Gallicynoic Acids A−I, Acetylenic Acids from the Basidiomycete *Coriolopsis gallica*

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Received November 12, 2007

Nine new acetylenic acids, gallicynoic acids A−I (**1**–**9**), have been isolated from a culture of the basidiomycete *Coriolopsis gallica*. The structures of **1**–**9** were elucidated on the basis of spectroscopic and chemical means.

The basidiomycete *Coriolopsis gallica* (Fr.) Ryvarden is a fungus belonging to the family Polyporaceae. Although the production of lactase from *C. gallica* has been reported,[1,2] there are few studies concerning the secondary metabolites produced by fungi of the genus *Coriolopsis*. Acetylenic acids are widespread in nature and are found in many organisms, but are especially common in plants of the Compositae/Asteraceae and the Umbelliferae/Apiaceae and fungi of the group Basidiomycete.[3,4] Over 600 naturally occurring acetylenic compounds are now known. Some of them exhibit diverse bioactivities, including cytotoxic, antimicrobial, enzyme–inhibitory, and anti-HIV activities.[4–10] In this paper, we report the isolation and structure elucidation of nine new compounds, gallicynoic acids A−I (**1**−**9**), from a culture of *C. gallica* collected in July 2005.

The organism was cultured in shakers (150 rpm) with modified PDA medium. After culturing for 30 days at 25 °C, the whole culture broth (18 L) was filtered and then the filtrate was extracted three times with EtOAc. The crude EtOAc extract (2.8 g) was subjected to repeated column chromatography to give pure **1** (12.8 mg), **2** (3.7 mg), **3** (65 mg), **4** (9.4 mg), **5** (4.8 mg), **6** (2.8 mg), **7** (15.3 mg), **8** (4.7 mg), and **9** (3.6 mg).

Results and Discussion

Gallicynoic acid A (**1**) was isolated as a colorless oil, in which the molecular formula was established as $C_{14}H_{22}O_4$ by negative HRESIMS. The IR spectrum showed the presence of both carbonyl (1710 cm^{-1}) and hydroxy groups (3332 cm^{-1}). The ^1H NMR spectrum revealed the occurrence of two olefinic (δ 5.50, 5.55), two oxymethine (δ 5.14, 4.32), and an allylic methylene (δ 2.18) proton and a methyl (δ 0.93) group. Correspondingly, the ^{13}C NMR spectrum exhibited the signals of two olefinic (δ 132.0, 131.9), two acetylenic quaternary (δ 86.6, 85.5), two oxymethine (δ 62.8, 58.5), and six methylene carbons (δ 23.4–38.7), as well as a methyl (δ 14.4) and a carbonyl (δ 177.4) group, typical of an acyclic fatty acid with a terminal methyl group. After treatment with $TMSCHN_2$, the methyl ester of **1** displayed a singlet at δ 3.66 integrating for three protons, confirming the presence of a carboxylic acid functional group. The HSQC data indicated that the proton at δ 5.14 was attached to the carbon resonating at δ 58.5, while the proton at δ 4.32 was attached to the carbon at δ 62.8. In the $^1H-^1H$ COSY and HMBC spectra, the olefinic protons showed correlations to the oxymethine (δ 5.14) and methylene (δ 2.18), whereas the resonances at δ 5.14 and 4.32 were correlated to two acetylenic quaternary carbons (δ 86.6, 85.5). COSY correlations between the oxymethine (δ 4.32) and the methylene (δ 1.68, 1H, H-11; 1.64, 1H, H-11) protons led to assignment of a partial structure, $CH_2-CH(OH)-C\equiv C-CH(OH)-CH=CH-CH_2$. On the basis of the chemical shift of the allylic carbon (δ 27.8), the configuration of the double bond was assigned as *Z*.[11] The two initially overlapped olefinic proton resonances were separated and gave a 10.3 Hz coupling constant after the formation of the MTPA ester of **1**. A fragment ion at *m/z* 111 [$CH_3 + 3CH_2 + CH(OH) + C\equiv C$] (Figure 1) in the FABMS, corresponding to α-cleavage at the allylic position, indicated that the olefin is located at C-5/C-6, which was supported by the above NMR data, including the COSY, DEPT, HSQC, and HMBC spectra. On the basis of all of these data, **1** was assigned as (*Z*)-7,10-dihydroxytetradec-5-en-8-ynoic acid.

Gallicynoic acids B−D (**2**–**4**) showed features similar to those of **1** in their NMR and IR spectra. Analysis of these NMR data together with the molecular formulas established by HRESIMS revealed that compounds **2**−**4** have one, two, and four more methylene groups than **1**, respectively. Taking the proposed biosynthetic pathway into consideration, it could be inferred that the methylene groups are inserted between the olefinic and carboxyl groups in **2**−**4**. This assignment was consistent with the ^{13}C NMR data, in which the chemical shifts of **1** at δ 14.4 (q), 23.4 (t), 28.6 (t), 38.7 (t), 62.8 (d), 86.6 (s), 85.5 (s), and 58.5 (d) were similar to those of compounds **2**−**4** in the corresponding regions of each spectrum. Similarly, a fragment ion at *m/z* 111 [$CH_3 + 3CH_2 + CH(OH) + C\equiv C$] was also observed for compounds **2**−**4** in the negative FABMS. On the basis of these data, the structures of gallicynoic acids B−D (**2**−**4**) were proposed as (*Z*)-8,11-dihydroxypentadec-6-en-9-ynoic acid, (*Z*)-9,12-dihydroxyhexa-dec-7-en-10-ynoic acid, and (*Z*)-11,14-dihydroxyoctadec-9-en-12-ynoic acid, respectively.

The modified Mosher method was applied to determine the absolute configuration at the carbinol centers in some of the acetynics obtained in this study.[12,13] From the values of $\Delta\delta$ ($\delta_S - \delta_R$) (Table S1, Supporting Information), the absolute configurations for **1** and **3** were assigned as 7*S*, 10*R* and 9*S*, 12*R*, respectively. The optical rotations and NMR data of compounds **1**–**4** are similar, suggesting that compounds **2** and **4** have the same configurations as **1** and **3**.

Gallicynoic acid E (**5**) was isolated as a minor constituent with a molecular formula of $C_{18}H_{30}O_5$. In its ^1H and ^{13}C NMR spectra, the signals of an oxymethine group (δ_H 3.97, δ_C 69.4) were observed instead of a methylene group (δ_H 1.60, δ_C 26.2) in **4**. The HMBC spectrum of **5** demonstrated correlations from H-2 (δ 2.36, 2.44) to C-1 (δ 176.1) and C-3 (δ 69.4). The methylene carbon resonance (C-2) of **5** at δ 43.4 was shifted to lower field than that of **4** at δ 35.2 (C-2), and the ^{13}C NMR spectrum of **5** showed a new methylene carbon resonance at δ 38.0. These observations indicated that a hydroxy group is located at C-3 in **5**. Consequently, the structure of **5** was proposed as (*Z*)-3,11,14-trihydroxyoctadec-9-en-12-ynoic acid. The absolute configuration was not determined because of the limited amount of compound available.

Gallicynoic acid F (**6**) was also isolated as a minor constituent with a molecular formula of $C_{18}H_{32}O_6$. Comparison of the ^1H and

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10.1021/np070638p CCC: $40.75
Published on Web 02/02/2008

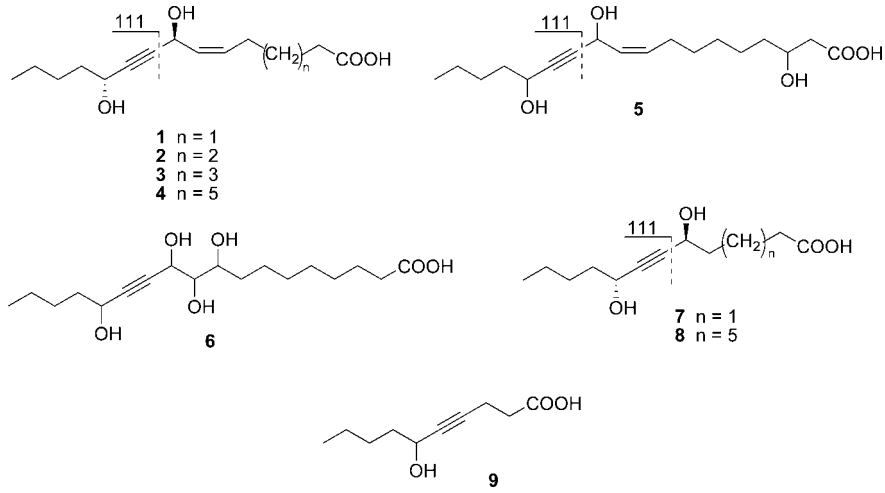

Figure 1. Structures of **1**−**9** and key MS fragmentations of **1**−**5** and **7**.

^{13}C NMR data of **6** with those of gallicynoic acids A−D (**1**–**4**) indicated that **6** lacks a double bond, since olefinic signals were absent, while resonances for two oxymethines (δ_H 3.37, δ_C 76.8; δ_H 3.83, δ_C 71.5) were apparent. In the ^{1}H−^{1}H COSY spectrum of **6**, correlation between H-10 (δ 3.37) and H-9 (δ 3.83) was observed. The HMBC spectrum of **6** showed correlations from H-10 (δ 3.37) to C-11 (δ 64.6) and C-12 (δ 84.9), H-11 (δ 4.40) to C-13 (δ 87.6), and H-14 (δ 4.33) to C-12 (δ 84.9). Therefore, a partial structure of CH(OH)−C≡C−CH(OH)−CH(OH)−CH(OH) could be assigned to **6**. Gallicynoic acid F (**6**) was proposed as 9,10,11,14-tetrahydroxyoctadec-12-ynoic acid.

The molecular formula of gallicynoic acid G (**7**) was found to be $C_{12}H_{22}O_4$ by negative HRESIMS. The lack of one double bond in **7** was confirmed by comparison of its ^{1}H and ^{13}C NMR data to those of **1**−**4**. The ^{13}C NMR data of carbons in the chain terminal (C7 through C12) in **7** were in good agreement with those of **1**−**4**. Further analysis of the NMR and FABMS data indicated that **7** possesses a chain two carbons shorter from the carboxyl terminal than **1**. The absolute configuration of gallicynoic acid G was determined as 5*S*, 8*R* by the modified Mosher method (Table S1, Supporting Information),[12,13] and the structure was assigned as 5*S*,8*R*-dihydroxydodec-6-ynoic acid.

The structure of gallicynoic H (**8**) was determined in a similar way to that of **7**. The optical rotations of **7** and **8** were found to be similar to each other, suggesting that **8** has the same absolute configuration as **7**. Accordingly, gallicynoic acid H (**8**) was proposed as 9*S*,12*R*-dihydroxyhexadec-10-ynoic acid.

Gallicynoic acid I (**9**) gave a molecular formula of $C_{10}H_{16}O_3$ based on its negative FABMS and NMR data. The ^{1}H and ^{13}C NMR spectra displayed signals for one oxymethine (H-6, δ_H 4.23, C-6, δ_C 62.9) and two methylene groups (H-3, δ_H 2.47; C-3, δ_C 15.4; H-2, δ_H 2.47, C-2, δ_C 34.6). HMBC correlations of protons H-2 and H-3 (δ_H2.47) with C-1 (δ_C 175.8), C-2 (δ_C 34.6), C-3 (δ_C 15.4), C-4 (δ_C 83.8), and C-5 (δ_C 83.1) revealed the presence of a C≡C−CH_2CH_2−COOH moiety. All of other NMR data of **9**, including the ^{1}H, ^{13}C NMR, HSQC, and HMBC spectra, were similar to those of **1**. Therefore, the structure of gallicynoic acid I (**9**) was determined as 6-hydroxydec-4-yoic acid.

It has been found that, in compounds isolated in the present study, the ^{1}H NMR resonances of the methine or the methylene group (CH_n, $n = 1$ or $n = 2$) adjacent to an acetylene unit, particularly the methine or the methylene group adjacent to an acetylene and an olefin or two acetylenes, were shifted to lower field, whereas the analogous ^{13}C NMR resonances were shifted to higher field, and these observations were in agreement with those reported in the literature for similar compounds.[14–16]

On comparing the structure of **4** with those of oleic, linoleic, and crepenynic acids, it is reasonable to assume that **4** is biosynthesized from crepenynic acid by allylic oxidation.[4b] Specially, a β-oxidation and a double β-oxidation of **4** would lead to a C_{16} acetylenic acid (**3**) and a C_{14} acetylenic acid (**1**), respectively. Compound **5** is probably derived from compound **4** by β-oxidation. While **2** may be formed by β-oxidation of the corresponding C_{17} acetylenic acid,[4c] even though this C_{17} acetylenic acid was not detected from *C. gallica* in the present investigation. Stymne and co-workers reported that the plant acetylenase enzyme catalyzes the formation of acetylenic bonds.[17] The results of the current study suggested that fungi may also contain a similar acetylenase.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Horiba SEPA-300 polarimeter. IR spectra were recorded with a Bruker Tensor 27 spectrometer. NMR spectra were acquired on a Bruker AM-400 or DRX-500 spectrometer in CD_3OD. FABMS were recorded with a VG Autospec-3000 spectrometer. ESIMS and HRESIMS were recorded with an API QSTAR Pulsar 1 spectrometer. Silica gel (200–300 mesh, Qingdao Marine Chemical Inc., People's Republic of China), RP-18 gel (40–75 μm, Fuji Silysia Chemicals Ltd., Aichi, Japan), and Sephadex LH-20 (Amersham Biosciences, Uppsala, Sweden) were used for column chromatography. Fractions were monitored by TLC, and spots were visualized by heating silica gel plates sprayed with 10% H_2SO_4 in ethanol.

Fungal Material and Cultivation Conditions. The fungus *C. gallica* was isolated from the tissue culture of its fruiting bodies collected at Ailao Mountains, Yunnan Province, People's Republic of China, in July 2005, and identified by Prof. Mu Zang, Kunming Institute of Botany. A voucher specimen (HFG05093) was deposited in the Herbarium of the Kunming Institute of Botany. The culture medium consisted of potato (peel), 200 g, glucose, 20 g, KH_2PO_4, 3 g, $MgSO_4$, 1.5 g, citric acid, 0.1 g, and thiamine hydrochloride, 10 mg, in 1 L of deionized H_2O. The pH was adjusted to 6.5 before autoclaving, and the fermentation was carried out on a shaker at 25 °C and 150 rpm for 30 days.

Extraction and Isolation. The whole culture broth of *C. gallica* (18 L) was initially filtered, and the filtrate extracted three times with EtOAc. The organic layer was concentrated under reduced pressure to give a crude extract (2.8 g), and this residue was subjected to column chromatography over silica gel (200–300 mesh, 3 × 45 cm), eluting with a $CHCl_3$−MeOH gradient, to afford fractions A−F. Fraction D eluted with $CHCl_3$−MeOH (9:1) was further purified on a silica gel column ($CHCl_3$−MeOH, 100:1–20:1) to give five subfractions, D1−D5. Each subfraction was further separated by repeated reversed-phased C_{18} (MeOH−H_2O) and Sephadex LH-20 ($CHCl_3$−MeOH, 1:1) column chromatography. Subsequently, **1** (12.8 mg) was obtained from subfraction D3, **2** (3.7 mg) and **3** (65 mg) from D2, **4** (9.4 mg), **8** (4.7 mg), and **9** (3.6 mg) from D1, **5** (4.8 mg) from D5, and **7** (15.3 mg) from D4, respectively. Fraction E, eluted with $CHCl_3$−MeOH (8:2), was again subjected using repeated reversed-phased C_{18} (MeOH−H_2O,

Table 1. ^{1}H NMR Data of Compounds **1**−**4** in CD_3OD at 400 MHz

position	1	2	3	4
2	2.31 (t, 7.4)	2.30 (t, 7.3)	2.27 (t, 7.2)	2.27 (t, 7.2)
3	1.69[a]	1.61[a]	1.60[a]	1.60[a]
4	2.18 (m)	1.44[a]	1.41[a]	1.38[a]
5	5.50[a]	2.15 (m)	1.42[a]	1.38[a]
6	5.55[a]	5.49[a]	2.13 (m)	1.38[a]
7	5.14 (br, d, 7.6)	5.51[a]	5.51[a]	1.38[a]
8		5.14 (br, d, 7.0)	5.48[a]	2.12 (m)
9			5.13 (br, d, 7.0)	5.50[a]
10	4.32 (br, t, 6.7)			5.50[a]
11	a 1.68[a], b 1.64[a]	4.31 (br, t, 6.8)		5.13 (br, d, 7.0)
12	1.43[a]	a 1.67[a], b 1.62[a]	4.31 (br, t, 6.5)	
13	1.34[a]	1.43[a]	a 1.68[a], b 1.61[a]	
14	0.93 (t, 7.4)	1.34[a]	1.42[a]	4.31 (br, t, 6.8)
15		0.93 (t, 7.3)	1.34[a]	a 1.66[a], b 1.63[a]
16			0.92 (t, 7.0)	1.43[a]
17				1.34[a]
18				0.93 (t, 7.0)

[a] Overlapped signals. Assignments are based on 2D NMR experiments.

Table 2. ^{1}H NMR Data of Compounds **5**−**9** in CD_3OD at 400 MHz

position	5	6	7	8	9
2	a 2.44 (dd, 15.1, 5.1) b 2.36 (dd, 15.1, 8.1)	2.20 (t, 7.2)	2.33 (t, 7.1)	2.27 (t, 7.6)	2.47 (br, s)
3	3.97 (m)	1.61[a]	1.76[a]	1.60[a]	2.47 (br, s)
4	1.48 (m)	1.36[a]	1.69[a]	1.35[a]	
5	1.42[a]	1.36[a]	4.36 (t, 6.5)	1.37[a]	
6	1.36[a]	1.36[a]		1.39[a]	4.23 (t, 6.7)
7	1.42[a]	1.36[a]		1.41[a]	a 1.67[a], b 1.62[a]
8	2.13 (m)	1.55[a]	4.32 (t, 6.7)	1.65[a]	1.43[a]
9	5.52[a]	3.83 (m)	1.62[a]	4.32 (t, 6.5)	1.33[a]
10	5.50[a]	3.37 (dd, 6.5, 2.9)	1.44[a]		0.92 (t, 7.0)
11	5.13 (br, d, 7.2)	4.40 (br, d, 6.6)	1.36[a]		
12			0.93 (t, 7.2)	4.32 (t, 6.5)	
13				1.65[a]	
14	4.31 (br, t, 6.7)	4.33 (br, t, 6.7)		1.43[a]	
15	a 1.67[a], b 1.62[a]	1.67[a]		1.35[a]	
16	1.43[a] (m)	1.45[a]		0.93 (t, 7.0)	
17	1.36[a] (m)	1.35[a]			
18	0.93 (t, 7.1)	0.93[a]			

[a] Overlapped signals. Assignments are based on 2D NMR experiments.

1:3) and Sephadex LH-20 ($CHCl_3$−MeOH, 1:1) column chromatography to give pure **6** (2.8 mg).

Gallicynoic acid A (1): colorless oil; $[\alpha]^{27}_D$ +132.5 (*c* 0.42, CH_3OH); IR (film) ν_{max} 3332, 3022, 2956, 2935, 2864, 2695, 2275, 1710, 1549, 1411, 1243, 1145 cm^{-1}; ^{1}H NMR data, see Table 1; ^{13}C NMR data, see Table 3; FABMS (negative) *m/z* 253 [M − H]$^-$, 507 [2 M − H]$^-$, 141, 111; HRESIMS (negative) *m/z* 253.1446 [M − H]$^-$, calcd for $C_{14}H_{21}O_4$, 253.1439.

Gallicynoic acid B (2): colorless oil; $[\alpha]^{27}_D$ +124.1 (*c* 0.18, CH_3OH); IR (KBr) ν_{max} 3407, 3021, 2955, 2934, 2863, 2310, 1711, 1657, 1549, 1459, 1409, 1279, 1145, 1037 cm^{-1}; ^{1}H NMR data, see Table 1; ^{13}C NMR data, see Table 3; FABMS (negative) *m/z* 267 [M − H]$^-$, 535 [2 M − H]$^-$, 155, 111; HRESIMS (negative) *m/z* 267.1595 [M − H]$^-$, calcd for $C_{15}H_{23}O_4$, 267.1596.

Gallicynoic acid C (3): colorless oil; $[\alpha]^{27}_D$ +135.8 (*c* 0.28, CH_3OH); IR (film) ν_{max} 3300, 3022, 2954, 2861, 2672, 1711, 1548, 1411, 1272, 1039 cm^{-1}; ^{1}H NMR data, see Table 1; ^{13}C NMR data, see Table 3; FABMS (negative) *m/z* 281 [M − H]$^-$, 563 [2 M − H]$^-$, 169, 111; HRESIMS (negative) *m/z* 281.1752 [M − H]$^-$, calcd for $C_{16}H_{25}O_4$, 281.1752.

Gallicynoic acid D (4): colorless oil; $[\alpha]^{27}_D$ +107.7 (*c* 0.33, CH_3OH); ^{1}H NMR data, see Table 1; ^{13}C NMR data, see Table 3; FABMS (negative) *m/z* 309 [M − H]$^-$, 198, 111; HRESIMS (negative) *m/z* 309.2073 [M − H]$^-$, calcd for $C_{18}H_{29}O_4$, 309.2065.

Gallicynoic acid E (5): colorless oil; $[\alpha]^{25}_D$ +36.6 (*c* 0.26, CH_3OH); ^{1}H NMR data, see Table 2; ^{13}C NMR data, see Table 3; FABMS (negative) *m/z* 326 [M − H]$^-$, 213, 111; HRESIMS (negative) *m/z* 325.2019 [M − H]$^-$, calcd for $C_{18}H_{29}O_5$, 325.2014.

Gallicynoic acid F (6): colorless oil; $[\alpha]^{25}_D$ −0.9 (*c* 0.19, CH_3OH); ^{1}H NMR data, see Table 2; ^{13}C NMR data, see Table 3; ESIMS (negative TOP) *m/z* 343 [M − H]$^-$, 687 [2 M − H]$^-$; HRESIMS (negative) *m/z* 343.2111 [M − H]$^-$, calcd for $C_{18}H_{31}O_6$, 343.2120.

Table 3. ^{13}C NMR Data of Compounds **1**−**9** in CD_3OD at 100 MHz

carbon	1	2	3	4	5	6	7	8	9
1	177.4	177.5	178.5	178.0	176.1	181.7	177.3	178.0	175.8
2	34.2	34.8	35.5	35.2	43.4	37.9	34.5	35.2	34.6
3	25.8	25.6	26.1	26.2	69.4	27.2	22.0	26.2[d]	15.4
4	27.8	29.9	29.8	30.1[a]	38.0	30.6[c]	38.3	30.2[e]	83.8
5	131.9	28.1	30.1	30.2[a]	26.5	30.6[c]	62.5	30.3[e]	83.1
6	132.0	132.5	28.2	30.3[a]	30.2[b]	30.7[c]	86.1	30.4[e]	62.9
7	58.5	131.4	132.7	30.4[a]	30.4[b]	26.9	86.7	26.3[d]	38.9
8	85.5	58.5	131.1	28.4	28.4	34.6	62.8	38.8[f]	28.6
9	86.6	85.5	58.5	132.9	132.9	71.5	38.7	62.8	23.5
10	62.8	86.5	85.5	131.1	131.1	76.8	28.6	86.4[g]	14.3
11	38.7	62.8	86.5	58.5	58.5	64.6	23.5	86.5[g]	
12	28.6	38.7	62.8	85.6	85.6	84.9	14.4	62.8	
13	23.4	28.6	38.6	86.5	86.5	87.6		39.0[f]	
14	14.4	23.5	28.5	62.8	62.8	62.9		28.6	
15		14.4	23.4	38.7	38.7	38.7		23.5	
16			14.4	28.6	28.6	28.6		14.4	
17				23.5	23.4	23.5			
18				14.4	14.4	14.4			

[a] Assignments may be interchanged. [b] Assignments may be interchanged. [c] Assignments may be interchanged. [d] Assignments may be interchanged. [e] Assignments may be interchanged. [f] Assignments may be interchanged. [g] Assignments may be interchanged.

Gallicynoic acid G (7): colorless oil; $[\alpha]^{27}_D$ −0.9 (*c* 0.37, CH_3OH); IR (KBr) ν_{max} 3386, 2957, 2935, 2871, 2020, 1713, 1549, 1459, 1409, 1242, 1035 cm^{-1}; ^{1}H NMR data, see Table 2; ^{13}C NMR data, see Table

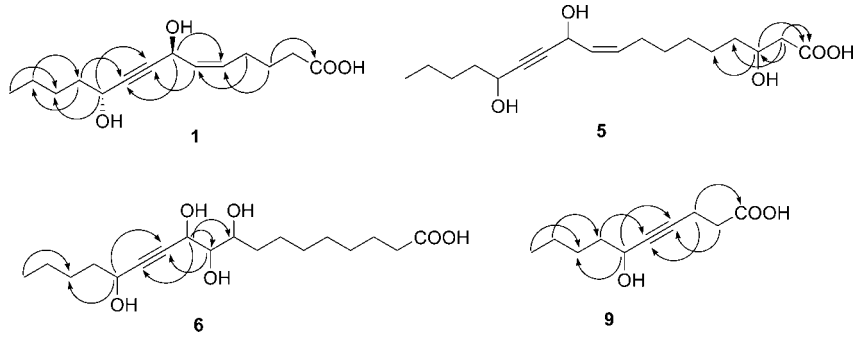

Figure 2. Key HMBC correlations of **1**, **5**, **6**, and **9**.

3; FABMS (negative) *m/z* 227 [M − H]$^-$, 115, 111; HRESIMS (negative) *m/z* 227.1280 [M − H]$^-$, calcd for $C_{12}H_{19}O_4$, 227.1283.

Gallicynoic acid H (8): colorless oil; $[\alpha]^{27}_D$ −8.3 (*c* 0.16, CH_3OH); ^{1}H NMR data, see Table 2; ^{13}C NMR data, see Table 3; FABMS (negative) *m/z* 283 [M − H]$^-$, HRESIMS (negative) *m/z* 283.1904 [M − H]$^-$, calcd for $C_{16}H_{27}O_4$, 283.1909.

Gallicynoic acid I (9): colorless oil; $[\alpha]^{27}_D$ +11.1 (*c* 0.17, CH_3COCH_3); IR (KBr) ν_{max} 3423, 2957, 2933, 2861, 2630, 2230, 1716, 1549, 1431, 1291, 1214 cm^{-1}; ^{1}H NMR data, see Table 2; ^{13}C NMR data, see Table 3; FABMS (negative) *m/z* 183 [M − H]$^-$, 367 [2 M − H]$^-$; HRESIMS (negative) *m/z* 183.1021 [M − H]$^-$, calcd for $C_{10}H_{15}O_3$, 183.1021.

MTPA Esters of Compounds 1, 3, and 7. The methyl ester by reaction with $TMSCHN_2$ was prepared from **1** by a procedure published in the literature.[18] A mixture of the methyl ester (3.3 mg), (*S*)-MTPA (31.3 mg), 4-(dimethylamino)pyridine (DMAP; 5.7 mg), and 1,3-dicyclohexylcarbodiimide (DCC; 26.2 mg) was dissolved in 10 mL of dry CH_2Cl_2 and stirred at room temperature for 24 h. The reaction mixture was filtered, and the concentrated filtrate was chromatographed over a silica gel (eluted with $CHCl_3$) and Sephadex LH-20 column (eluted with $CHCl_3$−MeOH, 1:1) to yield the purified Mosher ester of **1** (4.7 mg). Other MTPA esters were prepared in the same manner for **3** and **7** and characterized by measurement of their ^{1}H and ^{1}H−^{1}H COSY NMR spectroscopic data in $CDCl_3$.

Bis[(*S*)-MTPA] Ester of 1: ^{1}H NMR ($CDCl_3$) δ 6.29 (1H, d, J = 8.8 Hz, H-7), 5.63 (1H, dt, J = 10.3, 7.3 Hz, H-5), 5.53 (1H, t, J = 6.6 Hz, H-10), 5.44 (1H, dd, J = 10.3, 8.8 Hz, H-6), 2.29 (2H, t, J= 7.3 Hz, H-2), 2.18 (2H, m, H-4), 1.83 (2H, m, H-11), 1.69 (2H, m, H-3), 1.39 (2H, m, H-12), 1.32 (2H, m, H-13), 0.88 (3H, t, J = 7.3 Hz, H-14).

Bis[(*R*)-MTPA] Ester of 1: ^{1}H NMR ($CDCl_3$) δ 6.28 (1H, d, J = 9.5 Hz, H-7), 5.70 (1H, dt, J = 10.3, 7.3 Hz, H-5), 5.59 (1H, H-6), 5.56 (1H, H-10), 2.31 (2H, t, J = 7.3 Hz, H-2), 2.21 (2H, m, H-4), 1.73 (2H, m, H-11), 1.72 (2H, m, H-3), 1.24 (2H, m, H-12), 1.23 (2H, m, H-13), 0.82 (3H, t, J = 6.6 Hz, H-14).

Bis[(*S*)-MTPA] Ester of 3: ^{1}H NMR ($CDCl_3$) δ 6.31 (1H, d, J = 9.2 Hz, H-9), 5.65 (1H, dt, J = 10.4, 6.7 Hz, H-7), 5.55 (1H, dt, J = 6.7, 1.2 Hz, H-12), 5.39 (1H, dd, J = 10.4, 9.2 Hz, H-8), 2.29 (2H, t, J = 7.9 Hz, H-2), 2.13 (2H, m, H-6), 1.83 (2H, m, H-13), 1.61 (2H, m, H-3), 1.39 (2H, m, H-14), 1.35 (2H, m, H-5), 1.32 (2H, m, H-15), 1.31 (2H, m, H-4), 0.88 (3H, t, J = 6.7 Hz, H-16).

Bis[(*R*)-MTPA] Ester of 3: ^{1}H NMR ($CDCl_3$) δ 6.31 (1H, d, J = 8.5 Hz, H-9), 5.72 (1H, dt, J = 10.4, 7.3 Hz, H-7), 5.58 (1H, H-12), 5.54 (1H, H-8), 2.29 (2H, t, J = 7.3 Hz, H-2), 2.17 (2H, m, H-6), 1.73 (2H, m, H-13), 1.61 (2H, m, H-3), 1.39 (2H, m, H-5), 1.32 (2H, m, H-4), 1.24 (2H, m, H-14), 1.23 (2H, m, H-15), 0.82 (3H, t, J = 6.7 Hz, H-16).

Bis[(*S*)-MTPA] Ester of 7: ^{1}H NMR ($CDCl_3$) δ 2.33 (1H, t, J = 7.3 Hz, H-2), 2.26 (1H, t, J = 7.3 Hz, H-2), 1.833 (2H, m, H-9), 1.81 (2H, m, H-4), 1.75 (1H, m, H-3), 1.64 (1H, m, H-3), 1.39 (2H, m, H-10), 1.33 (2H, m, H-11), 0.88 (3H, t, J = 7.3 Hz, H-12).

Bis[(*R*)-MTPA] Ester of 7: ^{1}H NMR ($CDCl_3$) δ 2.34 (1H, t, J = 7.3 Hz, H-2), 2.27 (1H, t, J = 6.8 Hz, H-2), 1.86 (2H, m, H-4), 1.75 (2H, m, H-9), 1.77 (1H, m, H-3), 1.66 (1H, m, H-3), 1.26 (2H, m, H-10), 1.25 (2H, m, H-11), 0.83 (3H, t, J = 6.8 Hz, H-12).

Acknowledgment. This project was supported by the Chinese Academy of Sciences (KSCX1-YW-R-24; KSCX2-YW-G-025) and the National Natural Science Foundation of China (30671385).

Supporting Information Available: MS and 1D and 2D NMR spectra of **1**–**9**. IR spectra of **1**−**3**, **7**, and **9**. ^{1}H and ^{1}H−^{1}H COSY NMR spectra and $\Delta\delta$ ($\delta_S - \delta_R$, in ppm) of MTPA esters of **1**, **3**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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NP070638P