Chemical constituents from the roots of *Homonoia riparia*

YANG Shu-min[1,2], LIU Xi-kui[1*], QING Chen[3], WU Da-gang[1], ZHU Da-yuan[2]

(*1. State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, China; 2. State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences, Shanghai 201203, China; 3. Yunnan Pharmacological Laboratory of Natural Products, Kunming Medical College, Kunming 650031, China*)

Abstract: A new compound and twelve known compounds were isolated from the ethyl acetate extract of the roots of *Homonoia riparia* Lour, which are used in folk medicine for treatment of hepatitis, bellyache and scald, by the method of silica gel column chromatography repeatedly with a gradient of PE-EtOAc, PE-Me_2CO, $CHCl_3$-Me_2CO, $CHCl_3$-MeOH. Their structures were identified as a new compound 1-oxo-aleuritolic acid (**1**), and twelve known compounds aleuritolic acid (**2**), 3-acetoxy-aleuritolic acid (**3**), taraxerone (**4**), taraxerol (**5**), methyl 3-acetoxy-12-oleanen-28-oate (**6**), 3-acetoxy-12-oleanen-28-ol (**7**), ursolic acid (**8**), lupenol (**9**), 3β-acetoxy-lupenol (**10**), cleomiscosin A (**11**), chrysophanol (**12**), and gallic acid (**13**), which were obtained from this plant for the first time, by the spectroscopic techniques of NMR, HMBC, IR and MS, separately. Among the cytotoxicities evaluation of compounds **1** - **3** towards AGZY 83-a (human lung cancer cells) and SMMC-7721 (human liver cancer cells) tumor cells was assayed by MTT methods with *cis*-dichlorodiamminoplatinum (DDP) used as positive control. Compound **2** exerted weak activity against AGZY 83-a with the IC_{50} value of 33.055 $\mu g \cdot mL^{-1}$, while **1** and **3** showed no activity to these two cell lines.

Key words: *Homonoia riparia*; chemical constituent; 1-oxo-aleuritolic acid; cytotoxicity

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水杨柳根的化学成分

杨淑敏[1,2], 刘锡葵[1*], 卿 晨[3], 吴大刚[1], 朱大元[2]

(1. 中国科学院 昆明植物研究所 植物化学与西部植物资源持续利用国家重点实验室, 云南 昆明 650224;
2. 中国科学院 上海生命科学院 药物研究所 新药研究国家重点实验室, 上海 201203;
3. 昆明医学院 云南省天然药物药理实验室, 云南 昆明 650031)

摘要: 本文的目的是对水杨柳的根部进行化学成分研究, 采用硅胶柱色谱的方法分离和纯化化合物, 根据理化性质和波谱方法鉴定化合物结构。从水杨柳的根部分离得到了13个化合物, 包括1-羰基-油桐酸(**1**), 油桐酸(**2**), 3-乙酰氧基-油桐酸(**3**), 蒲公英赛酮(**4**), 蒲公英赛醇(**5**), 3-乙酰氧基-12-齐墩果烯-28-酸甲酯(**6**), 3-乙酰氧基-12-齐墩果烯-28-醇(**7**), 熊果酸(**8**), 羽扇豆醇(**9**), 乙酰氧羽扇豆醇酯(**10**), 臭矢菜素A(**11**), 大黄酚(**12**)和没食子酸(**13**)。化合物**1**为新的蒲公英赛烷三萜类化合物, 化合物**2**~**12**均为首次从该植物中分离得到。并用MTT法测定了化合物**1**~**3**对AGZY 83-a和SMMC-7721细胞的抑制作用。证明化合物**2**对AGZY 83-a细胞有弱抑制作用(IC_{50} 33.055 $\mu g \cdot mL^{-1}$)。

关键词: 水杨柳; 化学成分; 1-羰基-油桐酸; 细胞毒性

Homonoia Lour (Euphorbiaceae) is a small genus of shrubs or small arbor in the south and southwest of Asia, and only one of them, *Homonoia riparia* Lour, is found in South China. The roots of *H. riparia* are used in folk medicine for treatment of hepatitis, diarrhea,

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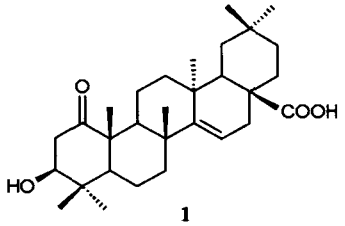
* Corresponding author Tel / Fax: 86 - 871 - 5215967,
E-mail: liuxikui@mail.kib.ac.cn

bellyache and scald[1]. In previous investigations three compounds including taraxerone, gallic acid and a flavone glucoside, were obtained from the leaves of *H. riparia*[2], but there is no report on the chemical constituents of its roots. This paper gives the first report on chemical examination of the roots of *H. riparia*, 13 compounds were isolated and identified as 1-oxo-aleuritolic acid (**1**), aleuritolic acid (**2**), 3-acetoxy-aleuritolic acid (**3**), taraxerone (**4**), taraxerol (**5**), methyl 3-acetoxy-12-oleanen-28-oate (**6**), 3-acetoxy-12-oleanen-28-ol (**7**), ursolic acid (**8**), lupenol (**9**), 3β-acetoxy-lupenol (**10**), cleomiscosin A (**11**), chrysophanol (**12**), gallic acid (**13**). Compound **1** was identified as a new taraxerane triterpene, and **2** – **12** were obtained from this plant for the first time. The bioactive experiments of **1** – **3** against AGZY 83-a (human lung cancer cells) and SMMC-7721 (human liver cancer cells) were also assayed.

Results and discussion

Compound **1** (Figure 1) was obtained as white crystals; mp 258 – 260 ℃; $[\alpha]_D^{27}$ +51.786 (*c* 0.56, MeOH). It showed a molecular ion peak at *m/z* 470 $[M]^+$ in the EI mass spectrum. Its molecular formula was determined to be $C_{30}H_{46}O_4$ by HRESIMS ($[M+Na]^+$, found 493.329 1, calcd. for $C_{30}H_{46}O_4Na$ 493.329 3). The IR spectrum revealed absorption bands for hydroxyl group (3 432 cm^{-1}) and carbonyl group (1 691 cm^{-1}). The ^1H and ^{13}C NMR spectra showed the presence of seven methyls, nine methylenes, four methines, one of which was oxygenated at δ_C 79.0 (d) and six quaternary carbons. In addition one trisubstituted double bond at δ_C 117.0 (d) and 160.4 (s), one carboxyl at δ_C 180.2 (s), and one ketone group at δ_C 212.5 (s) were detected (see Table 1).



1

Figure 1 The structure of compound **1**

Inspection of 1D and 2D NMR spectra of **1** proposed that it possessed a taraxerane triterpene skeleton [3], the ^1H and ^{13}C NMR spectral data were very similar to those of aleuritolic acid except for ring A[3]. Comparing the ^{13}C NMR spectrum of **1** with those of aleuritolic acid indicated that instead of a methylene group (δ_C 34.4) in aleuritolic acid, a carbonyl group (δ_C 212.5) was presented in **1**. Furthermore, the chemical shift values of C-2, C-3, C-5, C-10 were shifted downfield significantly in the ^{13}C NMR spectrum of **1**. All these indicated that a carbonyl group was located at C-1. The assignment was further confirmed by HMBC spectrum: δ_C 212.5 (s, C-1) showed cross peaks between δ_H 3.72 (1H, dd, J = 11.8, 4.5 Hz, H-3), 3.38 (1H, t, J = 11.7 Hz, H-2α), 2.66 (1H, dd, J = 11.8, 4.5 Hz, H-2β), 2.26 (1H, t, J = 9.6 Hz, H-9), 1.31 (3H, s, Me-25). In the ^1H NMR spectrum, the resonance of H-3 was observed as a double-doublets with the coupling constants 11.8, 4.5

Table 1 The NMR spectral data of compound **1** in $CDCl_3$

Position	δ_C	δ_H	HMBC
1	212.5	–	–
2	45.5	3.38(1H,t,11.7), 2.66(1H,dd,11.8,4.5)	C-1,3,4,10,25
3	79.0	3.72(1H,dd,11.8,4.5)	C-1,4,23,24
4	40.1	–	–
5	55.0	1.0(1H,d,10.2)	C-3,4,10,24
6	18.5	1.57(2H,m)	C-5,7,8
7	40.4	1.90(1H,brd,12.8), 1.27(1H,m)	C-5,6,8,26
8	39.0	–	–
9	42.2	2.26(1H,t,9.6)	C-5,8,10,11,14,25,26
10	54.4	–	–
11	19.0	1.54(2H,m)	C-8,9,10,12,13
12	34.2	1.98(1H,m), 1.76(1H,dd,14.3,9.1)	C-9,11,13,14,18,27
13	37.9	–	–
14	160.4	–	–
15	117.0	5.79(1H,dd,7.8,3.0)	C-8,13,16,17,27
16	32.6	2.79(1H,m), 2.12(1H,dd,14.2,3.0)	C-14,15,17,18,22,28, 28
17	51.2	–	–
18	42.3	2.81(1H,m)	C-12,13,14,16,17,19, 22,27,28
19	35.9	1.39,1.23(each 1H,m)	C-13,17,18,20,21,29
20	28.8	–	–
21	34.6	1.27(2H,m)	C-17,19,20,22
22	31.6	2.03,1.57(each 1H,m)	C-17,18,20,21
23	29.3	1.18(3H,s)	C-3,4,5,24
24	16.7	1.15(3H,s)	C-3,4,5,23
25	15.3	1.31(3H,s)	C-1,5,9,10
26	26.1	1.19(3H,s)	C-7,8,9,14
27	22.8	1.19(3H,s)	C-12,13,14,18
28	180.2	–	–
29	32.4	0.98(3H,s)	C-19,20,21,30
30	29.6	1.08(3H,s)	C-19,20,21,29

Hz, indicating that OH-3 was in equatorial position. Therefore **1** was determined to be 1-oxo-aleuritolic acid.

Compounds **1** – **3** were screened for cytotoxicity against AGZY 83-a and SMMC-7721, among **2** exerted weak activity against AGZY 83-a (IC_{50} 33.055 μg · mL^{-1}), **1** and **3** showed no activity to these two cell lines (IC_{50} > 100 μg · mL^{-1}).

Experimental

General experimental procedures Melting points were measured on an XRC-1 apparatus and uncorrected. Optical rotations were measured with a JASCO DIP-370 polarimeter. IR spectra were obtained on a Bio-Rad FTS-135 infrared spectrophotometer with KBr pellets. 1D and 2D NMR spectra were recorded on Bruker AM-400 and DRX-500 spectrometer with TMS as internal standard, δ in ppm, J in Hz. MS data recorded on an API Qstar Pulsar I spectrometer. The silica gel for TLC (GF_{254}) and column chromatography (CC, 200 – 300 mesh) were obtained from Qingdao Meijing Chemical Inc., China.

Plant material The roots of *H. riparia* were collected at Hekou County of Yunnan Province, China, in September 2003. The plant was identified by Professor De-ding TAO, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and isolation The air-dried and crashed roots of *H. riparia* (8.8 kg) were extracted three times with 95% EtOH under reflux. The concentrated extracts was partitioned between H_2O and EtOAc, The EtOAc fraction (70 g) was subjected to CC silica and eluted repeatedly with a gradient of PE-EtOAc, PE-Me_2CO, $CHCl_3$-Me_2CO, $CHCl_3$-MeOH, to yield **1** (27 mg), **2** (12 mg), **3** (18 mg), **4** (87 mg), **5** (38 mg), **6** (18 mg), **7** (41 mg), **8** (227 mg), **9** (17 mg), **10** (55 mg), **11** (10 mg), **12** (41 mg), **13** (32 mg).

Biological testing The cytotoxicity evaluation of compounds **1** – **3** towards AGZY 83-a and SMMC-7721 was examined, *cis*-dichlorodiamminoplatinum (DDP) was used as positive control and was purchased from Farmitalia Carlo Erba Ltd., the experimental procedure was just as reported in literature[4].

Identification

Compound 1 $C_{30}H_{46}O_4$, white crystal, mp 258 – 260 ℃. $[\alpha]_D^{27}$ +51.786° (*c* 0.56, MeOH); IR (KBr) ν_{max}: 3 432, 2 944, 2 867, 1 691, 1 638, 1 466, 1 387, 1 364, 1 296, 1 250, 1 210, 1 192, 1 132, 1 050, 1 022 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$), ^{13}C NMR (125 MHz, $CDCl_3$) and HMBC spectral data see Table 1; EI-MS *m/z*: 470 (M^+, 4), 452 (5), 424 (9), 409 (7), 391 (4), 373 (1), 316 (11), 301 (12), 283 (9), 255 (8), 248 (30), 234 (92), 219 (19), 203 (41), 189 (100), 173 (23), 149 (26), 133 (34), 119 (50), 105 (33), 95 (28), 81 (25), 69 (42), 55 (29). HR-ESI-MS *m/z*: 493.329 1 [M + Na]$^+$ (calculated for $C_{30}H_{46}O_4Na$ 493.329 3).

Compound 2 $C_{30}H_{48}O_3$, colorless crystal; ^1H NMR (C_5D_5N, 400 MHz) δ_H: 5.82 (1H, dd, J = 7.8, 3.1 Hz, H-15), 3.42 (1H, t, J = 7.9 Hz, H-3), 1.20 (3H, s, Me-23), 1.16 (3H, s, Me-26), 1.10 (3H, s, Me-27), 1.09 (3H, s, Me-30), 1.02 (3H, s, Me-24), 1.01 (3H, s, Me-29), 0.91 (3H, s, Me-25); ^{13}C NMR spectral data see Table 2; EI-MS *m/z*: 456 [M]$^+$. The spectral data are similar to aleuritolic acid in the reference[3].

Compound 3 $C_{32}H_{50}O_4$, white powder; ^1H NMR ($CDCl_3$, 400 MHz) δ_H: 5.51 (1H, dd, J = 7.7, 3.1 Hz, H-15), 4.46 (1H, m, H-3), 2.04, 1.03, 1.03, 0.95, 0.91, 0.91, 0.88, 0.85 (each 3H, s, Me × 8); ^{13}C NMR spectral data see Table 2; EI-MS *m/z*: 498 [M]$^+$. Compared to the reference [5], compound **3** was identified as 3-acetoxy-aleuritolic acid.

Compound 4 $C_{30}H_{48}O$, white needles; ^{13}C NMR spectral data see Table 2; EI-MS *m/z*: 424 [M]$^+$. The spectral data are similar to taraxerone in the reference[6].

Compound 5 $C_{30}H_{50}O$, white crystal; ^{13}C NMR spectral data see Table 2; EI-MS *m/z*: 426 [M]$^+$. The spectral data are similar to taraxerol in the reference[6].

Compound 6 $C_{33}H_{52}O_4$, white crystal; ^1H NMR ($CDCl_3$, 500 MHz) δ_H: 5.34 (1H, br s, H-12), 4.48 (1H, t-like, J = 8.0 Hz, H-3), 3.62 (3H, s, H-OCH_3), 2.04 (3H, s, $C\underline{H}_3COO$), 1.12, 1.92, 0.92, 0.89, 0.86, 0.85, 0.72 (each 3H, s, Me × 7); ^{13}C NMR spectral data see Table 2; EI-MS *m/z*: 512 [M]$^+$. The spectral data are similar to methyl 3-acetoxy-12-oleanen-28-oate in the reference[7].

Compound 7 $C_{32}H_{52}O_3$, white crystal; ^1H NMR ($CDCl_3$, 400 MHz) δ_H: 5.19 (1H, br s, H-12), 4.49 (1H, t, J = 7.9 Hz, H-3), 3.54, 3.21 (each 1H, d, J = 11.0 Hz, H-28), 2.04 (3H, s, $C\underline{H}_3COO$), 1.15, 0.95, 0.93, 0.88, 0.87, 0.87, 0.85 (each 3H, s, Me × 7); ^{13}C NMR spectral data see Table 2; EI-MS *m/z*: 484 [M]$^+$. The spectral data are similar to 3-

acetoxy-12-oleanen-28-ol in the reference[7].

Compound 8 $C_{30}H_{48}O_3$, white powder; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 5.50 (s, 1H, H-12), 3.46 (1H, m, H-3), 2.65 (1H, br d, J = 11.4 Hz, H-18); ^{13}C NMR data see Table 2; EI-MS m/z: 456 [M]$^+$. The spectral data are similar to ursolic acid in the reference[8].

Compound 9 $C_{30}H_{50}O$, colorless needles; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 4.62, 4.50 (each 1H, d, J = 1.8 Hz, H-29), 3.12 (1H, dd, J = 11.2, 4.8 Hz, H-3), 1.61 (3H, s, H-30), 1.27 (1H, d, J = 6.4 Hz, H-9), 0.96 (3H, s, Me-26), 0.90 (3H, s, Me-23), 0.88 (3H, s, Me-27), 0.76 (3H, s, Me-25), 0.72 (3H, s, Me-28), 0.69 (3H, s, Me-24); ^{13}C NMR spectral data see Table 2; EI-MS m/z: 426 [M]$^+$. The spectral data are similar to lupenol in the reference[9].

Compound 10 $C_{32}H_{52}O_2$, colorless needles; ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H: 4.66 (1H, d, J = 2.0 Hz, H-29a), 4.55 (1H, d, J = 2.0 Hz, H-29b), 4.50 (1H, dd, J = 13.0, 7.2 Hz, H-3), 2.02 (3H, s, H-32), 1.66 (3H, s, H-30); ^{13}C NMR spectral data see Table 2; EI-MS m/z: 468 [M]$^+$. Compared to the reference[10], compound **10** was identified as 3β-acetoxy-lupenol.

Compound 11 $C_{20}H_{18}O_8$, white crystal; ^{1}H NMR (C_5D_5N, 400 MHz) δ_H: 7.73 (1H, d, J = 9.5 Hz, H-4), 7.40 (1H, s, H-2′), 7.34 (1H, d, J = 8.1 Hz, H-5′), 7.29 (1H, d, J = 8.1 Hz, H-6′), 6.71 (1H, s, H-5), 6.43 (1H, d, J = 9.5 Hz, H-3), 5.57 (1H, d, J = 8.1 Hz, H-7′), 4.46 (1H, d, J = 8 Hz, H-9′b), 4.28 (1H, d, J = 12.9 Hz, H-9′a), 3.90 (1H, dd, J = 12.9, 2.7 Hz, H-8′), 3.78, 3.69 (each

Table 2 The ^{13}C NMR spectral data of compounds **2 – 10** ($CDCl_3$, 100 MHz)

Position	2	3	4	5	6	7	8	9	10
1	34.4 t	37.9 t	38.3 t	37.6 t	38.1 t	38.3 t	39.4 t	38.7 t	38.4 t
2	28.7 t	23.4 t	34.1 t	26.8 t	23.6 t	23.6 t	28.2 t	27.4 t	23.7 t
3	78.2 d	80.8 d	217.6 s	78.8 d	80.9 d	80.9 d	78.2 d	78.9 d	81.0 d
4	38.3 s	37.3 s	47.6 s	38.9 s	37.7 s	37.7 s	39.1 s	38.8 s	37.8 s
5	56.0 d	55.5 d	55.7 d	55.4 d	55.3 d	55.2 d	55.8 d	55.3 d	55.4 d
6	19.2 t	18.7 t	19.9 t	18.7 t	18.1 t	18.2 t	18.8 t	18.3 t	18.2 t
7	41.5 t	40.7 t	35.1 t	35.0 t	32.6 t	32.5 t	33.6 t	34.3 t	34.2 t
8	39.3 s	39.0 s	38.8 s	38.6 s	39.4 s	39.3 s	40.0 s	40.8 s	40.9 s
9	49.6 d	49.0 d	48.7 d	48.6 d	47.6 d	47.5 d	48.1 d	50.5 d	50.3 d
10	38.3 s	37.6 s	37.5 s	37.4 s	37.0 s	37.1 s	37.5 s	37.2 s	37.1 s
11	17.8 t	17.3 t	17.4 t	17.4 t	22.8 t	23.6 t	23.7 t	20.9 t	20.9 t
12	32.8 t	33.3 t	35.8 t	36.5 t	122.3 d	122.3 d	125.7 d	25.2 t	25.1 t
13	37.8 s	37.2 s	37.7 s	37.9 s	143.8 s	144.2 s	139.3 s	38.1 d	38.0 d
14	160.7 s	160.5 s	157.6 s	158.0 s	41.3 s	51.4 s	42.5 s	42.8 s	42.8 s
15	117.1 d	116.8 d	117.2 d	116.8 d	27.7 t	25.4 t	28.7 t	27.4 t	27.4 t
16	31.6 t	31.2 t	36.6 t	37.6 t	23.4 t	21.3 t	24.9 t	35.6 t	35.6 t
17	51.2 s	51.4 s	37.7 s	38.9 s	46.5 s	40.0 s	48.1 s	42.9 s	43.0 s
18	42.2 d	41.3 d	48.7 d	49.2 d	40.6 d	42.4 d	39.5 d	48.3 d	48.3 d
19	35.9 t	35.3 t	40.6 t	41.2 t	45.9 t	46.4 t	39.4 d	47.9 d	48.0 d
20	28.1 s	29.7 s	28.8 s	28.7 s	30.6 s	31.0 s	39.4 d	150.8 s	150.9 s
21	33.9 t	33.6 t	33.5 t	33.6 t	33.8 t	34.1 t	31.1 t	29.9 t	29.8 t
22	29.6 t	30.6 t	33.0 t	33.0 t	32.4 t	23.6 t	37.3 t	40.0 t	40.0 t
23	28.6 q	27.9 q	26.2 q	27.8 q	28.0 q	28.0 q	28.8 q	27.9 q	27.9 q
24	16.4 q	16.5 q	21.5 q	15.3 q	16.7 q	16.7 q	17.6 q	15.3 q	16.5 q
25	15.7 q	15.6 q	14.8 q	15.3 q	15.4 q	15.6 q	15.7 q	16.0 q	16.2 q
26	26.4 q	26.2 q	29.9 q	29.8 q	17.2 q	16.7 q	16.6 q	15.9 q	16.0 q
27	22.6 q	22.4 q	25.6 q	25.8 q	25.9 q	25.9 q	24.0 q	14.5 q	14.5 q
28	180.2 s	184.2 s	29.9 q	29.7 q	178.3 s	69.7 t	180.0 s	17.9 q	18.0 q
29	32.4 q	31.8 q	33.3 q	33.2 q	23.6 q	23.6 q	21.5 q	109.2 t	109.3 t
30	29.6 q	28.6 q	21.5 q	21.2 q	33.1 q	33.2 q	17.5q	19.3 q	19.3 q
–	–	170.9 s	171.0 s	171.0 s	–	171.0 s			
–	–	21.2 q	21.3 q	21.3 q	–	21.3 q			
–	–	–	51.5 q	–	–	–			

3H,s,2 × OMe); ^{13}C NMR(C_5D_5N, 100 MHz) δ_C: 160.9(s, C-2), 113.9(d, C-3), 144.6(d, C-4), 101.2(s, C-5), 146.5(d, C-6), 137.5(s, C-7), 133.2(s, C-8), 139.5(s, C-9), 112.0(s, C-10), 127.7(s, C-1′), 112.4(d, C-2′), 149.1(s, C-3′), 148.9(s, C-4′), 116.7(d, C-5′), 123.3(d, C-6′), 77.6(d, C-7′), 80.0(d, C-8′), 60.8(t, C-9′), 55.9, 56.2(q, OCH_3 × 2); EI-MS *m/z*: 386[M]$^+$. Compared to the reference[11], compound **11** was identified as cleomiscosin A.

Compound 12 $C_{15}H_{10}O_4$, yellow crystal; ^{1}H NMR($CDCl_3$, 500 MHz) δ_H: 7.78(1H, d, *J* = 7.4 Hz, H-5), 7.65(1H, t, *J* = 7.4 Hz, H-6), 7.27(1H, d, *J* = 7.4 Hz, H-7), 7.62(1H, s, H-4), 7.07(1H, s, H-2), 2.45(3H, s, Me), 12.0(1H, s, OH-1), 12.1(1H, s, OH-8); ^{13}C NMR($CDCl_3$, 100 MHz) δ_C: 162.7(s, C-1), 124.3(d, C-2), 149.3(s, C-3), 121.3(d, C-4), 119.9(d, C-5), 136.9(d, C-6), 124.5(d, C-7), 162.4(s, C-8), 192.5(s, C-12), 113.9(s, c-13), 133.3(s, C-14), 22.9(q, Me); EI-MS *m/z*: 239[M - Me]$^+$. Compared to the reference[12], compound **12** was identified as chrysophanol.

Compound 13 $C_7H_6O_5$, colorless needles; ^{13}C NMR(CD_3COCD_3, 100 MHz) δ_C: 122.1(s, C-1), 110.2(d, C-2), 146.0(s, C-3, 5), 138.7(s, C-4), 167.94(s, COOH); EI-MS *m/z*: 170[M]$^+$(100). Compared to the reference[13], compound **13** was identified as gallic acid.

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