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GANODERIC ACID G AND I AND GANOLUCIDIC ACID A AND B, NEW TRITERPENOIDS FROM GANODERMA LUCIDUM[1)]

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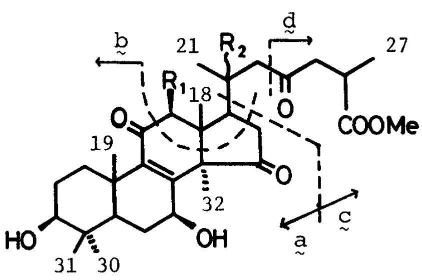
Four new highly oxidized lanostane-type triterpenoids, ganoderic acid G and I and ganolucidic acid A and B, were isolated from the fungus *ganoderma lucidum* and their structures were elucidated on the basis of spectral evidence.

KEYWORDS —— *Ganoderma lucidum*; triterpenoid; ganoderic acid G; ganoderic acid I; ganolucidic acid A; ganolucidic acid B; NMR

In the preceding communication,[2)] we reported the isolation of eleven new triterpenoids as the methyl esters and elucidated the structures of seven compounds: methyl ganoderate D, E, F, and H and methyl lucidenate D, E, and F. This communication deals with the structures of four new triterpenoids, ganoderic acid G[3)] and I and ganolucidic acid A and B, which were also obtained as the methyl esters, 1, 2, 4, and 5, respectively.

Methyl ganoderate G (1), $C_{31}H_{46}O_8$, was obtained as colorless prisms, mp 134-135°C, $[\alpha]_D$ +64° ($CHCl_3$), UV λ: 252.5 nm (log ε 4.01), IR ν: 3450, 1730, 1720, and 1660 cm^{-1}. It showed the molecular ion peak at m/z 546 and fragment peaks at m/z 375 (a), 306 (b + 1), 139 (c - CH_3OH), and 129 (d) in the mass spectrum. The ^{1}H-NMR spectrum of 1 showed signals due to three carbinol methine protons (δ 3.22, 4.38, and 4.80) along with two sec- and five tert-methyl signals, and the whole spectral pattern compared with that of methyl ganoderate B (3)[4)] suggested that the compound (1) may be the 12-hydroxy derivative of 3 (Table I). This was substantiated by comparison of the ^{13}C-NMR spectrum of 1 with that of 3; i. e., the signals assignable to C-12 and C-13 in 1 markedly shifted downfield, while the signal due to C-18 shifted upfield, relative to the corresponding signals in 3 (Table II). Furthermore, in the ^{1}H-NMR spectrum of the triacetate prepared by acetylation of 1, the methine proton at C-12 resonated at δ 5.69 (s), which showed ca. 10% NOE increase on irradiation at the 32-methyl protons (δ 1.42). Based on these findings, methyl ganoderate G was determined to be methyl 3β,7β,12β-trihydroxy-11,15,23-trioxo-5α-lanost-8-en-26-oate (1).

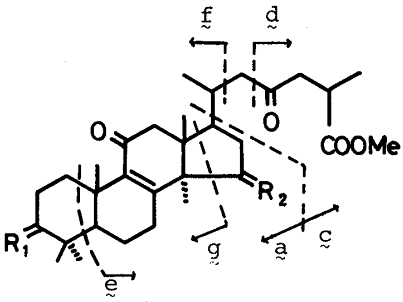
Methyl ganoderate I (2), $C_{31}H_{46}O_8$, colorless prisms, mp 279-281°C, $[\alpha]_D$ +132° ($CHCl_3$), UV λ: 254.5 nm (log ε 3.86), IR ν: 3450, 1730, 1710, and 1660 cm^{-1}, showed ^{1}H-NMR and ^{13}C-NMR spectra closely similar to those of 3, except for the downfield shift of a proton singlet (δ 1.40) assignable to the 21-methyl group and ^{13}C signals assignable to C-20, C-17, C-21, and C-22 (Table I and II). Therefore, methyl ganoderate I is considered to be the 20-hydroxy derivative of 3.



1 : $R_1 = OH$, $R_2 = H$

2 : $R_1 = H$, $R_2 = OH$

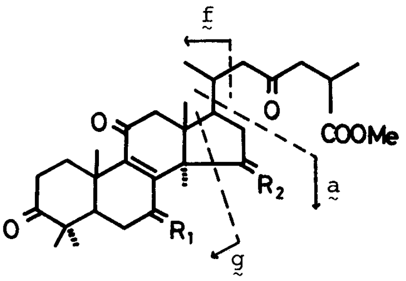
3 : $R_1 = R_2 = H$



4 : $R_1 = O$, $R_2 = \langle^{H}_{OH}$

5 : $R_1 = \langle^{OH}_{H}$, $R_2 = \langle^{H}_{OH}$

6 : $R_1 = R_2 = O$



7 : $R_1 = \langle^{OH}_{H}$, $R_2 = \langle^{H}_{OH}$

8 : $R_1 = R_2 = O$

Table I. ^{1}H-NMR (200 MHz) Spectral Data of Methyl Ganoderate A (7), B (3), G (1), and I (2) and Methyl Ganolucidate A (4) and B (5) and the Tetraoxo Ester (6) (δ in $CDCl_3$)

Compound / ^{1}H (J)	1	2	3[a]	4	5	6	7[a]
18-H_3 s	0.88	1.14	0.99	0.91	0.89	0.96	0.98
19-H_3 s	1.32	1.21	1.20	1.12	1.11	1.12[b]	1.25
21-H_3 d (6)	1.14	1.40(s)	0.99	0.86	0.84	0.98	0.88
27-H_3 d (7)	1.19	1.19	1.17	1.18	1.18	1.19	1.18
30-H_3 s	1.04	1.03	1.02	1.08	1.01	1.08	1.09
31-H_3 s	0.80	0.86	0.84	1.12	0.82	1.13[b]	1.11
32-H_3 s	1.43	1.35	1.33	1.18	1.16	1.31	1.27
COOMe s	3.68	3.71	3.67	3.70	3.68	3.70	3.68
3-H dd (10, 6)	3.22	3.22	3.21	—	3.25	—	—
7-H td (8.5, 4.5)	4.80	4.80	4.80	—	—	—	4.80(br t)
12-H d (2.5)	4.38	—	—	—	—	—	—
15-H dd (9, 5.5)	—	—	—	4.41	4.39	—	4.63
7-OH d (4.5)	4.43	4.12	4.05	—	—	—	—
12-OH d (2.5)	4.03	—	—	—	—	—	—

a) See reference 4. b) Assignments may be interchanged.

Methyl ganolucidate A (4), $C_{31}H_{46}O_6$, colorless needles, mp 192-194°C, $[\alpha]_D$ +188° ($CHCl_3$), UV λ: 256.5 nm (log 4.00), IR ν: 3450, 1730, 1710, and 1645 cm^{-1}, showed the molecular ion peak at m/z 514 and fragment ion peaks at m/z 417 (e + 1),[5] 371 (f), 287 (g + 1), 171 (c), 139 (c - CH_3OH), and 129 (d) in the mass spectrum. The ^{1}H-NMR spectrum of 4 exhibited signals due to a carbinol methine (δ 4.41) and two sec-methyl and five tert-methyl groups. Its spectral pattern resembled that of methyl ganoderate A (7)[4] except for the disappearance of another carbinol methine signal of 7 (Table I). The ^{13}C-NMR spectrum 4 was also closely similar to that of 7 except for the marked upfield shift of the C-7 and C-6 signals (Table II),

Table II. ^{13}C-NMR Spectral Data of Methyl Ganoderate A (7), B (3), G (1), and I (2) and Methyl Ganolucidate A (4), B (5), and the Tetraoxo Ester (6) (ppm in $CDCl_3$)

^{13}C \ Compd.	1	2	3	4	5	6	7
1	34.6 t	34.9 t	34.9 t	35.1 t	34.4 t	35.1 t	35.5 t
2	27.6 t	27.8 t	27.7 t	34.2 t	28.0 t	34.1 t	34.3 t
3	78.3 d	78.4 d	78.3 d	217.7 s	78.7 d	217.8 s	217.3 s
4	38.6 s	38.9 s	38.9 s	47.0a) s	39.0 s	44.8 s	46.8a) s
5	49.2 d	49.2 d	49.2 d	51.7 d	51.8 d	51.4 d	48.7b) d
6	26.9 t	26.7 t	26.7 t	18.7 t	17.4 t	18.6 t	29.0 t
7	66.2 d	66.9 d	66.9 d	29.6 t	30.4 t	29.2 t	68.9 d
8	157.4 s	156.6 s	156.9 s	163.2 s	162.9 s	160.3 s	159.3 s
9	141.9 s	142.3 s	142.7 s	138.6 s	140.0 s	139.3 s	140.1 s
10	38.4 s	38.7 s	38.7 s	37.1 s	37.8 s	37.5 s	38.0 s
11	199.3 s	197.8 s	197.8 s	198.1 s	198.3 s	197.0 s	199.6 s
12	77.9 d	50.7 t	50.3 t	51.7 t	52.1 t	49.8a) t	51.7 t
13	51.9 s	45.7 s	45.3 s	46.8a) s	47.2 s	47.0 s	46.6a) s
14	60.3 s	59.7 s	59.4 s	53.6 s	53.5 s	57.9 s	54.0 s
15	216.8 s	217.7 s	217.4 s	72.9 d	73.0 d	212.4 s	72.4 d
16	38.4 t	36.1 t	40.9 t	38.6 t	38.7 t	40.8 t	36.2 t
17	45.8 d	49.3 d	45.6 d	48.7 d	48.7 d	45.0 d	48.1b) d
18	12.0 q	19.0 q	17.4 q	17.2 q	17.1 q	17.0 q	17.3 q
19	18.8 q	18.4 q	18.5 q	18.8b) q	18.8a) q	18.9 q	19.5c) q
20	28.7 d	73.0 s	32.0 d	32.6 d	32.5 d	32.0 d	32.7 d
21	21.4 q	26.7 q	19.7 q	19.4 q	19.4 q	19.6 q	19.6c) q
22	48.4 t	52.7 t	49.1 t	49.6 t	49.7 t	49.3a) t	49.7 t
23	208.1 s	210.4 s	207.7 s	208.3 s	208.3 s	207.8 s	208.4 s
24	46.4 t	47.7 t	46.8 t	46.8 t	46.8 t	46.8 t	46.8 t
25	34.6 d	34.5 d	34.7 d	34.7 d	34.6 d	34.7 d	34.6 d
26	176.1 s	175.9 s	176.1 s	176.2 s	176.1 s	176.1 s	176.3 s
27	17.1 q	17.0 q	17.1 q	17.1 q	17.1 q	17.1 q	17.1 q
30	28.1 q	28.2 q	28.2 q	27.8 q	28.3 q	27.8 q	27.4 q
31	15.4 q	15.5 q	15.5 q	20.6 q	15.7 q	20.6 q	20.7 q
32	23.1 q	24.8 q	24.4 q	19.0b) q	19.0a) q	23.2 q	19.4c) q
OCH_3	51.9 q	52.0 q	51.9 q	51.9 q	51.9 q	51.9 q	52.0 q

a), b), c) Assignments may be interchanged in each compound.

suggesting that methyl ganolucidate A (4) may be the 7-deoxo derivative of methyl ganoderate A (7).

Oxidation of 4 with CrO_3 in AcOH afforded the tetraoxo ester (6), $C_{31}H_{44}O_6$, which showed the M^+ peak at m/z 512 together with fragment ion peaks at m/z 415 (e+1),[5] 350, 341 (a), 287 (g + 1), 171 (c), 139 (c - CH_3OH), and 129 (d). The ^{13}C-NMR spectrum of 6 compared with that of methyl ganoderate E (8)[2] indicated the apparent absence of oxygenic functional group at the C-7 position. Based on these data, methyl ganolucidate A was determined to be methyl 15α-hydroxy-3,11,23-trioxo-5α-lanost-8-en-26-oate (4).

Methyl ganolucidate B (5), $C_{31}H_{48}O_6$, colorless needles, mp 167-169°C, $[\alpha]_D$ +114° ($CHCl_3$), showed UV, IR, ^1H-NMR, and ^{13}C-NMR spectra similar to those of 4, except for a double doublet due to a methine proton (δ 3.25) and several signals arising from the ring-A carbons (Table I and II). In the mass spectrum of 5, the molecular ion peak appeared at m/z 516 and significant fragment ion peaks were observed at m/z 373 (f), 289 (g + 1), 171 (c), 139 (c - CH_3OH), and 129 (d). Finally, oxidation of 5 with CrO_3-AcOH gave the tetraoxo compound (6), identical with the sample (6) prepared by oxidation of 4. Thus, the structure of methyl ganolucidate B was assigned to the formula 5.

REFERENCES AND NOTES

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5) These MS peaks were tentatively assigned to the fragment (e + 1).

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