J Chin Med 14(4): 247-258, 2003

NEW ERGOSTANE AND LANOSTANE FROM *ANTRODIA CAMPHORATA*

Chien-Chang Shen[1], Yuh-Chi Kuo[1,2], Ray-Ling Huang[1], Lie-Chwen Lin[1], Ming-Jaw Don[1], Tun-Tschu Chang[3] and Cheng-Jen Chou[1]

[1]National Research Institute of Chinese Medicine,
[2]Institute of Life Science, Fu-Jen University,
[3]Division of Forest Protection, Taiwan Forestry Research Institute, Taipei, Taiwan
(Received 3rd September 2003, revised Ms received 7th October 2003, accepted 11th November 2003)

Fourteen compounds (one biphenyl, six ergostane, and seven lanostane derivatives) have been isolated from the fruiting body of *Antrodia camphorata*. They are 3β,15α-dihydroxylanosta-7,9(11),24-trien-21-oic acid, antcin K, dehydroeburicoic acid, eburicoic acid, methyl antcinate B, methyl antcinate H, zhankuic acid A, zhankuic acid B, dehydrosulphurenic acid, sulphurenic acid, 15α-acetyl-dehydrosulphurenic acid, versisponic acid D, zhankuic acid C, and 2,2′,5,5′-tetra-methoxy-3,4,3′,4′-bis(methlylenedioxy)-6,6′-dimethylbiphenyl. Among them, two lanostane-type compounds—sulphurenic acid and versisponic acid D were not previously reported from this fungus. 3β,15α-Dihydroxylanosta-7,9(11),24-trien-21-oic acid and antcin K are first found from nature and their structures were determined by spectroscopic methods.

Key words: *Antrodia camphorata*, Fungi, Ergostane, Lanostane, Biphenyl derivatives.

INTRODUCTION

The fruiting body of *Antrodia camphorata*[1] is well known in Taiwan by name niu-chang-chih or jang-jy. This fungus is known only in Taiwan and is restricted to *Cinnamomum kanehirai* Hay. (Lauraceae). The basidiomes have been used for the treatment of food and drug intoxication, diarrhea, abdominal pain, hypertension, skin itching, and cancer.[2] In the previous work, chemical investigation revealed that the constituents of niu-chang-chih contained triterpenes, steroids, and a sesquiterpene[3-8] and pharmacological studies of this fungus revealed that one component (Zhankuic acid A) showed cytotoxicity against P-388 murine leukaemia cell.[4] However, there has been a relative scarcity of papers on other anti-tumor, anti-hepatitis-B virus, and immune-pharmacological activities of *A. camphorata*. In the course of our search for physiologically active substances in nature, we found that water extract of *A. camphorata* suppressed proliferation in HMNC activated by PHA with IC_{50} of 17.5 μg/mL. It also possessed the

Correspondence to: Cheng-Jen Chou, National Research Institute of Chinese Medicine, Tel: 886-2-28201999 ext. 7101, Fax: 886-2-28264276, E-mail: choucj@cma23.nricm.edu.tw

activities of anti-hepatitis-B surface antigen and e antigen with EC_{50} of < 50 μg/mL and 86.5 μg/mL, respectively. In the anti-tumor experiment, ethanol extract of *A. camphorata* showed the inhibitory activities on K562 and Jurkat cell lines with IC_{50} of 17.5 μg/mL and 44 μg/mL, respectively. This observation led us to investigate the potential biologically active substances of the fruit-body of *A. camphorata*. In the present paper, we describe the isolation and identification of one biphenyl, six ergostane, and seven lanostane derivatives. Among them, two lanostane-type compounds-sulphurenic acid and versisponic acid D were not previously reported from this fungus.[9] Two other compounds are first found from nature; they are namely as 3β,15α-dihydroxylanosta-7,9(11),24-trien-21-oic acid (**1**) and antcin K (3α,4β,7β- trihydroxy-4α-methylergosta-8, 24(28)-dien-11-on-26-oic acid, **2**), respectively.

EXPERIMENTAL

General Experiment Procedures

Melting points were determined with a Yanaco MP-13 micro-melting point apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-370 polarimeter. HRFABMS spectra were recorded on a JEOL JMS-HX 110 spectrometer. EIMS spectra were recorded on a Finnigan MAT LCQ LC/MS spectrometer. ^{1}H, ^{13}C, and 2D NMR spectra were recorded on a Bruker AC-300P spectrometer or a Varian UNITY INOVA 500 MHz NMR spectrometer. Chemical shifts are shown in δ values (ppm) with deuterated solvents as internal standard.

Materials

A. camphorata (niu-chang-chih) was purchased from a Chinese medicinal store in Taipei, and identified by Dr. Tun-Tschu Chang of the Division of Forest Protection, Taiwan Forestry Research Institute. A voucher specimen was deposited in the herbarium of Taiwan Forestry Research Institute, Taipei, Taiwan.

Extraction and Isolation

The chipped fruiting bodies of *A. camphorata* (200 g) were extracted with distilled water at 80 °C for three times, to give 25.4 g of a solid extract. The residue of fruiting bodies was then refluxed four times with ethanol for 6 hr. The extracts were filtered and evaporated. The concentrate (51.8 g) was suspended in 1.5 L distilled water and partitioned between dichloromethane and water (1:1 v/v) to afford organic and aqueous fractions. The organic fraction (49.8 g) was dissolved in methanol and divided into methanol-soluble (38.1 g) and methanol-insoluble (1.21 g) portions. The methanol-soluble part was carried out on Sephadex LH-20 column chromatography with methanol, and five fractions (I-V) were collected. The fractions were collected in 250 mL portions and pooled according to their TLC profile in toluene–ethyl acetate–acetic acid solvent system. Fr-III (32.1 g) was redissolved in methanol and divided into

methanol-soluble and methanol-insoluble portions. The insoluble portion (1.1 g) was separated by HPLC (Cosmosil $5C_{18}$-AR- II column; MeOH/H_2O/AcOH solvent system) to afford dehydroeburicoic acid (**3**) and eburicoic acid (**4**). The MeOH-soluble portion (Fr-III-MS; 32.5 g) was chromatographed on silica gel MPLC (MeOH gradient in CH_2Cl_2) to give eight sub-fractions (Fr-III-MS-1~Fr-III-MS-8). Further chromatographic separation of Fr-III-MS-3 on silica gel MPLC (acetone gradient in hexane) and HPLC (Cosmosil $5C_{18}$-AR-II column; MeOH/H_2O/AcOH solvent system) afforded seven compounds: methyl-4α-methylergosta-8,24(28)-diene-3,7,11-trion-26-oate (**5**), methyl antcinate H (**6**), zhankuic acid A (**7**), zhankuic acid B (**8**), 3β,15α-dihydroxylanosta-7,9(11),24-trien-21-oic acid (**1**), dehydrosulphurenic acid (**9**), and sulphurenic acid (**10**). Fr-III-MS-4 was separated and purified similarly as above treatment to give 15α-acetyl-dehydrosulphurenic acid (**11**) and versisponic acid D (**12**). Fr-III-MS-6 was rechromatographed by silica gel column and eluted with hexane-acetone of increasing polarity to give six fractions (Fr-III-MS-6-1~Fr-III-MS-6-6). Fr-III-MS-6-5 was further purified by Sephadex LH-20 column and eluted with acetone to give zhankuic acid C (**13**). Fr-III-MS-8 was separated and purified similarly as above treatment to give antcin K (**2**). After chromatographic separation of Fr-V (1.2 g) on a Cosmosil $75C_{18}$-OPN column (methanol gradient in water), sub-fraction (Fr-V-5) was further purified by Sephadex LH-20 column and eluted with methanol to give 2,2′,5,5′-tetramethoxy-3,4,3′,4′-bis(methlylenedioxy)- 6,6′-dimethylbiphenyl (**14**).

3β,15α-Dihydroxylanosta-7,9(11),24-trien-21-oic acid (1)

White needles; mp 259-261 °C (MeOH); $[\alpha]_D$ +83.3° (c 0.3, MeOH); HRMS (Finnigan MAT-95XL): *m/z* 470.3415 $[M]^+$ ($C_{30}H_{46}O_4$ requires 470.3433.); ESI-MS (pos.): *m/z* 471 (M＋1); ^1H and ^{13}C NMR: see Table 1.

Antcin K (3α,4β,7β-trihydroxy-4α-methylergosta-8,24(28)-dien-11-on-26-oic acid, 2)

Colorless crystal; mp 227-230 °C (dil. MeOH); $[\alpha]_D$ +92.0° (c 0.25, MeOH); HRMS (Joel SX102A): *m/z* 488.3133 $[M]^+$ ($C_{29}H_{44}O_6$ requires 488.3134.); ESI-MS (neg.): *m/z* 487 (M−1); ^1H and ^{13}C NMR: see Table 2.

Dehydroeburicoic acid (24-methylenelanosta-7,9(11)-dien-3β-ol-21-oic acid, 3)[8]

White fine needles; mp 270-273 °C (MeOH); ^1H NMR (300 MHz, pyridine-d_5): δ 1.90 (2H, m, H-2), 3.43 (1H, t, *J* = 7.5 Hz, H-3), 1.26 (1H, H-5), 2.16 (2H, H-6), 5.61 (1H, br s, H-7), 5.36 (1H, d, *J* = 5.1 Hz, H-11), 2.50 (1H, H-12 α), 2.33 (1H, H-12 β), 0.99 (3H, s, H-18), 1.19 (3H, s, H-19), 2.64 (1H, td, *J* = 11.0, 3.0 Hz, H-20), 2.29 (1H, H-25), 1.02 (3H, d, *J* = 3.0 Hz, H-26 or H-27), 1.00 (3H, d, *J* = 3.0 Hz, H-27 or H-26), 4.88 (1H, br s, H-28a), 4.92 (1H, br s, H-28b), 1.11 (3H, s, H-29), 1.05 (6H, s, H-30, 31); ^{13}C NMR (75 MHz, pyridine-d_5): δ 36.4 (t, C-1), 28.7 (t, C-2), 78.0 (d, C-3), 39.4 (s, C-4), 49.1 (d, C-5), 23.6 (t, C-6), 121.3 (d, C-7), 142.8 (s, C-8), 146.6 (s, C-9), 37.9 (s, C-10), 116.6 (d, C-11), 36.0 (t, C-12), 44.3 (s, C-13), 50.5 (s, C-14), 31.8 (t, C-15), 27.3 (t, C-16), 48.1 (d, C-17), 16.3 (q, C-18),

23.0 (q, C-19), 49.8 (d, C-20), 178.5 (s, C-21), 32.8 (t, C-22), 31.6 (t, C-23), 155.9 (s, C-24), 34.3 (d, C-25), 21.9 (q, C-26), 22.0 (q, C-27), 107.1 (t, C-28), 25.9 (q, C-29), 28.8 (q, C-30), 16.6 (q, C-31); EIMS (GCQ, pos.): *m/z* 469 (M+1).

Table 1. NMR spectral data of 3β,15α-dihydroxylanosta-7,9(11),24-trien-21-oic acid (in pyridine-d_5; 500 MHz)[a]

Atom	^{13}C	^{1}H	HMBC
1	36.4 *t*	1.49, 1.96	H_3-19, H-5, H-2, H-3
2	28.7 *t*	1.92	
3	78.0 *d*	3.44 *br t* (7.0)	H_3-30, H_3-29, H-5, H-2, H-1
4	39.3 *s*		H_3-30, H_3-29, H-5, H-3, H-2
5	49.7 *d*	1.32 *dd* (4.5, 11.5)	H_3-30, H_3-29, H_3-19, H-7, H-6
6	23.5 *t*	2.11, 2.20	H-5, H-7
7	122.3 *d*	6.49 *d* (6.0)	H-5, H-6
8	141.9 *s*		H_3-28, H-6, H-11, H-12, H-15
9	146.9 *s*		H_3-19, H-5, H-7, H-12
10	37.92 *s*		H_3-19, H-1, H-2, H-5, H-11
11	116.3 *d*	5.38 *d* (6.5)	H-12
12	36.8 *t*	2.39 *dd* (6.5, 17.5)	H_3-18, H-11, H-17
13	44.9 *s*		H_3-18, H_3-28, H-12, H-17, H-20
14	52.5 *s*		H_3-18, H_3-28, H-12, H-15, H-7
15	73.7 *d*	4.77 *dd* (6.0, 10.0)	H_3-28, H-16
16	39.6 *t*	2.29	H-20, H-15, H-17
17	46.5 *d*	2.72	H-16, H_3-18, H-20
18	16.8 *q*	1.12 *s*	
19	23.2 *q*	1.08 *s*	H-1, H-5
20	48.8 *d*	2.65 *td* (3.5, 11.5)	H-17, H-22, H-23
21	178.7 *s*		H-22, H-20
22	33.3 *t*	1.78, 1.93	H-17, H-20, H-23, H-24
23	26.7 *t*	2.24, 2.34	H-20, H-22, H-24
24	124.8 *d*	5.28 *t* (7.0)	H_3-26, H_3-27, H-22, H-23
25	131.7 *s*		H_3-26, H_3-27, H-23
26	25.8 *q*	1.63 *s*	H_3-27, H-24
27	17.7 *q*	1.58 *s*	H_3-26, H-24
28	18.3 *q*	1.42 *s*	H-15
29	28.8 *q*	1.18 *s*	
30	16.6 *q*	1.10 *s*	

[a]Assignments were based on ^{13}C-DEPT, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC and HMBC spectra.

Eburicoic acid (24-methylenelanosta-8-en-3β-ol-21-oic acid, 4)[10]

White needles; mp 289-291 °C (MeOH); ^{1}H NMR (300 MHz, pyridine-d_5): δ 3.41 (1H, br t, J = 7.6 Hz, H-3), 1.00 (3H, s, H-18), 1.06 (3H, s, H-19), 2.63 (1H, td, J = 2.4, 10.6 Hz, H-20), 2.27 (1H, m, H-25), 1.00 (3H, H-26 or H-27), 1.01 (3H, H-27 or H-26), 4.87 (1H, br s, H-28a), 4.91 (1H, br s, H-28b), 1.05 (3H, s, H-29), 1.22 (3H, s, H-30), 1.00 (3H, s, H-31); ^{13}C NMR (75 MHz, pyridine-d_5): δ 36.1 (t, C-1), 28.6 (t, C-2), 78.0 (d, C-3), 39.5 (s, C-4), 50.9 (d,

C-5), 18.7 (t, C-6), 27.5 (t, C-7), 134.3 (s, C-8), 134.3 (s, C-9), 37.4 (s, C-10), 21.2 (t, C-11), 29.4 (t, C-12), 44.9 (s, C-13), 49.9 (s, C-14), 30.9 (t, C-15), 26.8 (t, C-16), 47.7 (d, C-17), 16.3 (q, C-18), 19.4 (q, C-19), 49.1 (d, C-20), 178.6 (s,

Table 2. NMR spectral data of antcin K (in pyridine-d_5; 500 MHz)[a]

Atom	^{13}C	^{1}H	HMBC
1	29.7 *t*	2.09, 3.10	H_3-19, H-3
2	26.7 *t*	1.92, 2.73	H-1
3	74.7 *d*	4.06 *br s*	H-1, H-2
4	73.9 *s*		H_3-29, H-5, H-3, H-2
5	43.5 *d*	2.17 *br d* (14.0)	H_3-19, H-6, H-3, H-1
6	30.1 *t*	2.42, 2.68	H-7, H-5
7	70.8 *d*	4.62 *t* (8.0)	H-6, H-5
8	154.3 *s*		H-14, H-15, H-6, H-7
9	143.9 *s*		H_3-19, H-5, H-12, H-7, H-14
10	38.7 *s*		H_3-19, H-2, H-1, H-6
11	201.5 *s*		H-12
12	58.8 *t*	2.44 *d* (13.4), 2.96 *d* (13.4)	H_3-18, H-14
13	47.9 *s*		H_3-18, H-17, H-15, H-14, H-12
14	53.7 *d*	2.64	H_3-18, H-12, H-7
15	25.4 *t*	2.08, 2.50	H-14, H-12 (2.96)
16	28.2 *t*	1.36, 1.92	H-15 (2.50)
17	54.8 *d*	1.41	H_3-18, H-22, H-14
18	12.5 *q*	0.89 *s*	H-12, H-14, H-17
19	20.9 *q*	2.05 *s*	H-1, H-5
20	36.2 *d*	1.40	H_3-21, H-17, H-22, H-23
21	18.6 *q*	0.88 *d* (7.5)	H-22
22	34.5 *t*	1.29, 1.74	H_3-21, H-23
23	31.7 *t*	2.19, 2.39	H-22, H-25, H-28
24	150.4 *s*		H_3-27, H-23, H-25, H-28
25	46.7 *d*	3.45 *q* (7.0)	H_3-27, H-23, H-28
26	176.8 *s*		H_3-27, H-25, H-28
27	17.2 *q*	1.47 *d* (7.0)	H-25
28	110.4 *t*	5.06 *br s*, 5.21 *br s*	H-23, H-25
29	28.0 *q*	1.73 *s*	H-3

[a]Assignments were based on ^{13}C-DEPT, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC and HMBC spectra.

C-21), 31.8 (t, C-22), 32.7 (t, C-23), 155.9 (s, C-24), 34.2 (d, C-25), 21.9 (q, C-26), 22.0 (q, C-27), 107.0 (t, C-28), 24.5 (q, C-29), 28.6 (q, C-30), 16.3 (q, C-31); EIMS (GCQ): *m/z* 471 (M+1).

Methyl antcinate B (methyl 4α-methylergosta-8,24(28)-diene-3,7,11-trion-26-oate, 5)[6]

Yellow powder; $[\alpha]_D$ +75.0° (c 0.28, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (1H, m, H-1α), 3.04 (1H, ddd, *J* = 2.8, 6.6, 13.1 Hz, H-1β), 2.40 (1H, m, H-2a), 2.53 (1H, m, H-2b), 2.47 (1H, m, H-4), 1.91 (1H, td, *J* = 4.0, 13.7 Hz, H-5), 2.41 (1H, m, H-6α), 2.53 (1H, m, H-6β), 2.37 (1H, br d, *J* = 14.1 Hz, H-12α), 2.92 (1H, d, *J* = 14.1 Hz, H-12β), 2.62 (1H, dd, *J* = 7.2, 11.7 Hz, H-14), 1.40 (1H, m, H-15a), 2.53 (1H, m, H-15b), 1.26 (1H, m, H-16a), 1.98 (1H, m, H-16b), 1.40 (1H, m, H-17), 0.67 (3H, s, H-18), 1.50 (3H, s, H-19), 1.40 (1H, m, H-20), 0.91 (3H, d, *J* = 3.9 Hz, H-21), 1.17 (1H, m, H-22a), 1.57 (1H, m, H-22b), 1.97 (1H, m, H-23a), 2.15 (1H, m, H-23b), 3.10 (1H, q, *J* = 7.2 Hz, H-25), 1.25 (3H, d, *J* = 7.1 Hz, H-27), 4.84 (1H, d, *J* = 3.0 Hz, H-28a), 4.88 (1H, d, *J* = 3.5 Hz, H-28b), 1.02 (3H, d, *J* = 6.4 Hz, H-29), 3.64 (3H, s, -COOC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 34.7 (t, C-1), 37.5 (t, C-2), 210.6 (s, C-3), 43.9 (d, C-4), 48.9 (d, C-5), 38.9 (t, C-6), 200.7 (s, C-7), 151.9 (s, C-8), 145.5 (s, C-9), 38.3 (s, C-10), 202.5 (s, C-11), 57.3 (t, C-12), 47.1 (s, C-13), 49.3 (d, C-14), 24.8 (t, C-15), 27.8 (t, C-16), 54.0 (d, C-17), 12.0 (q, C-18), 16.2 (q, C-19), 35.6 (d, C-20), 18.5 (q, C-21), 33.8 (t, C-22), 31.2 (t, C-23), 148.5 (s, C-24), 45.7 (d, C-25), 174.9 (s, C-26), 16.4 (q, C-27), 110.9 (t, C-28), 11.4 (q, C-29), 51.8 (q, -COO*C*H$_3$); APCI-MS (pos.): *m/z* 483 (M+1).

Methyl antcinate H (methyl 3α,12α-dihydroxy-4α-methylergosta-8,24(28)-diene-7,11-dion-26-oate, 6)[6]

Yellow needles; mp 158-160 °C (MeOH); $[\alpha]_D$ +86.9° (c 0.23, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.43 (1H, m, H-1α), 2.34 (1H, m, H-1β), 1.79 (2H, m, H-2), 3.76 (1H, d, *J* = 2.3 Hz, H-3), 1.72 (1H, m, H-4), 2.15 (1H, m, H-5), 2.22 (1H, m, H-6a), 2.40 (1H, m, H-6b), 4.03 (1H, s, H-12β), 3.00 (1H, dd, *J* = 7.5, 12.4 Hz, H-14), 1.49 (1H, m, H-15a), 2.52 (1H, m, H-15b), 1.26 (1H, m, H-16a), 1.95 (1H, m, H-16b), 1.83 (1H, m, H-17), 0.62 (3H, s, H-18), 1.27 (3H, s, H-19), 1.41 (1H, m, H-20), 0.94 (3H, d, *J* = 5.8 Hz, H-21), 1.17 (1H, m, H-22a), 1.57 (1H, m, H-22b), 1.89 (1H, m, H-23a), 2.17 (1H, m, H-23b), 3.11 (1H, q, *J* = 7.0 Hz, H-25), 1.26 (3H, d, *J* = 7.4 Hz, H-27), 4.86 (1H, d, *J* = 3.6 Hz, H-28a), 4.88 (1H, d, *J* = 4.3 Hz, H-28b), 0.92 (3H, d, *J* = 6.5 Hz, H-29), 3.65 (3H, s, -COOC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.8 (t, C-1), 28.9 (t, C-2), 70.3 (d, C-3), 34.5 (d, C-4), 40.7 (d, C-5), 38.1 (t, C-6), 201.6 (s, C-7), 144.6 (s, C-8), 152.2 (s, C-9), 38.3 (s, C-10), 202.5 (s, C-11), 80.8 (d, C-12), 49.5 (s, C-13), 41.8 (d, C-14), 23.9 (t, C-15), 26.9 (t, C-16), 45.6 (d, C-17 or C-25), 11.5 (q, C-18), 16.1 (q, C-19 or C-27), 35.4 (d, C-20), 17.9 (q, C-21), 33.9 (t, C-22), 31.4 (t, C-23), 148.6 (s, C-24), 45.7 (d, C-25 or C-17), 175.0 (s, C-26), 16.3 (q, C-27 or C-19), 110.9 (t, C-28), 15.6 (q, C-29), 51.9 (q, -COO*C*H$_3$).

Zhankuic acid A (4α-methylergosta-8, 24(28)-diene-3,7,11-trion-26-oic acid, 7)[4]

Yellow needles; mp 135-137 °C (hexane/acetone); $[\alpha]_D$ +54.3° (c 0.35, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (1H, m, H-1α), 3.05 (1H, ddd, *J* = 2.8, 6.6, 13.1 Hz, H-1β), 2.41 (1H, m, H-2a), 2.50 (1H, m, H-2b), 2.48 (1H, m, H-4), 1.90 (1H, td, *J* = 4.0, 13.7 Hz, H-5), 2.44 (1H, m, H-6α), 2.52 (1H, m, H-6β), 2.39 (1H, br d, *J* = 14.0 Hz, H-12α), 2.92 (1H, d, *J* = 14.0 Hz, H-12β), 2.63 (1H, dd, *J* = 7.1, 11.9 Hz, H-14), 1.41 (1H, m, H-15a), 2.53 (1H, m, H-

15b), 1.26 (1H, m, H-16a), 1.98 (1H, m, H-16b), 1.41 (1H, m, H-17), 0.68 (3H, s, H-18), 1.51 (3H, s, H-19), 1.41 (1H, m, H-20), 0.92 (3H, d, *J* = 5.7 Hz, H-21), 1.18 (1H, m, H-22a), 1.55 (1H, m, H-22b), 1.97 (1H, m, H-23a), 2.15 (1H, m, H-23b), 3.13 (1H, q, *J* = 7.1 Hz, H-25), 1.28 (3H, d, *J* = 7.0 Hz, H-27), 4.90 (1H, d, *J* = 2.4 Hz, H-28a), 4.96 (1H, br s, H-28b), 1.02 (3H, d, *J* = 6.6 Hz, H-29); ^{13}C NMR (75 MHz, $CDCl_3$): δ 34.7 (t, C-1), 37.5 (t, C-2), 210.6 (s, C-3), 43.9 (d, C-4), 48.9 (d, C-5), 38.9 (t, C-6), 200.7 (s, C-7), 145.5 (s, C-8), 151.9 (s, C-9), 38.3 (s, C-10), 202.5 (s, C-11), 57.3 (t, C-12), 47.1 (s, C-13), 49.3 (d, C-14), 24.8 (t, C-15), 27.8 (t, C-16), 54.0 (d, C-17), 11.9 (q, C-18), 16.2 (q, C-19), 35.6 (d, C-20), 18.4 (q, C-21), 33.7 (t, C-22), 31.3 (t, C-23), 148.0 (s, C-24), 45.5 (d, C-25), 179.7 (s, C-26), 16.1 (q, C-27), 111.4 (t, C-28), 11.4 (q, C-29); ESI-MS (neg.): *m/z* 467 (M–1).

Zhankuic acid B (3α-hydroxy-4α-methylergosta-8,24(28)-diene-7,11-dion-26-oic acid) (8)[4]

Pale yellow needles; mp 187-190 °C (dil. MeOH); $[\alpha]_D$ +23.1° (c 0.26, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (1H, m, H-1α), 2.50 (1H, m, H-1β), 1.70 (1H, m, H-2a), 1.80 (1H, m, H-2b), 3.77 (1H, d, *J* = 2.4 Hz, H-3), 1.72 (1H, m, H-4), 2.13 (1H, td, *J* = 2.9, 14.8 Hz, H-5), 2.39 (1H, dd, *J* = 2.8, 15.1 Hz, H-6α), 2.23 (1H, t, *J* = 14.7 Hz, H-6β), 2.38 (1H, br d, *J* = 13.5 Hz, H-12α), 2.87 (1H, d, *J* = 13.5 Hz, H-12β), 2.61 (1H, dd, *J* = 7.5, 11.9 Hz, H-14), 1.40 (1H, m, H-15a), 2.50 (1H, m, H-15b), 1.25 (1H, m, H-16a), 1.98 (1H, m, H-16b), 1.40 (1H, m, H-17), 0.65 (3H, s, H-18), 1.29 (3H, s, H-19), 1.40 (1H, m, H-20), 0.91 (3H, d, *J* = 5.4 Hz, H-21), 1.18 (1H, m, H-22a), 1.57 (1H, m, H-22b), 1.95 (1H, m, H-23a), 2.16 (1H, m, H-23b), 3.13 (1H, q, *J* = 7.1 Hz, H-25), 1.27 (3H, d, *J* = 7.0 Hz, H-27), 4.89 (1H, br s, H-28a), 4.95 (1H, br s, H-28b), 0.94 (3H, d, *J* = 6.8 Hz, H-29); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.8 (t, C-1), 29.0 (t, C-2), 70.3 (d, C-3), 34.5 (d, C-4), 41.0 (d, C-5), 38.0 (t, C-6), 202.3 (s, C-7), 144.6 (s, C-8), 153.7 (s, C-9), 38.7 (s, C-10), 202.9 (s, C-11), 57.5 (t, C-12), 47.3 (s, C-13), 49.5 (d, C-14), 24.9 (t, C-15), 27.8 (t, C-16), 53.9 (d, C-17), 11.9 (q, C-18), 16.2 (q, C-19 or C-27), 35.6 (d, C-20), 18.5 (q, C-21), 33.9 (t, C-22), 31.2 (t, C-23), 148.1 (s, C-24), 45.5 (d, C-25), 179.3 (s, C-26), 15.9 (q, C-27 or C-19), 111.3 (t, C-28), 15.9 (q, C-29), APCI-MS (neg.): *m/z* 469 (M–1).

Dehydrosulphurenic acid (24-methylenelanosta-7,9(11)-diene-3β,15α-diol-21-oic acid, 9)[8]

White powder; $[\alpha]_D$ +60.0° (c 0.25, MeOH); ^{1}H NMR (300 MHz, pyridine-d_5): δ 1.90 (2H, m, H-2), 3.43 (1H, t, *J* = 7.6 Hz, H-3), 1.32 (1H, m, H-5), 2.16 (2H, m, H-6), 6.48 (1H, br s, H-7), 5.39 (1H, d, *J* = 6.0 Hz, H-11), 2.37 (1H, H-12β) 2.70 (1H, H-12α), 4.75 (1H, dd, *J* = 5.9, 9.3 Hz, H-15), 1.09 (3H, s, H-18), 1.10 (3H, s, H-19), 2.23 (1H, H-25), 1.01 (3H, d, *J* = 6.8 Hz, H-26), 0.99 (3H, d, *J* = 6.8 Hz, H-27), 4.85 (1H, br s, H-28a), 4.88 (1H, br s, H-28b), 1.42 (3H, s, H-29), 1.17 (3H, s, H-30), 1.12 (3H, s, H-31); ^{13}C NMR (75 MHz, pyridine-d_5): δ 36.9 (t, C-1), 28.7 (t, C-2), 78.0 (d, C-3), 39.4 (s, C-4), 49.8 (d, C-5), 23.6 (t, C-6), 122.3 (d, C-7), 142.0 (s, C-8), 147.1 (s, C-9), 38.0 (s, C-10), 116.3(d, C-11), 36.5 (t, C-12), 45.0 (s, C-13), 52.6 (s, C-14), 73.8 (d, C-15),39.6 (t, C-16), 46.5 (d, C-17), 16.9 (q, C-18), 23.1 (q, C-19), 48.9 (d, C-20), 178.6 (s, C-21), 32.8 (t, C-22), 31.9 (t, C-23), 155.9 (s, C-24), 34.3 (d, C-25), 21.9

(q, C-26), 22.0 (q, C-27), 107.1 (t, C-28), 18.3 (q, C-29), 28.8 (q, C-30), 16.6 (q, C-31); APCI-MS (pos.): *m/z* 485 (M+1).

Sulphurenic acid (24-methylenelanosta-8-ene-3β,15α-diol-21-oic acid, 10)[9]

White powder; mp 246-248 °C (MeOH); $[\alpha]_D$ +36.4° (c 0.22, MeOH); ^{1}H NMR (300 MHz, pyridine-d_5): δ 3.41 (1H, dd, *J* = 7.0, 8.3 Hz, H-3), 4.61 (1H, dd, *J* = 6.2, 8.9 Hz, H-15), 1.05 (3H, s, H-18), 1.05 (3H, s, H-19), 1.00 (3H, d, *J* = 6.9 Hz, H-26), 0.99 (3H, d, *J* = 6.8 Hz, H-27), 4.84 (1H, br s, H-28a), 4.87 (1H, br s, H-28b), 1.34 (3H, s, H-29), 1.20 (3H, s, H-30), 1.17 (3H, s, H-31); ^{13}C NMR (75 MHz, pyridine-d_5): δ 36.2 (t, C-1), 28.7 (t, C-2), 78.1 (d, C-3), 39.3 (s, C-4), 50.9 (d, C-5), 18.9 (t, C-6), 27.7 (t, C-7), 134.9 (s, C-8), 135.2 (s, C-9), 37.3 (s, C-10), 21.2 (t, C-11), 30.2 (t, C-12), 45.2 (s, C-13), 52.2 (s, C-14), 72.5 (t, C-15), 39.5 (t, C-16), 46.7 (d, C-17), 16.9 (q, C-18), 19.4 (q, C-19), 49.0 (d, C-20), 178.7 (s, C-21), 31.9 (t, C-22), 32.7 (t, C-23), 155.9 (s, C-24), 34.2 (d, C-25), 21.9 (q, C-26), 22.0 (q, C-27), 107.1 (t, C-28), 18.1 (q, C-29), 28.6 (q, C-30), 16.3 (q, C-31); APCI-MS (pos.): *m/z* 467 (M+1).

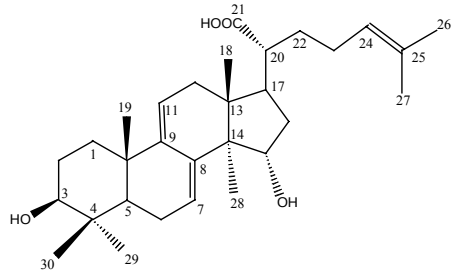
15α-Acetyl-dehydrosulphurenic acid (15α-acetoxy-24-methylenelanosta-7,9(11)-dien-3β-ol-21-oic acid, 11)[8]

White needless; $[\alpha]_D$ +57.1° (c 0.21, MeOH); ^{1}H NMR (300 MHz, pyridine-d_5): δ 3.44 (1H, t, *J* = 6.5 Hz, H-3), 5.85 (1H, d, *J* = 5.8 Hz, H-7), 5.37 (1H, d, *J* = 6.0 Hz, H-11), 5.48 (1H, dd, *J* = 5.5, 9.6 Hz, H-15), 1.05 (3H, s, H-18), 1.09 (3H, s, H-19), 2.23 (1H, H-25), 1.02 (3H, d, *J* = 6.8 Hz, H-26), 1.00 (3H, d, *J* = 6.8 Hz, H-27), 4.85 (1H, br s, H-28a), 4.88 (1H, br s, H-28b), 1.04 (3H, s, H-29), 1.56 (3H, s, H-30), 1.05 (3H, s, H-31), 2.15 (3H, s, -OCOC*H*$_3$); ^{13}C NMR (75 MHz, pyridine-d_5): δ 36.3 (t, C-1), 28.7 (t, C-2), 78.1 (d, C-3), 39.3 (s, C-4), 49.6 (d, C-5), 23.6 (t, C-6), 122.3 (d, C-7), 140.9 (s, C-8), 146.7 (s, C-9), 38.0 (s, C-10), 116.5 (d, C-11), 36.6 (t, C-12), 44.8 (s, C-13), 51.7 (s, C-14), 77.4 (d, C-15), 36.4 (t, C-16), 46.3 (d, C-17), 16.6 (q, C-18), 23.0 (q, C-19), 48.7 (d, C-20), 178.3 (s, C-21), 32.7 (t, C-22), 31.9 (t, C-23), 155.8 (s, C-24), 34.3 (d, C-25), 21.9 (q, C-26), 22.0 (q, C-27), 107.2 (t, C-28), 18.9 (q, C-29), 28.9 (q, C-30), 16.6 (q, C-31), 170.9 (s, -O*C*OCH$_3$), 21.3 (q, -OCO*C*H$_3$); APCI-MS (pos.): *m/z* 527 (M+1).

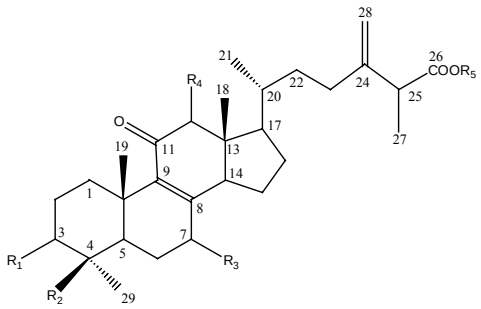
Versisponic acid D (15α-acetoxy-24-methylenelanosta-8-en-3β-ol-21-oic acid, 12)[9]

White needless; $[\alpha]_D$ +61.5° (c 0.26, MeOH); ^{1}H NMR (300 MHz, pyridine-d_5): δ 1.18 (1H, m, H-1a), 1.60 (1H, m, H-1b), 3.42 (1H, dd, *J* = 7.0, 8.3 Hz, H-3), 1.14 (1H, m, H-5), 1.50 (1H, m, H-6a), 1.72 (1H, m, H-6b), 2.08 (1H, m, H-7a), 2.26 (1H, m, H-7b), 1.88 (1H, m, H-11a), 1.98, (1H, m, H-11b), 1.90 (1H, m, H-12a), 2.09 (1H, m, H-12b), 5.41 (1H, dd, *J* = 5.5, 9.6 Hz, H-15), 1.92 (1H, m, H-16a), 2.37 (1H, m, H-16b), 2.60 (1H, m, H-17), 1.12 (3H, s, H-18), 1.01 (3H, s, H-19), 2.56 (1H, m, H-20), 1.78 (1H, m, H-22a), 2.00 (1H, m, H-22b), 2.24 (1H, m, H-23a), 2.39 (1H, m, H-23b), 2.24 (1H, m, H-25), 1.01 (3H, d, *J* = 6.8 Hz, H-26), 1.00 (3H, d, *J* = 6.8 Hz, H-27), 4.87 (1H, br s, H-28a),

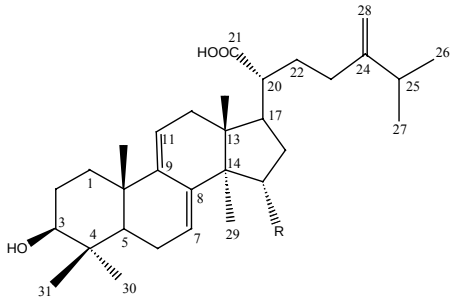
4.89 (1H, br s, H-28b), 1.20 (3H, s, H-29), 1.22 (3H, s, H-30), 1.04 (3H, s, H-31), 2.13 (3H, s, -OCOC*H*$_3$); ^{13}C NMR (75 MHz, pyridine-d$_5$): δ 36.1 (t, C-1), 28.6 (t, C-2), 78.1 (d, C-3), 39.6 (s, C-4), 50.8 (d, C-5), 18.6 (t, C-6), 26.9 (t, C-7), 133.1 (s, C-8), 136.3 (s, C-9), 37.6 (s, C-10), 21.1 (t, C-11), 29.6 (t, C-12), 45.3 (s, C-13), 51.3 (s, C-14), 76.0 (t, C-15), 36.1 (t, C-16), 46.6.(d, C-17), 16.7 (q, C-18), 19.4 (q, C-19), 48.9 (d, C-20), 178.4 (s, C-21), 31.9 (t, C-22), 32.7 (t, C-23), 155.9 (s, C-24), 34.3 (d, C-25), 21.9 (q, C-26), 22.0 (q, C-27), 107.1 (t, C-28), 18.7 (q, C-29), 28.7 (q, C-30), 16.3 (q, C-31), 170.8 (s, -O*C*OCH$_3$), 21.3 (q, -OCO*C*H$_3$); APCI-MS (neg.): *m/z* 527 (M−1).



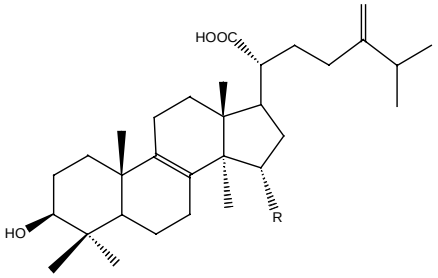
3β,15α-Dihydroxylanosta-7,9(11),24-trien-21-oic acid (**1**)



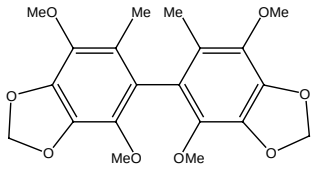
Antcin K (**2**): R_1= (α-OH), R_2=R_3= (β-OH), R_4=H, R_5=H
Zhankuic acid A (**7**): R_1=R_3= (=O), R_2=H, R_4=H, R_5=H
Zhankuic acid B (**8**): R_1= (α-OH), R_2=H, R_3= (=O), R_4=H, R_5=H
Zhankuic acid C (**13**): R_1=R_4= (α-OH), R_2=H, R_3= (=O), R_5=H
Methyl antcinate B (**5**): R_1=R_3= (=O), R_2=H, R_4=H, R_5=CH_3
Methyl antcinate H (**6**): R_1=R_4= (α-OH), R_2=H, R_3= (=O), R_5=CH_3



Dehydroeburicoic acid (**3**): R=H
Dehydrosulphurenic acid (**9**): R=OH
15α-Acetyl-dehydrosulphurenic acid (**11**): R=OAc



Eburicoic acid (**4**): R=H
Sulphurenic acid (**10**): R=OH
Versisponic acid D (**12**): R=OAc



2,2',5,5'-Tetramethoxy-3,4,3',4'-bis(methyl-enedioxy)-6,6'-dimethylbiphenyl (**14**)

Fig. 1. Structures of fourteen compounds isolated from the fruit-body of *Antrodia camphorata*.

Zhankuic acid C (3α,12α-dihydroxy-4α-methylergosta-8,24(28)-diene-7,11-dion-26-oic acid, 13)[4]

Yellow fine needles; mp 170-173 °C (dil. MeOH); $[\alpha]_D$ +71.4° (c 0.28, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.77 (1H, br s, H-3), 4.02 (1H, s, H-12β), 2.98 (1H, dd, *J* = 7.5, 12.0 Hz, H-14), 0.61 (3H, s, H-18), 1.26 (3H, s, H-19), 0.91 (3H, d, *J* = 6.3 Hz, H-29), 3.15 (1H, q, *J* = 7.1 Hz, H-25), 1.27 (3H, d, *J* = 7.0 Hz, H-27), 4.90 (1H, br s, H-28a), 4.95 (1H, br s, H-28b), 0.91 (3H, d, *J* = 6.3 Hz, H-29); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.7 (t, C-1), 28.8 (t, C-2), 70.3 (d, C-3), 34.5 (d, C-4), 40.7 (d, C-5), 38.1 (t, C-6), 201.8 (s, C-7), 144.8 (s, C-8), 152.3 (s, C-9), 38.3 (s, C-10), 202.9 (s,

C-11), 80.7 (d, C-12), 49.6 (s, C-13), 41.9 (d, C-14), 23.9 (t, C-15), 26.9 (t, C-16), 45.6 (d, C-17 or C-25), 11.4 (q, C-18), 16.1 (q, C-19 or C-27), 35.4 (d, C-20), 17.9 (q, C-21), 33.7 (t, C-22), 30.9 (t, C-23), 148.0 (s, C-24), 45.7 (d, C-25 or C-17), 179.5 (s, C-26), 15.9 (q, C-27 or C-19), 111.4 (t, C-28), 15.6 (q, C-29); EIMS (GCQ, pos.): *m/z* 487 (M+1).

2,2′,5,5′-Tetramethoxy-3,4,3′,4′-bis(methlylenedioxy)-6,6′-dimethylbiphenyl (14)[5]

White crystal; mp 144-146 °C (MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.94 (4H, s), 3.90 (6H, s), 3.71 (6H, s), 1.77 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.86 (s), 137.28 (s), 136.84 (s,), 136.49 (s), 123.11 (s), 101.03 (t), 59.85 (q); APCI-MS (pos.): *m/z* 391 (M+1).

RESULTS AND DISCUSSION

A concentrated ethanol extract of the fruiting bodies of *A. camphorata* was taken in dichloromethane, and the soluble part was concentrated and chromatographed to give one biphenyl, six ergostanes, and seven lanostanes. By analysis of their physical and spectral properties (mp, [α], MS, ^{1}H and ^{13}C NMR spectra), twelve known compounds were identified as dehydroeburicoic acid (24-methylenelanosta-7,9(11)-dien-3β-ol-21-oic acid, **3**),[8] eburicoic acid (24-methylenelanosta-8-en-3β-ol-21-oic acid, **4**),[10] methyl antcinate B (methyl 4α-methylergosta-8,24(28)-diene-3,7,11-trion-26-oate, **5**),[6] methyl antcinate H (methyl 3α,12α-dihydroxy-4α-methylergosta-8,24(28)-diene-7,11-dion-26-oate, **6**),[6] zhankuic acid A (4α-methylergosta-8,24(28)-diene-3,7,11-trion-26-oic acid, **7**),[4] zhankuic acid B (3α-hydroxy-4α-methylergosta-8,24(28)-diene-7,11-dion-26-oic acid, **8**),[4] dehydrosulphurenic acid (24-methylenelanosta-7,9(11)-diene-3β,15α-diol-21-oic acid, **9**),[8] sulphurenic acid (24-methylenelanosta-8-ene-3β,15α-diol-21-oic acid, **10**),[9] 15α-acetyl-dehydrosulphurenic acid (15α-acetoxy-24-methylenelanosta-7,9(11)-dien-3β-ol-21-oic acid, **11**),[8] versisponic acid D (15α-acetoxy-24-methylenelanosta-8-en-3β-ol-21-oic acid, **12**),[9] zhankuic acid C (3α,12α-dihydroxy-4α-methylergosta-8,24(28)-diene-7,11-dion-26-oic acid, **13**),[4] and 2,2′,5,5′-tetramethoxy-3,4,3′,4′-bis(methlylenedioxy)-6,6′-dimethylbiphenyl (**14**).[5]

Compound **1** was obtained as fine needles, mp 259-261 °C (dil. MeOH), [α] +83.3 (c 0.3, MeOH); its molecular formula $C_{30}H_{46}O_4$ was determined by HRMS, which showed the molecular ion at *m/z* 470.4315. Compared with dehydrosulphurenic acid, compound **1** lacked one carbon and two hydrogens. Its ^{1}H and ^{13}C NMR spectra were similar to those of dehydrosulphurenic acid except the region of the long side chain on D-ring. Compound **1** showed an olefinic proton at δ_H 5.28 instead of δ_H 4.84 and 4.88 methylene signals in dehydrosulphurenic acid. Besides, two doublets at δ_H 0.99 and 0.98 from the methyl groups (H-26 and H-27) of isopropyl in dehydrosulphurenic acid disappeared and two singlets at δ_H 1.63 (3H) and 1.58 (3H) were observed in **1**, which indicated that there existed an internal double bond between C-24 and C-25. The complete analysis of NMR spectra (^{1}H, ^{13}C, DEPT, HMQC, and

HMBC) is shown in Table 1. From these spectral data, **1** was established as 3β,15α-dihydroxylanosta-7,9(11),24-trien-21-oic acid.

Compound **2** was also obtained as white needles, mp 227-230 °C (dil. MeOH), [α] +92.0 (c 0.25, MeOH); its EIMS (ESI, neg.) showed $[M-1]^-$ at *m/z* 487 and HRMS showed a molecular ion peak at *m/z* 488.3133, which was analyzed for $C_{29}H_{44}O_6$. The ^1H and ^{13}C NMR spectra of **2** were similar to those of zhankuic acid B; however, compound **2** showed a triplet at δ_H 4.62 (1H), which was correlated to δ_C 70.8 in HMQC and to C-6, C-8, C-9, and C-14 in HMBC spectra. This revealed that a hydroxyl group was attached to the methine of C-7. Moreover, a signal at δ_C 73.9 correlated to H-2, H-3, H-5, and H-29 in HMBC spectrum indicated that another hydroxyl group was attached to C-4. The stereochemistry of C-4 and C-7 was established by NOESY experiment. Cross peaks between H-29 and H-3, H-5 in NOESY spectrum indicated that the methyl group at C-4 was in α position. In addition, the α configuration of H-7 (δ 4.62, t, J = 8.0 Hz) was confirmed by cross peaks between H-7 and H-5, H-6α. Table 2 shows the complete analysis of NMR spectra (^1H, ^{13}C, DEPT, HMQC, and HMBC). The structure of **2** was thus determined to be 3α,4β,7β-trihydroxy-4α-methylergosta-8,24(28)-dien-11-on-26-oic acid, and named as antcin K.

ACKNOWLEDGMENT

The authors thank the National Science Council of the Republic of China for financial support (NSC 90-2113-M-077-004).

REFERENCES

1. Wu SH, Ryvarden L, Chang TT. *Antrodia camphorata* (niu-chang-chih), new combination of a medicinal fungus in Taiwan. Bot. Bull. Acad. Sin. 38: 273-275, 1997.
2. Tsai ZT, Liaw SL. The use and the effect of Ganoderma. Sheng-Yun Publishers, Inc., Taichung, Taiwan, 1982.
3. Cherng IH, Chiang HC, Cheng MC, Wang Y. Three new triterpenoids from *Antrodia cinnamomea.* J. Nat. Prod. 58: 365-371, 1995.
4. Chen CH, Yang SW, Shen YC. New steroid acids from *Antrodia cinnamomea,* a fungal parasite of *Cinnamomum micrantham.* J. Nat. Prod. 58: 1655-1661, 1995.
5. Chiang HC, Wu DP, Cherng IW, Ueng CH. A sesquiterpene lactone, phenyl and biphenyl compounds from *Antrodia cinnamomea.* Phytochemistry, 39: 613-616, 1995.
6. Wu DP, Chiang HC. Constituents of *Antrodia cinnamomea.* J. Chin. Chem. Soc. 42: 797-800, 1995.
7. Cherng IH, Wu DP, Chiang HC. Triterpenoids from *Antrodia cinnamomea.* Phytochemistry, 41: 263-267, 1996.
8. Yang SW, Shen YC, Chen CH. Steroids and triterpenoids of *Antrodia cinnamomea* - a fungus parasitic on *Cinnamomum micranthum.* Phytochemistry, 41: 1389-1392, 1996.
9. Yoshikawa K, Matsumoto K, Mine C, Bando S, Arihara S. Five lanostane triterpenoids and three saponins from

the fruit body of *Laetiporus versisporus*. Chem. Pharm. Bull. 48: 1418-1421, 2000.

10. Tai T, Akahori A, Shingu T. Triterpenes of *Poria cocos* Phytochemistry, 32: 1239-1244, 1993.

J Chin Med 14(4): 247-258, 2003

牛樟芝成分之研究

沈建昌[1]　郭育綺[1,2]　黃瑞齡[1]　林麗純[1]　董明兆[1]　張東柱[3]　周正仁[1]

[1]國立中國醫藥研究所

[2]輔仁大學生命科學研究所

[3]農委會林業試驗所森林保護系

台北，台灣

(2003 年 9 月 3 日受理，2003 年 10 月 7 日收校訂稿，2003 年 11 月 11 日接受刊載)

樟薄孔菌（*Antrodia camphorata*）又名牛樟芝或樟芝，為台灣特有真菌，生長在台灣本土特有牛樟樹（*Cinnamomum kanehirae*）上，民間傳頌牛樟芝具有藥食物中毒之解毒作用，亦可治療腹瀉、肚子痛，高血壓，皮膚癢，及肝癌等。經本次實驗研究，從牛樟芝子實體酒精抽取物分離出十四種成分，分別為 3β,15α-dihydroxylanosta-7,9(11),24-trien-21-oic acid、antcin K、dehydroeburicoic acid、eburicoic acid、methyl antcinate B、methyl antcinate H、zhankuic acid A、zhankuic acid B、dehydrosulphurenic acid、sulphurenic acid、15α-acetyl-dehydrosulphurenic acid、versisponic acid D、zhankuic acid C、和 2,2′,5,5′-tetramethoxy-3,4,3′,4′-bis(methlylenedioxy)-6,6′-dimethylbiphenyl。其中四種成分 3β,15α-dihydroxylanosta-7,9(11),24-trien-21-oic acid (**1**)、antcin K (**2**)、sulphurenic acid 及 versisponic acid D，係首次從牛樟芝獲得，成分 **1** 及 **2** 兩種更是首次在天然物界發現。

關鍵詞：牛樟芝，真菌，麥角甾酸，羊毛甾酸，雙苯環類。

聯絡人：周正仁，國立中國醫藥研究所，電話：02-28201999 轉 7101，傳真：02-28264276，E-mail：choucj@cma23.nricm.edu.tw。