.33 *s*	1.44 *s*
20	2.18 *m*	—	—	2.00 *m*	2.00 *m*		—
Me-21	1.09 *d* (6.8)	1.41 *s*	1.67 *s*	0.86 *d* (6.4)	0.85 *d* (6.4)	0.98 *d* (6.2)	2.31 *d* (1.0)
22	2.41 *dd* (16.1, 8.3)	2.66 *d* (16.5)	2.85 *d* (14.7)	2.42 *dd* (16.6, 2.4)	2.38 *dd* (16.1, 2.9)		6.15 *d* (1.0)
22	2.37 *dd* (6.1, 4.4)	2.49 *d* (16.5)	2.82 *d* (14.7)	2.25 *dd* (16.6, 9.7)	2.25 *dd* (16.1, 9.3)		—
24	2.87 *dd* (17.6, 8.3)	2.95 *m*	3.0 *m*	2.82 *dd* (17.7, 8.3)	2.83 *dd* (17.7, 8.6)	2.83 *dd* (17.2, 8.8)	2.95 *m*
24	2.47 *dd* (17.6, 5.4)	2.45 *m*	2.70 *dd* (17.0, 4.0)	2.46 *dd* (17.7, 5.1)	2.46 *dd* (17.7, 5.4)	2.42 *dd* (17.2, 5.0)	2.53 *m*
25	2.96 *m*	2.95 *m*	3.0 *m*	2.94 *m*	2.95 *m*	2.96 *ddq* (8.8, 5.0, 7.0)	2.95 *m*
Me-27	1.19 *d* (7.3)	1.20 *d* (7.0)	1.16 *d* (7.3)	1.18 *d* (7.3)	1.18 *d* (7.3)	1.18 *d* (7.0)	1.19 *d* (7.3)
Me-28	1.10 *s*	1.11 *s*	1.06 *s*	1.03 *s*	1.05 *s*	1.03 *s*	1.13 *s*
Me-29	1.14 *s*	1.12 *s*	1.11 *s*	0.89 *s*	0.84 *s*	0.82 *s*	1.13 *s*
Me-30	1.32 *s*	1.34 *s*	1.92 *s*	1.29 *s*	1.27 *s*	1.73 *s*	1.51 *s*
COOMe	3.69 *s*	3.69 *s*	3.62 *s*	3.67 *s*	3.68 *s*	3.67 *s*	3.69 *s*
OAc-12	—	—	—	—		2.24 *s*	—

*Measured at 500 MHz.

†Measured at 270 MHz.

**Values in parentheses are coupling constants in Hz.

Table 2. ^{13}C NMR spectral data of compounds **2**, **5**, **8**, **9** and **14** [67.8 MHz, $CDCl_3$ (**2**, **14**) or C_5D_5N (**5**, **8**, **9**), TMS as int. standard]

C	2	5	8	9	14
1	35.7 (2)**	35.2 (2)	35.4 (2)	36.7 (2)	33.3 (2)
2	34.3 (2)	28.9 (2)	28.3 (2)	27.9 (2)	27.4 (2)
3	217.8 (0)*	77.9 (1)	72.0 (1)	70.7 (1)	77.5 (1)
4	45.3 (0)	39.5 (0)*	43.0 (0)	43.6 (0)	40.4 (0)
5	49.4 (1)†	49.4 (1)	42.5 (1)	44.5 (1)	51.4 (1)
6	27.7 (2)	27.7 (2)	27.8 (2)	34.1 (2)	36.7 (2)
7	66.3 (1)	68.0 (1)	66.7 (1)	200.4 (0)	194.1 (0)
8	157.6 (0)	161.3 (0)	158.8 (0)	152.2 (0)	151.6 (0)
9	141.0 (0)	141.2 (0)	142.9 (0)	147.4 (0)	146.0 (0)
10	38.3 (0)	39.4 (0)*	39.2 (0)	40.8 (0)	39.1 (0)
11	197.6 (0)	199.6 (0)	198.3 (0)	199.8 (0)	198.9 (0)
12	50.5 (2)	52.8 (2)	51.1 (2)	49.9 (2)	79.4 (1)
13	46.8 (0)	47.8 (0)	45.6 (0)	44.5 (0)	48.0 (0)
14	59.7 (0)	54.2 (0)	59.2 (0)	57.6 (0)	58.5 (0)
15	216.8 (0)*	71.8 (1)	216.8 (0)	208.0 (0)	206.0 (0)
16	36.3 (2)	38.0 (2)	41.4 (2)	40.5 (2)	37.6 (2)
17	49.0 (1)†	46.9 (1)	46.2 (1)	45.5 (1)	45.5 (1)
18	19.3 (3)	17.4 (3)	17.8 (3)	16.4 (3)	12.1 (3)
19	18.1 (3)	17.8 (3)	19.2 (3)	18.6 (3)	18.0 (3)
20	72.9 (0)	33.0 (1)	35.4 (1)	35.5 (1)	33.0 (1)
21	26.7 (3)	19.4 (3)	18.1 (3)	18.2 (3)	20.2 (3)
22	52.7 (2)	49.7 (2)	31.0 (2)	31.0 (2)*	30.1 (2)
23	210.4 (0)	208.5 (0)	31.0 (2)	31.1 (2)*	31.7 (2)
24	47.7 (2)	46.9 (2)	174.0 (0)	174.0 (0)	173.7 (0)
25	34.5 (1)	35.1 (1)	66.6 (2)	65.1 (2)	27.9 (3)
26	175.9 (0)	176.2 (0)	13.2 (3)	13.1 (3)	15.6 (3)
27	17.0 (3)	17.2 (3)	24.8 (3)	21.6 (3)	21.4 (3)
28	27.0 (3)	28.8 (3)	—	—	—
29	20.8 (3)	16.8 (3)	—	—	—
30	25.1 (3)	21.7 (3)	—	—	—
COOMe	52.0 (3)	51.6 (3)	51.4 (3)	51.4 (3)	51.6 (3)
12AcMe	—	—	—	—	20.8 (3)
12AcCO	—	—	—	—	170.1 (0)

*,† Assignments may be reversed.
** Number of bonded H in parenthesis.

however, it contained no signals for methine groups bearing a hydroxyl group. By analogy with methyl ganoderate N (**2**), alkaline treatment of **3** gave a *retro*-aldol condensation product (**16**) (Fig. 2), which was also derived from lucidone B (**15**) on treatment with pyridinium dichromate (PDC) [16]. From these data, methyl ganoderate O was concluded to be methyl 3,7,11,15,24-pentaoxo-5α-lanost-8-en-26-oate (**3**).

Compound **4**, $C_{31}H_{46}O_7$, gave a ^1H NMR spectrum (Table 1) similar to that of methyl ganoderate J [4], but the signal at δ 3.28 (1H, *dd*, J = 11.7, 6.5) showed the presence of a β-hydroxyl group at C-3 instead of a carbonyl group. Thus, **4** was identified as methyl ganoderate K, whose structure had been presented by Kikuchi *et al.* [13].

Compound **5** was formulated as $C_{31}H_{48}O_7$ and its ^{13}C NMR spectrum (Table 2) indicated the presence of three methine carbons each bearing a hydroxyl group (δ 77.9, 77.8 and 68.0). Its ^1H NMR spectrum (Table 1) also indicated the presence of three methine protons each bearing a hydroxyl group [δ 3.31 (1H, *dd*, J = 10.5, 5.4), 4.5–4.6 (2H, overlapped)]. Acetylation of **5** gave a diacetate (**5a**) as a major product, the ^1H NMR spectrum of which showed the signals due to the above methine protons at δ 5.28 (1H, *dd*, J = 9.3, 5.7), 4.57 (1H, *dd*, J = 11.2, 5.3), and 4.31 (1H, *m*). The two signals at δ 5.28 and 4.57 indicated the presence of an α-acetoxyl group at C-15 and a β-acetoxyl group at C-3, respectively. On the other hand, the signal at δ 4.31 indicated the presence of an α-hydroxyl group at C-7, the presence of which was also observed in the mycelial components, ganoderic acids U, V and W [14, 15]. These observations indicated that **5** was an epimer at C-7 of methyl ganoderate C_2 (reported as ganoderic C in ref. [7] and as ganoderic acid D in ref. [8]) and was identical with 'Compound B9' [13], whose structure had been presented by Kikuchi *et al.* Furthermore, this structure was confirmed by oxidation of **5** with PDC to give a pentaketo compound (**5b**) [6].

Compound **6** exhibited a molecular ion peak at *m/z* 586 and was assigned the molecular formula $C_{33}H_{46}O_9$. Its ^1H NMR data (Table 1) entirely agreed with that of methyl ganoderate H [8, 10]. Thus, **6** was identified as methyl ganoderate H.

The molecular formula of compound **7**, methyl ganoderate E, was determined to be $C_{31}H_{42}O_8$. Its UV spectrum contained an absorption maximum at 247 nm

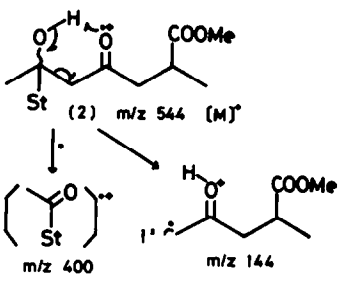
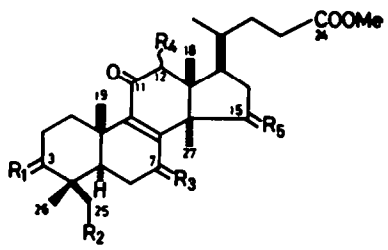


Fig. 1. McLafferty rearrangement and consequent cleavage between C-20 and C-22 in the mass spectrum of compound 2.



(8) R_1=R_3=β-OH, R_2=OH, R_4=H, R_5=O

(8a) R_1=, R_3=β-OH, R_4=H, R_5=O
R_2=

(9) R_1=β-OH, R_2=OH, R_3=R_5=O, R_4=H

(10) R_1=R_4=β-OH, R_2=OH, R_3=R_5=O

(11) R_1=R_3=R_5=O, R_2=H, R_4=α-OH

(12) R_1=R_4=β-OH, R_2=H, R_3=R_5=O

(13) R_1=β-OH, R_2=R_4=H, R_3=R_5=α-OH

(14) R_1=β-OH, R_2=H, R_3=R_5=O, R_4=β-OAc

(ε 11760). The large ε value of which indicated the presence of two α,β-unsaturated carbonyl groups. In the ^{1}H NMR spectrum of 7 (Table 1), the signals due to a olefinic methyl group at δ 2.31 (3H, *d*, *J* = 1.0) and 6.15 (1H, *d*, *J* = 1.0) suggested the presence of a *E*-double bond between C-20 and C-22 by analogy with ganoderenic acids A–D [11]. The signals at δ4.84 (1H, *dd*, *J* = 8.6, 8.6) and 4.46 (1H, *s*) revealed the presence of 7β- and 12β-hydroxyl groups. From these data, the structure of methyl ganoderenate E was concluded to be methyl 7β,12β-dihydroxy-3,11,15,23-tetraoxo-5α-lanosta-8,20*E*-dien-26-oate (7).

Compound **8**, methyl lucidenate H, was formulated as $C_{28}H_{42}O_7$. Its ^{13}C NMR spectrum (Table 2) showed the presence of two methine carbons (δ 72.0, 66.7) and one methylene (δ 66.6) carbon which possessed the hydroxyl group, in addition to a carbonyl (δ 216.8), an α,β-unsaturated carbonyl (δ 198.3, 158.8, 142.9) and an ester carboxyl (δ 174.0) group. In the ^{1}H NMR spectrum of **8** (Table 3), the signals at δ4.30 (1H, *dd*, *J* = 11.7, 5.5) and 5.25 (1H, *dd*, *J* = 7.5, 7.5) revealed the presence of 3β- and 7β-hydroxyl groups, and the AB-doublet signals at δ 4.24 (1H, *d*, *J* = 10.4) and 3.78 (1H, *d*, *J* = 10.4) indicated the presence of an α-hydroxymethyl group at C-4. These ^{1}H NMR data are in marked contrast with those of ganolucidic acid C [4], which possesses a β-hydroxymethyl group at C-4. On the basis of these observations, the structure of methyl lucidenate H was concluded to be methyl 3β,7β-dihydroxy-4α-hydroxymethyl-4β,14α-dimethyl-11,15-dioxo-5α-chol-8-en-24-oate (**8**). This structure was confirmed by converting **8** into **8a** by treating it with cupric sulphate–acetone. The ^{1}H NMR data of **8a** (experimental) was in good agreement with that of the acetonide derived from a triterpene which has 3β-hydroxyl and 4α-hydroxymethyl groups [17].

The molecular formula of compound **9**, methyl lucidenate I, was assigned as $C_{28}H_{40}O_7$. By analogy with methyl lucidenate H (**8**), the ^{1}H NMR signals of **9** at δ 4.29 (1H, *dd*, *J* = 11.2, 5.3), 4.16 (1H, *d*, *J* = 10.8) and 3.61 (1H, *d*, *J* = 10.8) established the presence of 3β-hydroxyl and 4α-hydroxymethyl groups, and the absence of a 7β-hydroxyl group (Table 3). Moreover, the ^{13}C NMR signal of **9** at δ 200.4 indicated the presence of a conjugated carbonyl group at C-7 (Table 2). Thus, the structure of methyl lucidenate I was established to be methyl 3β-hydroxy-4α-hydroxymethyl-4β,14α-dimethyl-7,11,15-trioxo-5α-chol-8-en-24-oate (**9**).

Compound **10**, methyl lucidenate J, $C_{28}H_{40}O_8$, had a ^{1}H NMR spectrum closely similar to that of methyl lucidenate I (**9**) (Table 3). However, a signal at δ 4.92 (1H, *s*) revealed the presence of an additional β-hydroxyl group at C-12. So, the structure of methyl lucidenate J was determined to be methyl 3β,12β-dihydroxy-4α-hydroxymethyl-4β,14α-dimethyl-7,11,15-trioxo-5α-chol-8-en-24-oate (**10**).

Compound **11**, methyl lucidenate K, was formulated as $C_{28}H_{38}O_7$. Its ^{1}H NMR spectrum (Table 3) resembled that of lucidenic acid E_1 [2] and a signal at δ 3.94 (1H, *s*) indicated the presence of an α-hydroxyl group at C-12. However the ABX type signals at δ 2.68 (1H, *dd*, *J* = 15.1, 14.6), 2.39 (1H, *dd*, *J* = 14.6, 3.4) and 2.54 (1H, *dd*, *J* = 15.1, 3.4) implied the presence of a carbonyl group at C-

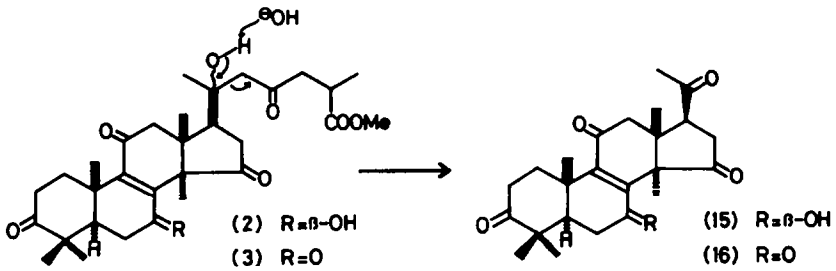


Fig. 2. *retro*-Aldol condensations of compounds 2 and 3.

Table 3. ^{1}H NMR spectral data of compounds 8–14 [C_5D_5N (8–10) or $CDCl_3$ (11–14), TMS as int. standard]

H	8*	9*	10*	11†	12*	13*	14*
1α	1.29 *ddd* (13.6, 12.5, 6.9)**	1.45 *m*	1.35 *m*	2.08 *m*	1.14 *ddd* (13.6, 13.6, 5.8)		1.18 *ddd* (13.9, 13.2, 5.5)
1β	3.27 *ddd* (13.6, 3.5, 3.5)	3.10 *ddd* (13.6, 3.5, 3.5)	2.97 *ddd* (13.5, 3.5, 3.5)	2.78 *ddd* (14.2, 8.3, 5.8)	2.76 *ddd* (13.6, 3.7, 3.5)	3.00 *ddd* (13.2, 3.5, 3.5)	2.74 *ddd* (13.9, 3.7, 3.7)
2α	2.05 *m*	2.05 *m*	2.05 *m*	2.55 *ddd* (15.6, 8.3, 7.8)	1.75 *m*		1.70 *m*
2β	2.05 *m*	2.05 *m*	2.05 *m*	2.61 *ddd* (15.6, 8.8, 5.8)	1.75 *m*		1.70 *m*
3α	4.30 *dd* (11.7, 5.5)	4.29 *dd* (11.2, 5.3)	4.27 *dd* (11.5, 5.2)	—	3.27 *dd* (9.9, 6.2)	3.32 *dd* (11.1, 4.7)	3.26 *dd* (10.4, 4.6)
5α	1.91 *d* (12.7)	2.65 *dd* (13.6, 2.6)	2.65 *dd* (13.6, 2.6)	2.39 *dd* (14.6, 3.4)	1.55 *dd* (14.3, 2.6)		1.56 *dd* (14.3, 2.9)
6α	2.58 *dd* (12.1, 7.5)	2.92 *dd*, (13.9, 2.6)	2.93 *dd* (13.6, 2.6)	2.54 *dd* (15.1, 3.4)	2.58 *dd* (14.3, 2.6)		2.58 *dd* (14.3, 2.9)
6β	1.95 *m*	2.80 *dd* (13.9, 13.6)	2.83 *dd* (13.6, 13,6)	2.68 *dd* (15.1, 14.6)	2.70 *dd* (14.3, 14.3)		2.68 *dd* (14.3, 14.3)
7α	5.25 *dd* (7.5, 7.5)	—	—	—	—	—	—
7β	—	—	—	—	—	4.55 *m*	—
12α	2.95 *dq* (16.8, 1.0)	3.09 *d* (15.3)	4.92 *s*	—	4.51 *s*	2.76 *d* (17.6)	5.63 *s*
12β	2.81 *d* (16.8)	2.81 *d* (15.3)	—	3.94 *s*	—	2.40 *d* (17.6)	—
15β	—	—	—	—	—	4.58 *dd* (9.9, 5.1)	—
16α	2.77 *dd* (19.2, 8.1)	2.78 *m*	2.87 *dd* (17.6, 9.2)	2.84 *dd* (18.6, 9.3)	2.74 *dd* (18.0, 9.9)		2.79 *dd* (18.3, 9.7)
16β	2.21 *dd* (19.2, 9.9)	2.10 *m*	2.26 *dd* (17.6, 8.1)	2.07 *dd* (18.6, 9.3)	2.06 *dd* (18.0, 8.1)		2.08 *dd* (18.3, 8.1)
17	2.0 *m*	2.05 *m*	2.70 *ddd* (8, 8, 8)	2.07 *ddd* (9.3, 9.3, 9.3)	2.55 *ddd* (9.9, 8.1, 8.3)		2.28 *ddd* (8.3, 8.3, 8.3)
Me-18	1.10 *s*	0.93 *s*	0.98 *s*	0.84 *s*	0.64 *s*	0.84 *s*	0.89 *s*
Me-19	1.54 *s*	1.47 *s*	1.52 *s*	1.23 *s*	1.37 *s*	1.06 *s*	1.33 *s*
20	1.50 *m*	1.45 *m*	1.95 *m*	1.55 *m*	1.80 *m*		1.70 *m*
Me-21	0.86 *d* (6.2)	0.86 *d* (6.6)	1.28 *d* (6.6)	1.06 *d* (6.8)	1.11 *d* (7.0)	0.85 *d* (5.8)	0.99 *d* (6.6)
22	1.80 *m*	1.80 *m*	1.95 *m*	1.82 *m*	1.80 *m*		1.85 *m*
22	1.30 *m*	1.40 *m*	1.41 *m*	1.43 *m*	1.30 *m*		1.30 *m*
23	2.43 *ddd* (15.0, 9.5, 5.5)	2.45 *ddd* (15.1, 9.3, 5.2)	2.48 *ddd* (16.2, 9.2, 5.8)	2.43 *ddd* (16.1, 9.3, 5.4)	2.41 *ddd* (15.8, 9.2, 5.5)		2.44 *ddd* (15.8, 8.6, 7.3)
23	2.30 *ddd* (15.0, 8.8, 7.0)	2.31 *ddd* (15.1, 8.8, 7.0)	2.37 *ddd* (16.2, 8.7, 6.9)	2.30 *ddd* (16.1, 8.8, 7.3)	2.27 *ddd* (15.8, 8.8, 7.0)		2.41 *ddd* (15.8, 9.2, 5.7)
25	4.24 *d* (10.4)	4.16 *d* (10.8)	4.16 *d* (10.6)	—	—	—	—
25	3.78 *d* (10.4)	3.61 *d* (10.8)	3.61 *d* (10.6)	—	—	—	—
Me-25	—	—	—	1.12 *s*	1.04 *s*	1.05 *s*	1.03 *s*
Me-26	1.11 *s*	1.05 *s*	1.04 *s*	1.15 *s*	0.90 *s*	0.84 *s*	0.83 *s*
Me-27	1.30 *s*	1.63 *s*	1.78 *s*	1.58 *s*	1.69 *s*	1.28 *s*	1.73 *s*
COOMe	3.65 *s*	3.65 *s*	3.65 *s*	3.68 *s*	3.66 *s*	3.67 *s*	3.67 *s*
OAc-12	—	—	—	—	—	—	2.22 *s*

*270 MHz.
†500 MHz.
**Values in parentheses are coupling constants in Hz.

7 for **11** instead of the β-hydroxyl group for lucidenic acid E_1. Thus, the structure of methyl lucidenate K was concluded to be methyl 12α-hydroxy-4,4,14α-trimethyl-3,7,11,15-tetraoxo-5α-chol-8-en-24-oate (**11**).

The molecular formula of compound **12**, methyl lucidenate L, was assigned as $C_{28}H_{40}O_7$. Its UV spectrum gave a absorption maximum at 255 nm (ε 6930). The detailed analysis of the ^{1}H NMR spectrum (Table 3) indicated structure **12** for methyl lucidenate L. The signals at δ 4.58 (1H, *s*) and 3.27 (1H, *dd*, J = 9.9, 6.2) suggested the presence of 12β- and 3β-hydroxyl groups, respectively. Thus, the structure of methyl lucidenate L was determined

to be methyl 3β,12β-dihydroxy-4,4,14α-trimethyl-7,11,15-trioxo-5α-chol-8-en-24-oate (12).

Compound 13, methyl lucidenate M, gave a molecular ion peak at *m/z* 476 and was formulated as $C_{28}H_{44}O_6$. Its UV spectrum gave a absorption maximum at 255 nm (ε 7900), which indicated the presence of an α,β-unsaturated carbonyl group. Although the ^{1}H NMR spectrum of 13 (Table 3) was not clearly observed because of its small amount, the signals at δ 3.32 (1H, *dd*, *J* = 11.1, 4.7), 4.55 (1H, overlapped) and 4.58 (1H, *dd*, *J* = 9.9, 5.1) implied the presence of 3β-, 7α- and 15-α-hydroxyl groups similar to compound B9 (5). Five singlet and one doublet methyl signal were also observed in higher field and their chemical shifts were in good agreement with those of the corresponding methyl groups of compound B9 (5). From these observations, it was deduced that the structure of 13 was the same as that of 5 except for the side-chain moiety. Therefore, the structure of methyl lucidenate M was elucidated to be methyl 3β,7α,15α-trihydroxy-4,4,14α-trimethyl-11-oxo-5α-chol-8-en-24-oate (13).

The molecular formula of compound 14 was assigned as $C_{30}H_{42}O_8$. Its ^{1}H NMR (Table 3) and ^{13}C NMR (Table 2) spectra entirely agreed with those of methyl lucidenate E_2 [8], which is unique in having the β-acetoxyl group at C-12. So, compound 14 was identified as methyl lucidenate E_2.

Alkaline treatment of methyl ganoderates N (2) and O (3) afforded the corresponding *retro*-aldol condensation products 15 (lucidone B) and 16, respectively. Taking account of this observation, it appears that lucidones A, B and C [2, 5] might be artifacts generated under the alkaline conditions (satd aq. $NaHCO_3$) used during the isolation procedure.

EXPERIMENTAL

Mps (Yanako micro-melting point apparatus) are uncorr.; ^{1}H NMR: 270 and 500 MHz, $CDCl_3$, TMS as int. standard; ^{13}C NMR: 270 MHz, $CDCl_3$.

Extraction and isolation. Dried chipped fruiting bodies of *G. lucidum* (a mixture of two strains [18], 6 kg) were extracted with EtOH. The extract was concd and partitioned between $CHCl_3$ and H_2O. The $CHCl_3$ layer was alkalinized with sat. aq. $NaHCO_3$ and the H_2O phase acidified to pH 3–4 with 6M HCl. The resulting ppt was dissolved in $CHCl_3$ and then evapd to yield an acidic residue, which was chromatographed on silica gel (fractions 1–11, $CHCl_3$–MeOH, 49:1; fraction 12, $CHCl_3$–MeOH, 9:1; fraction 13, MeOH).

Fraction 5 was rechromatographed 3 times on a silica gel column ($CHCl_3$–MeOH, 19:1) to give several fractions, some of which were treated with etheral CH_2N_2. The methylated fractions were separated by the combination of prep. TLC (C_6H_6–EtOAc, 1:1 or 2:1) and silica gel ($CHCl_3$–MeOH, 99:1) or reverse-phase LC (MeOH–H_2O, 7:3, Lobar RP-18). These separations gave compounds 1, 2, 3, 6, 7, 11, 12 and 14. Fractions 10 and 11 were combined and subjected to silica gel CC to give ganoderic acid C_2 as crude crystals, which were methylated with 3% methanolic HCl. Purification of the methylated products by reverse-phase LC (MeOH–H_2O, 3:1, RP-18) and HPLC (MeOH–H_2O, 3:1, μ Bondapak C18) gave compound 4 as one of the impurities. Fraction 12 was subjected to reverse-phase LC (MeOH–H_2O, 13:7, Lobar RP-8) and separated into four fractions (12a–12d). Fraction 12b was treated with etheral CH_2N_2 and the methylated products were separated on a silica gel column (×3) ($CHCl_3$–Me_2CO, 2:1, $CHCl_3$–MeOH, 19:1, C_6H_6–EtOAc, 1:6) and reverse-phase LC (MeOH–H_2O, 7:3, RP-8) to yield compounds 8, 9 and 10. Fractions 12c and 12d were also methylated with etheral CH_2N_2. Compound 5 was purified by silica gel column chromatography ($CHCl_3$–MeOH, 3:1) of the methylated product of fraction 12c. Compound 13 was isolated from the methylated product of fraction 12d by a combination of silica gel CC ($CHCl_3$–MeOH, 9:1), prep. TLC ($CHCl_3$–Me_2CO, 2:1) and reverse-phase HPLC (MeOH–H_2O, 3:2, μ Bondapak C18).

Methyl ganoderate M (1). Compound 1 was crystallized from MeOH as needles (1.5 mg), mp 206–210°. EIMS *m/z* (rel. int.): 544.3058 $[M]^+$ ($C_{31}H_{44}O_8$, calc. 544.3037) (3), 526 (6), 355 (6), 304 (100), 139 (23), 129 (31), 69 (25), 59 (37); IR ν_{max}^{film} cm^{-1}: 3450, 2900, 1710, 1660, UV λ_{max}^{MeOH} nm (ε): 258 (2940); CD λ^{MeOH} nm (Δε): 292 (−1.0), 282 (0), 257 (+7.3), 230 (0), 218 (−2.8).

Methyl ganoderate N (2). Compound 2 was crystallized from EtOAc–cyclohexane as prisms (22.7 mg), mp 164–167°, $[\alpha]_D^{24}$ +153° (*c* = 0.2, MeOH). FDMS *m/z* (rel. int.): 544 $[M]^+$ (10), 400 (100), 187 (77), 144 (43); EIMS *m/z* (rel. int.): 544.3057 $[M]^+$ ($C_{31}H_{44}O_8$, calc. 544.3037) (0.06), 400 $[C_{24}H_{32}O_5]^+$ (2), 372 (5), 129 (7), 112 (18), 87 (21), 59 (21), 43 (100); IR ν_{max}^{film} cm^{-1}: 3450, 2950, 1720, 1700, 1650; UV λ_{max}^{MeOH} nm (ε): 254 (7180); CD λ^{MeOH} nm (Δε): 292 (−2.5), 280 (0), 255 (+18.1), 229 (0), 215 (−7.3).

Alkaline treatment of 2. Compound 2 (1.3 mg) in MeOH (0.2 ml) was treated with 1M KOH (0.2 ml). After 30 min, the reaction mixture was diluted with H_2O and extracted with Et_2O (15 ml). The organic layer was dried (Na_2SO_4) and concd to give compound 15 (1.5 mg): $[M]^+$, *m/z* 400 ($C_{24}H_{32}O_5$); ^{1}H NMR: identical to that of lucidone B [2].

Methyl ganoderate O (3). Compound 3 was obtained as pale yellow needles (3.5 mg, from Et_2O–hexane), mp 168–171°. FDMS *m/z* (rel. int.): 542 $[M]^+$ (100), 398 (43), 355 (20), 187 (90), 144 (31); EIMS *m/z* (rel. int.): 398 $[C_{24}H_{30}O_5]^+$ (6), 355 (4), 300 (42), 215 (23), 87 (15), 59 (15), 43 (100); IR ν_{max}^{film} cm^{-1}: 3475, 2950, 1740, 1700; UV λ_{max}^{MeOH} nm (ε): 252 (6610); CD λ^{MeOH} nm (Δε): 330 (0), 305 (−5.0), 290 (0), 277 (+5.1), 259 (0), 252 (−1.5), 243 (0), 225 (+8.4), 212 (0).

Alkaline treatment of 3. Compound 3 (0.9 mg) in MeOH (0.2 ml) was treated with 1 M KOH. After 35 min, the reaction mixture was diluted with H_2O and extracted with EtOAc. The organic layer was dried (Na_2SO_4) and concd to yield compound 16 (0.7 mg). Compound 16, a colourless syrup, $C_{24}H_{30}O_5$ (calc. 398.2094, $[M]^+$, *m/z* 398.2080). EIMS *m/z* (rel. int.): 398 $[M]^+$ (9), 300 (60), 215 (33), 187 (20), 163 (19), 69 (25), 55 (28), 43 (100); ^{1}H NMR: δ 3.38 (1H, *dd*, *J* = 8.8, 8.8, H-17), 3.07 (1H, *dq*, *J* = 15.8, 1.1, H-12α), 2.90 (1H, *ddd*, *J* = 14.5, 8.1, 6.1, H-1β), 2.85 (1H, *dd*, *J* = 19.0, 8.8, H-16), 2.84 (1H, *d*, *J* = 15.8, H-12β), 2.70 (1H, *dd*, *J* = 14.7, 13.6, H-6β), 2.63 (1H, *ddd*, *J* = 15.6, 9.5, 6.1, H-2), 2.62 (1H, *dd*, *J* = 19.0, 8.8, H-16), 2.49 (1H, *dd*, *J* = 13.6, 2.6, H-6α), 2.48 (1H, *ddd*, *J* = 15.6, 8.1, 6.1, H-2), 2.32 (1H, *dd*, *J* = 14.7, 2.6, H-5α), 2.21 (3H, *s*, H-21), 1.75 (1H, *ddd*, *J* = 14.7, 9.5, 6.1, H-1α), 1.70 (3H, *s*, H-24), 1.28 (3H, *s*, H-19), 1.15 (3H, *s*, H-23), 1.12 (3H, *s*, H-22), 0.78 (3H, *d*, *J* = 1.1, H-18). From these data, compound 16 was determined to be 4,4,14α-trimethyl-3,7,11,15,20-pentaoxo-5α-pregn-8-en, which was also prepared by oxidation of lucidone B (15).

Oxidation of lucidone B (15). Lucidone B (16.9 mg) was reacted with pyridinium dichromate (60 mg) in DMF (0.15 ml) for 18 hr at room temp. The reaction mixture was diluted with H_2O and then extracted with Et_2O (30 ml). After drying (Na_2SO_4), the organic layer was concentrated and subjected to prep. TLC (C_6H_6–EtOAc, 1:1, two developments). Oxidized lucidone B was obtained as a pale yellow syrup and was identical to compound 16 (MS and ^{1}H NMR).

Methyl ganoderate K (4). Compound 4 was obtained as a pale yellow syrup (1.7 mg). EIMS *m/z* (rel. int.): 530.3204 $[M]^+$

($C_{31}H_{46}O_7$, calc. 530.3245) (80), 512 (7), 368 (71), 171 (28), 139 (41), 129 (62), 69 (49), 59 (100), 43 (66); IR ν_{max}^{film} cm^{-1}: 3450, 2975, 2930, 1710, 1665; UV λ_{max}^{EtOH} nm (ε): 272 (6570). CD λ^{EtOH} nm (Δε): 314 (0), 272 (+5.5), 238 (0).

'Compound B9' (**5**). Compound **5** was crystallized from EtOH–H_2O as needles (20.2 mg), mp 213–216°, $[\alpha]_D^{23}$ +156° (*c* = 0.1, MeOH). EIMS *m/z* (rel. int.): 532.3317 $[M]^+$ ($C_{31}H_{48}O_7$, calc. 532.3401) (8), 364 (5), 236 (10), 129 (16), 83 (100); IR ν_{max}^{film} cm^{-1}: 3380, 2925, 1710, 1650; UV λ_{max}^{MeOH} nm (ε): 254 (10430). CD λ^{MeOH} nm (Δε): 355 (−2.9), 291 (0), 257 (+21.9), 233 (0), 222 (−3.22).

Acetylation of **5**. Ac_2O–C_5H_5N treatment of **5** (6.3 mg) overnight at room temp. gave a diacetate **5a** (3.8 mg) as a major product, which was purified by prep. TLC ($CHCl_3$–MeOH, 49:1). EIMS and ^1H NMR spectrum of **5** were as follows. EIMS *m/z* (rel. int.): 616.3575 $[M]^+$ ($C_{35}H_{52}O_9$, calc. 616.3613) (5), 556 (28), 496 (13), 412 (30), 278 (42), 171 (23), 129 (53), 69 (45), 59 (70), 43 (100); ^1H NMR: δ 5.28 (1H, *dd*, *J* = 9.3, 5.7, H-15β), 4.57 (1H, *dd*, *J* = 11.2, 5.3, H-3α), 4.31 (1H, *m*, H-7β), 2.99 (1H, *ddd*, *J* = 13.6, 3.5, 3.5, H-1β), 2.82 (1H, *dd*, *J* = 17.6, 8.1, H-24), 2.77 (1H, *d*, *J* = 17.6, H-12α), 2.43 (1H, *dd*, *J* = 17.6, 5.1, H-24), 2.42 (1H, *dd*, *J* = 17.6, H-12β), 2.12 (3H, *s*, OAc), 2.06 (3H, *s*, OAc), 1.36 (3H, *s*, H-30), 1.17 (3H, *d*, *J* = 7.0, H-27), 1.06 (3H, *s*, H-19), 0.93 (3H, *s*), 0.92 (3H, *s*), 0.90 (3H, *s*), 0.86 (3H, *d*, *J* = 5.9, H-21).

Oxidation of **5**. Compound **5** (8.3 mg) was reacted with pyridinium dichromate (50 mg) in DMF (0.1 ml) for 14 hr at room temp. The reaction mixture was added to H_2O and extracted with Et_2O (20 ml). After drying (Na_2SO_4), the organic layer was concd and subjected to prep. TLC ($CHCl_3$–MeOH, 49:1) to yield a pentaketo compound, the EIMS and ^1H NMR data of which were identical with those of the pentaketo compound (**5b**) derived from methyl ganoderates A and B [6].

Methyl ganoderate H (**6**). Compound **6** was obtained as a pale yellow syrup (11.6 mg), $[\alpha]_D^{24}$ +54° (*c* = 0.2, MeOH). EIMS *m/z* (rel. int.): 586.3129 $[M]^+$ ($C_{33}H_{46}O_9$, calc. 586.3134) (1.1), 544 (13), 304 (13), 191 (12), 129 (41), 69 (31), 59 (61), 43 (100); IR ν_{max}^{film} cm^{-1}: 3500, 2930, 1740, 1690; UV λ_{max}^{MeOH} nm (ε): 256 (6270); CD λ^{MeOH} nm (Δε): 336 (0), 305 (−6.4), 290 (0), 278 (+6.6), 264 (0), 252 (−4.4), 241 (0), 225 (+11.2), 210 (0).

Methyl ganoderenate E (**7**). Compound **7** was crystallized from EtOAc–MeOH as needles (2.1 mg), mp 227–229°. EIMS *m/z* (rel. int.): 542.2874 $[M]^+$ ($C_{31}H_{42}O_8$, calc. 542.2881) (5), 524 (19), 464 (9), 304 (39), 165 (28), 129 (100), 95 (27), 59 (49); IR ν_{max}^{film} cm^{-1}: 3450, 2950, 1725, 1700, 1660, 1610; UV λ_{max}^{MeOH} nm (ε): 247 (11760); CD λ^{MeOH} nm (Δε): 290 (−2.1), 279 (0), 255 (+11.5), 228 (0).

Methyl lucidenate H (**8**). Compound **8** was crystallized from EtOAc–cyclohexane as pale yellow prisms (34.2 mg), mp 190–192°, $[\alpha]_D^{23}$ +136° (*c* = 0.2, MeOH). EIMS *m/z* (rel. int.): 490.2932 $[M]^+$ ($C_{28}H_{42}O_7$, calc. 490.2932) (38), 472 (22), 462 (30), 347 (100), 334 (63), 322 (36), 107 (61), 95 (35), 81 (36), 69 (43), 55 (66), 43 (88); IR ν_{max}^{film} cm^{-1}: 3400, 2925, 1720, 1655; UV λ_{max}^{MeOH} nm (ε): 255 (7550); CD λ^{MeOH} nm (Δε): 293 (−3.3), 280 (0), 255 (+14.9), 230 (0), 210 (−8.3).

Methyl lucidenate H acetonide (**8a**). Compound **8** (5 mg) in Me_2CO (2 ml) was shaken with anhydrous $CuSO_4$ (50 mg) at room temp. for 4 hr. Filtration and evapn of the solvent gave a colourless solid, which was purified by prep. TLC ($CHCl_3$–MeOH, 19:1) to yield acetonide **8a** (4.4 mg). EIMS *m/z* (rel. int.): 530.3238 $[M]^+$ ($C_{31}H_{46}O_7$, calc. 530.3245) (31), 515 (46), 502 (21), 472 (24), 455 (23), 437 (51), 386 (46), 361 (35), 333 (31), 298 (20), 55 (65), 43 (100); ^1H NMR: δ 4.79 (1H, *ddd*, *J* = 8.3, 8.3, 4.4, H-7α), 4.08 (1H, *d*, *J* = 4.4, 7β-OH), 3.68 (3H, *s*, COOMe), 3.59 (1H, *d*, *J* = 10.6, H-25), 3.49 (1H, *dd*, *J* = 11.7, 4.0, H-3α), 3.42 (1H, *d*, *J* = 10.6, H-25), 2.94 (1H, *ddd*, *J* = 13.5, 3.5, 3.5, H-1β), 2.79 (1H, *dd*, *J* = 19.3, 8.1, H-16), 2.79 (1H, *d*, *J* = 16.0, H-12α), 2.70 (1H, *d*, *J* = 16.0, H-12β), 2.40 (1H, *ddd*, *J* = 16.2, 9.2, 5.2, H-23), 2.28 (1H, *d*, *J* = 16.2, 8.1, 6.9, H-23), 2.12 (1H, *dd*, *J* = 19.3, 9.5, H-16), 1.99 (1H, *dd*, *J* = 9.5, 9.5, 8.1, H-17), 1.87 (1H, *ddd*, *J* = 13.3, 8.1, 1.7, H-6α), 1.44 (3H, *s*, acetonide), 1.42 (3H, *s*, acetonide), 1.36 (3H, *s*, H-27), 1.26 (3H, *s*, H-19), 1.11 (3H, *s*, H-26), 1.08 (1H, *ddd*, *J* = 13.8, 13.8, 4.4, H-1α), 0.97 (3H, *s*, H-18), 0.97 (3H, *d*, *J* = 6.2, H-21).

Methyl lucidenate I (**9**). Compound **9** was obtained as a pale yellow syrup (12.6 mg), $[\alpha]_D^{23}$ +118° (*c* = 0.1, MeOH). EIMS *m/z* (rel. int.): 488.2796 $[M]^+$ ($C_{28}H_{40}O_7$, calc. 488.2775) (30), 470 (12), 265 (20), 141 (33), 109 (42), 95 (36), 81 (33), 69 (40), 55 (73), 44 (100); IR ν_{max}^{film} cm^{-1}: 3400, 2925, 1735, 1675; UV λ_{max}^{MeOH} nm (ε): 262 (6830); CD λ^{MeOH} nm (Δε): 333 (0), 305 (−4.9), 292 (0), 275 (+8.3), 245 (0), 231 (+0.2), 225 (0), 207 (−4.4).

Methyl lucidenate J (**10**). Compound **10** was obtained as a pale yellow syrup (4.7 mg), $[\alpha]_D^{25}$ +78° (*c* = 0.1, MeOH). EIMS *m/z* (rel. int.): 504.2746 $[M]^+$ ($C_{28}H_{40}O_8$, calc. 504.2724) (51), 458 (25), 371 (65), 353 (33), 155 (39), 115 (42), 95 (34), 55 (67), 43 (100); IR ν_{max}^{film} cm^{-1}: 3430, 2930, 1740, 1680; UV λ_{max}^{MeOH} nm (ε): 255 (6400); CD λ^{MeOH} nm (Δε): 346 (0), 308 (−6.0), 292 (0), 279 (+6.0), 262 (0), 255 (−1.2), 248 (0), 228 (+5.7), 215 (0).

Methyl lucidenate K (**11**). Compound **11** was obtained as a pale yellow syrup (1.6 mg). EIMS *m/z* (rel. int.): 486.2601 $[M]^+$ ($C_{28}H_{38}O_7$, calc. 486.2618) (63), 458 (19), 371 (39), 353 (22), 302 (100), 287 (35), 55 (55), 43 (57); IR ν_{max}^{film} cm^{-1}: 3450, 2920, 1735, 1700, 1680; UV λ_{max}^{MeOH} nm (ε): 258 (5440); CD λ^{MeOH} nm (Δε): 337 (0), 308 (−4.1), 291 (0), 272 (+4.4), 233 (+3.4), 218 (0).

Methyl lucidenate L (**12**). Compound **12** was obtained as a pale yellow syrup (2.2 mg). EIMS *m/z* (rel. int.): 488.2766 $[M]^+$ ($C_{28}H_{40}O_7$, calc. 488.2775) (10), 304 (100), 191 (21), 129 (35), 95 (21), 69 (26), 55 (43), 43 (78); IR ν_{max}^{film} cm^{-1}: 3450, 2920, 1740, 1680; UV λ_{max}^{MeOH} nm (ε): 255 (6930); CD λ^{MeOH} nm (Δε): 345 (0), 307 (−7.1), 291 (0), 278 (+6.2), 264 (0), 256 (−2.1), 246 (0), 227 (+8.3), 213 (0).

Methyl lucidenate M (**13**). Compound **13** was obtained as a syrup (1.0 mg). EIMS *m/z* (rel. int.): 476.3105 $[M]^+$ ($C_{28}H_{44}O_6$, calc. 476.3139) (100), 458 (37), 336 (56), 236 (53), 69 (58), 55 (92), 43 (96); UV λ_{max}^{EtOH} nm (ε): 7900.

Methyl lucidenate E_2 (**14**). Compound **14** was crystallized as pale yellow needles (51.3 mg), mp 161–164°, $[\alpha]_D^{24}$ +65° (*c* = 0.2, MeOH). EIMS *m/z* (rel. int.): 530.2851 $[M]^+$ ($C_{30}H_{42}O_8$, calc. 530.2881) (2.2), 470 (6), 304 (100), 185 (27), 167 (35), 107 (16), 55 (25), 43 (81); IR ν_{max}^{film} cm^{-1}: 3500, 2925, 1740, 1690; UV λ_{max}^{MeOH} nm (ε): 258 (5990); CD λ^{MeOH} nm (Δε): 335 (0), 305 (−6.1), 290 (0), 278 (+6.8), 264 (0), 253 (−4.5), 242 (0), 225 (+10.6).

Acknowledgements—We are thankful to Mr. A. Honda for supplying the fruiting bodies of *G. lucidum*. We are also grateful to Miss Y. Misu (^1H and ^{13}C NMR, 270 MHz), Dr. M. Ikura (^1H NMR, 500 MHz), Mr. K. Watanabe (FDMS), Miss Y. Atsuta (EIMS) and their associates, Hokkaido University, for spectral measurements.

REFERENCES

1. Nishitoba, T., Sato, H., Kasai, T., Kawagishi, H. and Sakamura, S. (1984) *Agric. Biol. Chem.* **48**, 2905.
2. Nishitoba, T., Sato, H. and Sakamura, S. (1985) *Agric. Biol. Chem.* **49**, 1547.
3. Nishitoba, T., Sato, H., Kasai, T., Kawagishi, H. and Sakamura, S. (1985) *Agric. Biol. Chem.* **49**, 1793.
4. Nishitoba, T., Sato, H. and Sakamura, S. (1985) *Agric. Biol. Chem.* **49**, 3637.
5. Nishitoba, T., Sato, H. and Sakamura, S. (1986) *Agric. Biol. Chem.* **50**, 809.

6. Kubota, T., Asaka, Y., Miura, I. and Mori, H. (1982) *Helv. Chim. Acta* **65**, 611.
7. Kohda, H., Tokumoto, W., Sakamoto, K., Fujii, M., Hirai, Y., Yamasaki, K., Komoda, Y., Nakamura, H., Ishihara, S. and Uchida, M. (1985) *Chem. Pharm. Bull.* **33**, 1367.
8. Kikuchi, T., Matsuda, S., Kadota, S., Murai, Y. and Ogita, Z. (1985) *Chem. Pharm. Bull.* **33**, 2624.
9. Kikuchi, T., Matsuda, S., Murai, Y. and Ogita, Z. (1985) *Chem. Pharm. Bull.* **33**, 2628.
10. Hirotani, M., Furuya, T. and Shiro, H. (1985) *Phytochemistry* **24**, 2055.
11. Komoda, Y., Nakamura, H., Ishihara, S., Uchida, M., Kohda, H. and Yamasaki, K. (1985) *Chem. Pharm. Bull.* **33**, 4829.
12. Hirotani, M. and Furuya, T. (1986) *Phytochemistry* **25**, 1189.
13. Kikuchi, T., Kanomi (nee Matsuda), S., Kadota, S., Murai, Y., Tsubono, K. and Ogita, Z. (1986) *Chem. Pharm. Bull.* (in press).
14. Toth, J. O., Luu, B. and Ourisson, G. (1983) *Tetrahedron Letters* **24**, 1081.
15. Toth, J. O., Luu, B., Beck, J. P. and Ourisson, G. (1983) *J. Chem. Res.* (*S*) 299; (1983) *J. Chem. Res.* (*M*) 2722.
16. Corey, E. J. and Schmidt, G. (1979) *Tetrahedron Letters* 399.
17. Tsuda, Y., Sano, T., Isobe, K. and Miyauchi, M. (1974) *Chem. Pharm. Bull.* **22**, 2396.
18. Nishitoba, T., Sato, H., Shirasu, S. and Sakamura, S. (1986) *Agric. Biol. Chem.* **50**, 2151.