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TRITERPENOIDS FROM *ANTRODIA CINNAMOMEA*

I-HWA CHERNG, DE-PENG WU and HUNG-CHEH CHIANG*

Institute of Chemistry, National Taiwan Normal University, Taipei 117, Taiwan

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Key Word Index—*Antrodia cinnamomea*; Polyporaceae; triterpenoids, antcin; methyl antcinate.

Abstract—Four novel ergostane-type triterpenoids (antcins E and F and methyl antcinates G and H) were isolated from the fruiting body of the fungus *Antrodia cinnamomea*, a newly identified species of *Antrodia*, Polyporaceae in Taiwan. Their structures were elucidated by spectroscopic methods.

INTRODUCTION

Several highly oxygenated triterpenoids from *Ganoderma lucidum* were isolated previously [1, 2] whose biological activities included histamine release-inhibition [3], inhibition or stimulation of platelet aggregation [4, 5], cytotoxicity to hepatoma cells [6], inhibition of angiotensin-converting enzyme [7], hypolipidemic activity and inhibition of cholesterol synthesis [8].

Antrodia cinnamomea Chang & Chou, sp. nov. growing rarely on the inner cavity wall of *Cinnamomum kanehirai* Hay was identified as a new species of *Antrodia* in 1994 [9]. It was initially identified as a new *Ganoderma species*, *Ganoderma camphoratum* in 1990 [10] because there were several similar characteristics. However, it tastes more bitter than *G. lucidum* and the percentage of methanolic extract from *Antrodia cinnamomea* (30%) is 10 times higher than that of *G. lucidum* (3%) [11]. *Antrodia cinnamomea* is used as an antidote, anticancer and anticnesmatic (anti-itching) drug, but no phytochemical or biological studies have been published. This study attempts to explore the differences between *Antrodia cinnamomea* and *G. lucidum* in their constituents and biological activities by constituent analysis. Previously, three triterpenoids were isolated and determined from *Antrodia cinnamomea* which were designated as antcin A (**1**, 4α-methylergost-8,4(8)-diene-3,11-dion-26-oic acid), antcin B (**2**, 4α-methylergost-8,4(8)-diene-3,7,11-trion-26-oic acid) and antcin C (**3**, 7β-hydroxy-4α-methylergost-8,4(8)-diene-3,11-dion-26-oic acid) [12]. In this paper we report five additional triterpenoids isolated from the methanolic extract of *Antrodia cinnamomea*. They are antcin D (**4**, 14-hydroxy-4α-methyl-3,7,11-trioxo-ergost-8,24(28)-dien-26-oic acid), antcin E (**5**, 3,11-dioxo-4α-methylergost-8,14,24(28)-trien-26-oic acid), antcin F (**6**, 3,11-dioxo-7β-hydroxy-4α-methylergost-8,14,24(28) trien-26-oic acid), methyl antcinate G (**7a**, 7α-acetoxy-3,11-dioxo-4α-methylergost-8,24(28)-dien-26-oate), and methyl antcinate H (**8a**, 3α, 12α-dihydroxy-7,11-dioxo-4α-methylergost-8,24(28)-dien-26-oate). With the exception of antcin D, the other four triterpenoids reported in this study are new.

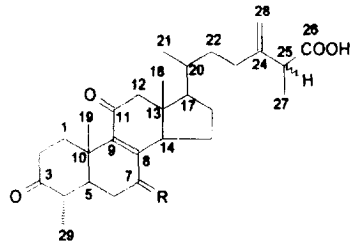
RESULTS AND DISCUSSION

In this study, five compounds from *Antrodia cinnamomea* were isolated from the MeOH extraction and are designated as compounds **4**, **5**, **6**, **7a** and **8a**.

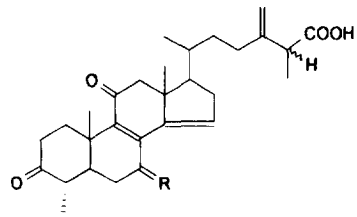
Compound **4**, antcin D, analysed for $C_{29}H_{40}O_6$ by HRMS, had an absorption at 256 nm ($\log\varepsilon$ 3.92), in the UV spectrum characteristic of an α,β-unsaturated carbonyl group [13]. Its IR absorption bands were observed at 3400–2500 (br., carboxylic acid), 1710 (carbonyl), 1680 (α,β-unsaturated carbonyl), and 875 cm^{-1} (terminal methylene). Compound **4** gave a M^+ at *m/z* 484 $[M]^+$, and a fragment ion peak by the elimination of water at *m/z* 466 $[M - H_2O]^+$. The fragment ion peaks at *m/z* 440 $[M - CO_2]^+$, 371 $[M - C_6H_9O_2]^+$, and *m/z* 329 $[M - C_9H_{15}O_2]^+$ suggested that the side chain was of the 24(28)-ene-26-carboxylic type [14]. The latter fragment ion peak results from cleavage of the side chain, and the peak at *m/z* 371 results from the allylic cleavage between C-22 and C-23. In the ^{13}C NMR spectrum of **4**, four carbonyl carbon signals (δ210.7, 202.9, 201.3 and 179.7), three quaternary olefinic carbon signals (δ152.0, 148.1 and 144.2) and a secondary olefinic carbon signal (δ111.4) suggested the presence of a conjugated 8-ene-7, 11-dione system, a 24(28)-ene-26-carboxylic side chain and a saturated, six-membered cyclic ketone at C-3 [13]. In addition, a quaternary carbon signal bearing a hydroxyl group was observed at δ81.0.

The ^1H NMR spectrum of **4** showed two methyl singlets at δ1.53 and 0.81, three methyl doublets at δ1.30 (*d*, $J = 7.3$), δ1.06 (*d*, $J = 6.4$) and δ0.94 (*d*, $J = 6.4$) and two singlets at δ4.97 and 4.92. Its ^1H NMR spectral pattern resembled that of antcin B (**2**), but the signal of the

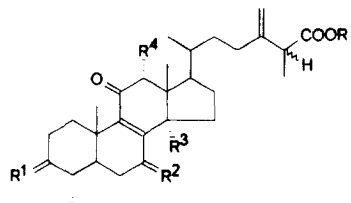
*Author to whom correspondence should be addressed



	R
1	H_2
2	O
3	β-OH α-H



	R
5	H_2
6	α-H β-OH



	R^1	R^2	R^3	R^4	R
4	O	O	α-OH	H_2	H
7a	O	α-OAc β-H	α-H	H_2	CH_3
8a	α-OH β-H	O	α-H	α-OH β-H	CH_3

18-methyl was more downfield than that in **2**. The ^{13}C NMR spectrum of **4** also resembled that of **2**, except for the presence of a quaternary carbon signal at δ81.0. The ^1H–^1H and ^1H–^{13}C shift correlation NMR spectra were analyzed to examine the proton and carbon sequences in **4**. Comparison of its ^{13}C NMR data with those of **2** indicated that the chemical shifts of the carbons in rings A and B, and in the side chain, were practically the same as those of the corresponding carbons in **2** [12]. Furthermore, from a consideration of the ^1H splitting pattern and the coupling constants, together with a comparison of its ^1H NMR and ^{13}C NMR data with those of **2**, it could be deduced that the skeleta of **2** and **4** were similar. The signal due to the quaternary carbon with a hydroxy group at δ81.0 and the ^{13}C NMR spectrum of **4**, which showed a more upfield shift for the 18-methyl signal at δ17.2 than that in **2**. The γ-effect of 14α-hydroxy group, coupled with a blue shift due to the substitution of a 14α-hydroxy in the UV spectrum (265 nm, log ε 3.27 for **2**), led to the formulation of **4** as 14-hydroxy-4α-methyl-3,7,11-trioxo-ergost-8,24(28)-dien-26-oic acid [15].

Compound **5**, antcin E ($[M]^+$, *m/z* 452), was assigned the molecular formula $C_{29}H_{40}O_6$ by HRMS. The IR spectrum of **5** showed the presence of a carboxylic acid group (3400–2400, 1710 cm^{-1}), a saturated carbonyl group (1705 cm^{-1}), an α,β-unsaturated carbonyl group (1658 cm^{-1}) and a terminal methylene group (891 cm^{-1}). The side chain could be identified by its fragment ion peaks at *m/z* 408 $[M - CO_2]^+$ and 297 $[M - C_9H_{15}O_2]^+$ as of the 24(28)-ene-26-carboxylic type. The ^{13}C NMR spectrum showed signals due to three carbonyl carbons at δ213.1, 200.6, and 179.9, four olefinic quaternary carbons at δ148.4, 148.0, 143.0, and 138.0, one olefinic methine at δ126.0, and one olefinic methylene at δ111.3, which had one more extending olefinic double bond and one less carbonyl group than **4**. The ^{13}C NMR and UV absorption at 295 nm (log ε 3.95) suggested that the conjugated system contained an 8,14-dien-11-one, a carbonyl group at C-3 and a 24(28)-ene-26-carboxylic side chain. The ^1H NMR spectrum of **5** exhibited three methyl doublets similar to those of **4**, a more downfield signal of H_3-18, and broad singlet of H-15 at δ5.87. Thus, the structure of **5** can be assigned as 3,11-dioxo-4α-methylergost-8,14,24(28)-trien-26-oic acid.

The HRMS of compound **6**, antcin F, revealed the molecular formula to be $C_{29}H_{40}O_5$, i.e. one additional oxygen atom than **5**. The mass spectrum of compound **6** revealed fragment ion peaks at *m/z* 450 $[M - H_2O]^+$, 313 $[M - C_9H_{15}O_2]^+$ and 295 $[M - C_9H_{15}O_2 - H_2O]^+$, showing that **6** has the same side chain and an additional hydroxy group in comparison with **5**. The UV, IR and ^1H NMR spectra of **6** closely resembled those of **5**, but a signal due to a carbinol methine proton at δ4.66

(*dd*, $J = 7.3, 9.3$), and assigned to H-7 was not observed in the ^{1}H NMR spectrum of **5**. The ^{13}C NMR spectrum of compound **6** was also similar to that of compound **5**, except for the tertiary carbon at δ67.0 (C-7) and the chemical shifts of several proximate carbons (C-8, C-9, C-14, C-15). Thus, the structure of compound **6** can be formulated as 3,11-dioxo-7β-hydroxy-4α-methylergost-8,14,24(28)trien-26-oic acid.

Compound **7a**, methyl antcinate G, analysed for $C_{32}H_{46}O_6$ by HRMS, and showed in the UV spectrum an absorption at 249.5 nm ($\log\varepsilon$ 4.05). The IR spectrum showed a carboxylate group (1735 cm^{-1}), two keto groups (1706, 1665 cm^{-1}), and a terminal methylene (890 cm^{-1}). The MS spectrum of **7a** showed a base peak at *m/z* 466 $[M - HOAc]^+$ and fragment ion peaks at *m/z* 357 $[M - C_{10}H_{17}O_2]^+$, *m/z* 325 $[M - C_8H_{13}O_2 - HOAc]^+$, *m/z* 339 $[M - C_7H_{11}O_2 - HOAc]^+$, and *m/z* 297 $[M - C_8H_{13}O_2 - HOAc]^+$, indicating the presence of a methyl 24(28)-ene-26-carboxylate side chain and an acetoxy group. The ^{13}C NMR spectrum showed signals due to the carbonyl carbons at δ212.5 (C-3) and δ200.3 (C-11), two carboxylate carbons at δ175.0 (C-26) and δ170.0 (OAc), three quaternary olefinic carbons at δ150.0 (C-9), δ148.4 (C-24) and δ142.8 (C-8), a secondary olefinic carbon at δ110.9 (C-28), and two carbons bearing oxygens at δ68.4 (C-7) and δ51.9 (OCH_3). The ^{1}H NMR contained four methyl singlets at δ3.68 ($COOCH_3$), δ2.08 (acetoxy), δ1.32 (19-methyl), δ0.71 (18-methyl), three methyl doublets, an acetoxymethine proton signal at δ5.36 (*br s*, 7β-H), and two olefinic protons slightly shifted upfield to δ4.93, 4.88 (28-CH_2), in comparison with **4**. In the ^{1}H–^{1}H COSY, the H-7 was coupled with the 6-CH_2 protons at δ1.82, 1.61, while the 6-CH_2 protons were coupled with H-5 proton at δ1.66, which was assigned by the correlation between H-4 and the relation between H-4 and H_3-29. The configuration of H-7 was determined by its coupling constant. The clear doublet of doublets for the H-7 α proton signal ($J = 8.5, 8.5$) of the acetylated derivative of ganodermic acid E [12] indicated that H-7 of compound **7a** should be a 7β-configuration proton which had a broad singlet at δ5.36. Thus, compound **7a** can be assigned as methyl 7α-acetoxy-3,11-dioxo-4α-methylergost-8,24(28)-dien-26-oate.

Compound **8a**, methyl antcinate H, has the molecular formula $C_{30}H_{44}O_6$ as confirmed by the HRMS data. The UV spectrum of **8a** showed an absorption band at 274 nm ($\log\varepsilon$ 3.79) and its IR spectrum showed the presence of a hydroxy group (3435 cm^{-1}, *br*), an ester group (1728 cm^{-1}), an α,β-unsaturated carbonyl group (1676 cm^{-1}) and a terminal methylene (879 cm^{-1}). The MS spectrum of **8a** showed a molecular ion peak at *m/z* 500 $[M]^+$, and other fragment ion peaks at *m/z* 482 $[M - H_2O]^+$, *m/z* 469 $[M - OCH_3]^+$, *m/z* 441 $[M - COOCH_3]^+$, *m/z* 359 $[M - C_8H_{13}O_2]^+$, and *m/z* 331 $[M - C_{10}H_{17}O_2]^+$, indicating the presence of a hydroxy group and a side chain, the same as in **7a**. The ^{13}C NMR spectrum showed signals at δ202.6 (C-11), δ201.7 (C-7), δ152.2 (C-9) and δ144.6 (C-8) similar to that of **4**. Also, in the ^{13}C NMR spectrum are signals due to an 8-ene-7,11-dione system, similar to that of **7a**, and two tertiary carbon signals at δ80.7 and δ70.4. Comparing the ^{13}C NMR spectrum with those of **4** and **7a**, it can be observed that the 3-carbonyl carbon signal (*ca* δ210) is absent and that the signals due to ring A are changed. The ^{1}H NMR spectrum of compound **8a** exhibited more upfield tertmethyl signals (δ0.96, *d*, $J = 7.3$, 29-methyl; δ0.97, *d*, $J = 6.8$, 21-methyl; and δ1.27, *d*, $J = 6.8$, 27-methyl), a broad singlet at δ3.79 and a singlet at δ4.05 due to two carbinol methine protons. Only the 12-carbinol methine proton resulted in the singlet at δ4.05 and in the ^{1}H–^{1}H COSY, the absence of the cross peak by the W conformation of 18-methyl and H-12α and the NOE of H-12β and H_3-18 suggested that the hydroxy group is attached at 12-α site. The other hydroxy group was assigned at 3-α site by the chemical shift difference and coupling constant of 3β-carbinol proton (δ3.79, *brs*) from that of 3α-carbinol proton (*ca* δ3.24, $J = ca$ 11 and 5) [14]. Thus, the compound **8a** can be formulated methyl 3α,12α-dihydroxy-7,11-dioxo-4α-methylergost-8,24(28)-dien-26-oate.

Finally, in comparison with constituents from *G. ludicum* and *A. cinnamomea*, the former are triterpenoids of the lanostane type, which have two methyl groups at C-4 [6, 7, 16, 17] and a side-chain with a trisubstituted allylic group at C-24 (25) [6, 7, 17], whereas *A. cinnamomea* has a terminal allyic group at C-2 (28) and only one methyl group at C-4.

EXPERIMENTAL

General. Mps (Yamato MP-21 MEL-TEMP apparatus) are uncorr.; IR: $CHCl_3$ soln. in CaF_2 cell or KBr disc (only compound **7a**). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 and 100 MHz, respectively, with TMS as int. standard. EIMS: 30 eV. HPLC was performed with *n*-Hexane–EtOAc or EtOAc–$CHCl_3$ on a Si60 (Waters, 6 μm, 7.8 × 300 nm) column employing a refractive index detector at a flow rate of 2.0 ml min^{-1}.

Extraction and separation. Antrodia cinnamomea, growing in Pin-Tung, Taiwan, was collected and identified by Prof. Chiu-Yuan Chien, Institute of Biological Sciences, National Taiwan Normal University. A Voucher specimen was deposited by Dr T. T. Chang to the Division of Forest Protection, Taiwan Forestry Research Institute. The dry fruit bodies of *Antrodia cinnamomea* (300 g) were cut into small pieces and refluxed × 6 with MeOH (2 l) for 5 hr. The concd MeOH ext was partitioned between H_2O and $CHCl_3$, and the $CHCl_3$ fr. (70 g) was CC on Si gel (800 g) by stepwise elution with *n*-Hexane–EtOAc (7:3), *n*-Hexane–EtOAc (1:1), and *n*-Hexane–EtOAc (2:3). The *n*-Hexane–EtOAc (7:3) elution was cc on HPLC using *n*-Hexane–EtOAc (3:1) to give **7a** (10 mg). The *n*-Hexane–EtOAc (1:1) elution was chromatographed on Si gel repeatedly (EtOAc–$CHCl_3$, 2:3) and then separated by HPLC (*n*-Hexane–EtOAc, 55:45) to afford **5** (14 mg), **4** (24 mg) and **8a** (21 mg). The 60% EtOAc–*n*-Hexane elution was separated by HPLC (*n*-Hexane–EtOAc, 2:3) to give **6** (7 mg).

Table 1. ^{1}H NMR spectral data of compounds **4**, **5**, **6**, **7a** and **8a***

Atom	4	5	6	7a	8a
1	1.56, 3.02	1.29, 2.91	2.83, 1.26	1.42, 3.10	2.34, 1.43
2	2.60, 2.44	2.53, 2.18	2.64, 2.33	2.40, 2.55	1.79, 1.79
3	—	—	—	—	3.79
4	2.50	2.40	2.40	2.35	1.72
5	2.01	1.45	1.40	1.66	2.14
6	2.46, 2.53	1.84, 1.48	2.30, 1.53	1.61, 1.82	2.40, 2.22
7	—	2.49, 2.46	4.66 *dd* (J = 7.3, 9.3)	5.36 *br s*	—
12β	3.18 *d* (J = 13.7)	2.66 *d* (J = 13.2)	2.74 *d* (J = 13.7)	2.86 *d* (J = 14.6)	4.05 *s*
12α	2.50 *d* (J = 13.7)	2.53 *d* (J = 13.2)	2.54 *d* (J = 13.7)	2.38 *d* (J = 14.6)	—
14	—	—	—	2.69 *dd*	3.02 *dd*
15	1.88, 2.34	5.87 *br s*	6.04 *br s*	1.45, 1.61	2.53, 1.49
16	1.38, 2.07	2.52, 2.50	2.40, 2.40	1.36, 1.96	1.95, 1.26
17	2.04	1.75	1.66	1.48	1.83
18	0.81 *s*	0.92 *s*	0.98 *s*	0.71 *s*	0.64 *s*
19	1.53 *s*	1.41 *s*	1.51 *s*	1.32 *s*	1.30 *s*
20	1.42	1.60	1.64	1.45	1.40
21	0.94 *d* (J = 6.4)	0.92 *d* (J = 5.4)	0.95 *d* (J = 6.4)	0.93 *d* (J = 5.8)	0.97 *d* (J = 6.8)
22	1.25, 1.62	1.62, 1.26	1.59, 1.27	1.20, 1.52	1.57, 1.17
23	1.98, 2.17	2.20, 2.05	2.20, 2.05	1.93, 2.13	2.17, 1.89
25	3.15 *q* (J = 7.3)	3.14 *q* (J = 6.8)	3.17 *q* (J = 6.8)	3.13 *q* (J = 6.8)	3.14 *q* (J = 6.8)
27	1.30 *d* (J = 7.3)	1.30 *d* (J = 6.8)	1.31 *d* (J = 6.8)	1.28 *d* (J = 6.8)	1.27 *d* (J = 6.8)
28	4.97, 4.92	4.98, 4.93	4.99, 4.95	4.88, 4.93	4.92, 4.89
29	1.06 *d* (J = 6.4)	1.05 *d* (J = 6.8)	1.08 *d* (J = 6.8)	1.00 *d* (J = 6.8)	0.96 *d* (J = 7.3)
OAc	—	—	—	2.08 *s*	—
OCH_3	—	—	—	3.68 *s*	3.68 *s*

*Values in parentheses are coupling constants in Hz ($CDCl_3$, TMS as int. standard, 400 MHz).

Antcin D (**4**). Compound **4** was crystallized from *n*-Hexane–$CHCl_3$ as yellow needles (24 mg), mp 173–176°, $[\alpha]^{24}$ + 109° ($CHCl_3$; *c* 0.55) IR: (CaF_2, $CHCl_3$) ν_{max} cm^{-1}: 3400, 3020, 2978, 1720, 1709, 1680, 1460, 1421, 1377, 1230, 1174, 1107, 875; UV λ^{MeOH} nm (log ε): 256 (3.92). HRMS *m/z* 484.2831 $[M]^+$ $C_{29}H_{40}O_6$ requires: 484.2826. EIMS (30 ev) *m/z* (rel. int.): 484 $[M]^+$ (100), 466 (33), 456 (65), 440 (20), 404 (18), 371 (18), 369 (19), 358 (38), 356 (30), 329 (32), 312 (30), 274 (50), 262 (50), 162 (32), 109 (43). ^{1}H NMR ($CDCl_3$): (Table 1). ^{13}C NMR ($CDCl_3$): (Table 2).

Antcin E (**5**). Compound **5** was obtained as a yellow syrup (14 mg). $[\alpha]^{24}$ + 76.7° ($CHCl_3$; *c* 1.2). IR: (CaF_2, $CHCl_3$) ν_{max} cm^{-1}: 3400, 3024, 2970, 2934, 2881, 1720, 1705, 1658, 1616, 1570, 1458, 1423, 1377, 1236, 1195, 906, 891. UV λ^{MeOH} (log ε) 295 nm (3.95). HRMS *m/z* 452.2930 $[M]^+$ $C_{29}H_{40}O_4$ requires: 452.2928. EIMS (30 ev) *m/z* (rel. int.): 452 (46), 438 (9), 408 (9), 378 (100), 379 (35), 370 (5), 363 (9), 323 (35), 297 (11), 281 (8), 199 (5), 159 (9), 121 (15), 109 (8), 95 (5). ^{1}H NMR ($CDCl_3$): (Table 1). ^{13}C NMR ($CDCl_3$): (Table 2).

Antcin F (**6**). Compound **6** was crystallized from EtOAc–$CHCl_3$ as needles (7 mg). $[\alpha]^{24}$ + 120° ($CHCl_3$; *c* 0.15). IR: (CaF_2, $CHCl_3$) ν_{max} cm^{-1}: 3400, 3038, 3020, 2934, 1720, 1707, 1666, 1608, 1458, 1377, 1234, 1087, 898, 873, 854. UV λ^{MeOH} (log ε) 294 (3.87), 230 (3.49). HRMS *m/z* 468.2878 $[M]^+$ $C_{29}H_{40}O_5$ requires: 468.2877. EIMS (30 ev) *m/z* (rel. int.): 468 (30) $[M]^+$, 450 (88), 404 (3), 394 (100), 395 (33), 377 (40), 339 (6), 323 (10), 313 (5), 295 (15), 253 ((8), 225 (5), 172 (10), 171 (12), 154 (35), 137 (8), 109 (16), 91 (3). ^{1}H NMR ($CDCl_3$): (Table 1). ^{13}C NMR ($CDCl_3$): (Table 2).

Methyl antcinate G (**7a**). Compound **7a** was a colourless liquid. (10 mg). $[\alpha]^{24}$ + 114.5° ($CHCl_3$; *c* 1.1). IR: (KBr, $CHCl_3$) ν_{max} cm^{-1}: 1735, 1707, 1666, 1373, 1226, 1192, 890; UV λ^{CHCl_3} nm (log ε) 249.50 (4.05). HRMS *m/z* 526.3285 $[M]^+$ $C_{32}H_{46}O_6$ requires: 526.3294. EIMS (30 ev) *m/z* (rel. int.): 526 (2) $[M]^+$, 466 (100) $[M - HOAc]^+$, 484 (12), 467 (25), 419 (20), 357 (6), 339 (10), 325 (52), 297 (20), 245 (22), 171 (10), 135 (15), 109 (22), 95 (8). ^{1}H NMR ($CDCl_3$): (Table 1). ^{13}C NMR ($CDCl_3$): (Table 2).

Methyl antcinate H (**8a**). Compound **8a** was crystallized from *n*-Hex-$CHCl_3$ as yellow needles (21 mg), mp 170–173°. $[\alpha]^{24}$ + 102° ($CHCl_3$; *c* 0.45). IR: (CaF_2, $CHCl_3$) ν_{max} cm^{-1}: 3437, 3634, 3018, 2935, 1730, 1676,

Table 2. ^{13}C NMR spectral data of compounds **4**, **5**, **6**, **7a** and **8a**

Atom	4	5	6	7a	8a
1	35.6	35.0	35.2	34.7	27.8
2	37.4	36.1	36.5	37.6	28.9
3	210.7	213.1	212.1	212.5	70.4
4	44.0	44.2	43.8	43.5	34.5
5	48.8	50.3	47.1	45.3	40.7
6	38.9	20.7	30.6	27.8	38.1
7	201.3	27.8	67.0	68.4	201.7
8	144.2	138.0	145.0*	142.8	144.6
9	152.0	143.0	144.0*	150.0	152.2
10	38.4	36.7	37.1	37.1	38.3
11	202.9	200.6	200.9	200.3	202.6
12	50.1	55.8	56.1	57.6	80.7
13	49.3	48.3	49.5	47.4	49.5
14	81.0	148.0	140.0*	51.0	41.8
15	33.3	126.0	121.6	22.9	23.9
16	26.6	37.8	37.7	27.4	26.9
17	48.3	56.5	56.3	55.0	45.5
18	17.2	17.4	17.3	11.9	11.4
19	16.3	18.0	17.8	16.3	16.1
20	35.4	33.4	33.4	35.7	35.4
21	18.5	18.3	18.5	18.4	18.0
22	34.1	33.6	33.7	33.8	33.8
23	31.4	31.2	31.1	31.1	31.3
24	148.1	148.4	148.1	148.4	148.5
25	45.4	45.4	45.5	45.6	45.6
26	179.7	179.9	179.0	175.0	175.0
27	16.2	16.2	16.3	16.3	16.3
28	111.4	111.3	111.4	110.9	110.9
29	11.5	11.6	11.6	51.9	15.6
OCH_3	—	—	—	51.9	51.9
OCOMe	—	—	—	170.0	—
OCOMe	—	—	—	21.2	

*Assignments may be reversed ($CDCl_3$, TMS as int. standard, 100 MHz).

1458, 1437, 1377, 1238, 1170, 1055, 896, 877. UV λ^{MeOH} nm (log ε) 274 (3.79). HRMS *m/z* 500.3140 $[M]^+$ $C_{30}H_{44}O_6$ requires: 500.3139. EIMS (30 ev) *m/z* (rel. int.): 500 (100) $[M]^+$, 482 (5), 441 (7), 423 (6), 413 (5), 359 (3), 341 (11), 331 (6), 329 (14), 313 (13), 277 (12), 275 (24), 215 (21), 201 (22), 75 (25), 121 (24), 109 (39), 95 (13). ^{1}H NMR ($CDCl_3$): (Table 1). ^{13}C NMR ($CDCl_3$): (Table 2).

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