

短角湿生冷水花化学成分的研究

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摘要:为研究短角湿生冷水花(*Pilea aquarum* subsp. *brevicornuta*)化学成分。实验采用色谱法从中分离得到7个化合物,包括5个五环三萜、一个甾醇和一个木脂素。利用波谱学方法鉴定了它们的结构,分别鉴定为pilearbornol(1)、rubiaronone D(2)、camarolide(3)、表齐墩果酸(4)、齐墩果酮酸(5)、5,8-epidioxy-(3β,5α,8α,22E)-ergosta-6,9(11),22-trien-3-ol(6)和桉脂素(7)。其中,化合物1和2属于乔木萜烷型(arborane)三萜,化合物1为新化合物,化合物2的绝对构型首次通过X-射线单晶衍射得到了确定。所有化合物均为首次从该植物中分离得到,这也是首次从荨麻科植物中分离得到乔木萜烷型三萜化合物。

关键词:短角湿生冷水花;乔木萜烷;三萜;绝对构型

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Chemical constituents from *Pilea aquarum* subsp. *brevicornuta*

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Abstract: The study was focus on the chemical constituents of *Pilea aquarum* subsp. *brevicornuta* and seven compounds were obtained. Their structures were identified as pilearbornol (1), rubiarbonone D (2), camarolide (3), epi-oleanolic acid (4), oleanonic acid (5), 5,8-epidioxy-(3β,5α,8α,22E)-ergosta-6,9(11),22-trien-3-ol (6) and eudesmin (7), respectively, by spectroscopic methods. Among them, compounds 1 and 2 belong to arborane-type triterpenoids and compound 1 is new. In addition, the absolute configuration of compound 2 was determined by X-ray crystal diffraction. All isolates were discovered from this plant for the first time and this is the first time to report arborane triterpenoids from Urticaceae family.

Key words: *Pilea aquarum* subsp. *brevicornuta*; arborane; triterpenoids; absolute configuration

荨麻科(Urticaceae)冷水花属(*Pilea*)植物全球共有六百多种,其中中国境内大约分布90多种^[1]。部分冷水花属植物有一定药用价值,可以清热、解毒、利湿等,如波缘冷水花(*P. cavaleriei*)、西南冷水花(*P. plataniflora*)、冷水花(*P. notata*)和粗齿冷水花(*P. fasciata*)^[2]。目前国内外对该属植物的化学成分研究主要集中在波缘冷水花等为数不多的几种植物,所报道的化合物类型包括倍半萜^[3,4],木脂素^[5]和三萜类化合物^[6,7],其中一些化合物显示抗菌和细胞毒等作用^[3]。短角湿生冷水花 *P. aquarum* subsp. *brevicornuta* (Hayata) C. J. Chen 是一种多年生

草本植物,分布于我国福建、广东、贵州和云南等南方地区。到目前为止,短角湿生冷水花的化学成分还没有文献报道。近几年来,我们开始关注并探索天然产物中潜在抗炎活性成分的发现^[8,9]。作为该研究工作的一部分,我们对短角湿生冷水花的化学成分进行了研究。经硅胶、微孔树脂(MCI)、葡聚糖凝胶(Sephadex LH-20)以及半制备HPLC等多种色谱方法从中共分离、鉴定了五个五环三萜类化合物:pilearbornol(1),rubiarbonone D(2),camarolide(3),表齐墩果酸(4),齐墩果酮酸(5);一个甾醇类化合物:5,8-epidioxy-(3β,5α,8α,22E)-ergosta-6,9(11),22-trien-3-ol(6)和一个木脂素:桉脂素(7)。其中,化合物1和2均为乔木萜烷型三萜,且化合物1为新化合物。化合物2的绝对构型首次通过X-射线单晶衍射得到了确定。结合生源关系,通过与化合

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物²的比较对化合物¹的绝对构型也进行了合理推定。经查阅文献后发现,这是第一次从荨麻科植物中发现乔木萜烷型的三萜。

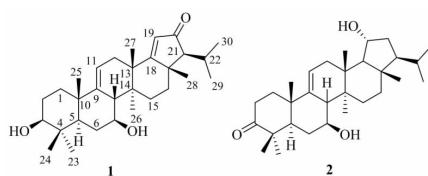


图 1 化合物¹和²的结构式

Fig. 1 Chemical structures of compounds **1** and **2**

1 仪器与材料

核磁共振仪: Varian Mercury Plus 400 MHz 和 Bruker Avance III 600 MHz; MCI(75 ~ 150 μm)为日本三菱公司产品; Sephadex LH-20 为瑞士 GE Healthcare 公司产品; UV 光谱和 IR 光谱数据分别由 Hitachi U-2900E 紫外光谱仪和 Thermo Scientific Nicolet iS 5 FTIR 型红外光谱仪获得; Rudolf Autopol IV 旋光仪; ESI-MS 数据由 Agilent 1100 series 仪器获得; HR-ESIMS 采集于 AB Sciex Triple TOFTM 5600 高分辨质谱仪; X-射线单晶衍射采集于 Bruker D8 Venture; 半制备高效液相色谱 HPLC 为 Waters e2695, 配备 2998 PDA 检测器; 半制备色谱柱为 Waters Sunfire ODS(5 μm , 250 \times 10 mm); SGW X-4 显微熔点仪为上海精密科学仪器有限公司; 硅胶(100~200 目, 200 ~ 300 目)为青岛海洋化工有限公司产品; 分析纯石油醚(PE)、乙酸乙酯(EtOAc)、甲醇(MeOH)和正丁醇(n-BuOH)等为国药集团化学试剂化学有限公司产品, 色谱级甲醇为上海星可高纯溶剂有限公司产品。

短角湿生冷水花全草 2015 年 4 月采集于贵州省贵阳市清镇市九龙山, 并由李振元教授鉴定, 凭证标本(No:20150412)保存于复旦大学药学院天然药物化学教研室。

2 实验方法

晾干粉碎后的短角湿生冷水花全草(3.0 kg)用 75% EtOH 在室温下浸提六次(每次 24 小时、5.0 L 溶剂)。合并提取液, 减压浓缩后得到的总浸膏(630.0 g)均匀分散在 1.0 L 水中, 依次用石油醚(1.0 L \times 3)、乙酸乙酯(1.0 L \times 4)和正丁醇(1.0 L \times 3)萃取。将石油醚浸膏(113.0 g)进行硅胶柱(100 ~ 200 目)色谱分离, 用 PE-EtOAc(150 \times 800 mm, 15:1 ~ 0:1, v/v)进行梯度洗脱共得到五个组分(Fr. 1 ~ Fr. 5)。对 Fr. 2(1.4 g)进行 MCI 柱色谱

(35 \times 500 mm, MeOH: H₂O, 7:3 ~ 1:0, v/v)层析并得到八个组分(Fr. 2A ~ Fr. 2H)。Fr. 2C(312.0 mg)经 Sephadex LH-20 柱层析(35 \times 1 200 mm, MeOH)层析后经硅胶(200 ~ 300 目)柱层析(20 \times 300 mm, PE: EtOAc, 8:1, v/v)纯化得到化合物⁶(1.1 mg)。将 Fr. 2D(903.0 mg)再一次经 Sephadex LH-20 柱层析(35 \times 1 200 mm, MeOH)分离得到化合物⁴(500.0 mg)。组分 Fr. 4(6.8 g)经 MCI 柱色谱(35 \times 500 mm, MeOH: H₂O, 7:3 ~ 1:0, v/v)层析后由 Sephadex LH-20 柱层析(35 \times 1 200 mm, MeOH)分离得到化合物⁵(300.0 mg)。Fr. 3(5.5 g)经 MCI 柱色谱(35 \times 500 mm, MeOH: H₂O, 7:3 ~ 1:0, v/v)层析得到八个亚组分(Fr. 3A ~ Fr. 3H), 对组分 Fr. 3D(33.0 mg)进行 Sephadex LH-20(20 \times 1 200 mm, MeOH)柱层析后进一步通过半制备高效液相色谱纯化得到化合物³(1.5 mg, MeOH: H₂O, 75:25, $t_{\text{R}} = 15.0 \text{ min}$, 3 mL/min)。Fr. 5(7.5 g)经 MCI 梯度(35 \times 500 mm, MeOH: H₂O, 7:3 ~ 1:0, v/v)柱层析同样得到八个亚组分(Fr. 5A ~ Fr. 5H), Fr. 5B(301.0 mg)经 Sephadex LH-20(35 \times 1 200 mm, MeOH)凝胶层析和硅胶柱层析(200 ~ 300 目, 20 \times 300 mm, PE: EtOAc, 8:1, v/v)后进一步用半制备高效液相色谱对它们进行纯化, 分别得到化合物²(8.5 mg, MeOH: H₂O, 78:22, $t_{\text{R}} = 13.8 \text{ min}$, 3 mL/min)和¹(1.1 mg, MeOH: H₂O, 80:20, $t_{\text{R}} = 13.3 \text{ min}$, 3 mL/min)。Fr. 5H(14.0 mg)经 Sephadex LH-20(20 \times 1 200 mm, MeOH)柱层析后进一步通过半制备高效液相色谱纯化得到化合物⁷(4.0 mg, MeOH: H₂O, 20:80, $t_{\text{R}} = 13.7 \text{ min}$, 3 mL/min)。

3 实验结果

化合物¹为白色无定形粉末, $[\alpha]_D^{25} -14.31$ (*c* 0.11, MeOH); 由 HR-ESIMS 中的准分子离子峰 *m/z* 455.3517 [M + H]⁺ 推测其分子式为 C₃₀H₄₆O₃ (C₃₀H₄₇O₃ 的计算值为 455.3520)。根据其分子式计算该化合物含有八个不饱和度。红外光谱在 3 438 cm⁻¹较强加宽信号峰表明分子中含有羟基, 1 690 cm⁻¹的信号峰表明可能含有不饱和共轭羰基。紫外光谱在波长 235 nm(log ε 为 2.30, MeOH)的吸收进一步说明分子中存在共轭结构单元。¹H NMR 数据(表 1)显示, 在高场区含有六个单峰甲基(δ_{H} 0.82, 0.85, 1.00, 1.10, 1.16, 1.31)和一个异丙基(δ_{H} 1.08, d, *J* = 6.4 Hz; 1.21, d, *J* = 6.4 Hz; 2.01, m); 在低场区, 出现两个烯氢(δ_{H} 5.44, dd, *J* = 6.8, 3.3

Hz, H-11; 5.74, s, H-19)信号和两个连氧次甲基碳上质子信号(δ_H 3.24, dd, $J = 11.4, 3.2$ Hz, H-3; 3.68, ddd, $J = 10.9, 10.7, 5.3$ Hz, H-7); 13 C NMR 和 HSQC(表1)数据表明以下特征信号:八个甲基,六个亚甲基,八个次甲基(两个烯碳分别在 δ_c 116.2 (C-11)和 126.4 (C-19);两个连氧碳分别在 δ_c 72.6 (C-7)和 78.6 (C-3))和八个季碳(两个烯碳分别在 δ_c 145.8 (C-9)和 191.5 (C-18);一个羰基碳 δ_c 209.1 (C-20))。通过以上 1H - ^{13}C NMR, HSQC 数据, 结合 1H - 1H COSY 和 HMBC(图3)相关实验, 我们确立了化合物1的平面结构如图1所示。乔木萜烷和羊齿烷型(fernane)三萜分子具有相同的平面结构, 不同之处在于 C-8, 13, 17, 18, 21 的构型差异, 可分析 1H NMR 和 ROESY 相关图谱进行区分^[10]。 1H NMR 揭示 H-3 ($J = 11.4$ Hz) 和 H-8 ($J = 10.9$ Hz) 都拥有较大的耦合常数, 表明 H-3 处于 α -直立键而 H-8 处于 α -直立键。考虑到与 H-8 耦合的质子只有 H-7, 因此可确定 H-7 一定位于 α -直立键。通过 ROESY 实验(图3), 表明 H-5 和 H-3,7 以及 H-7 和 Me-26 的相关信号, 这表明 H-3, H-5, H-7 和 Me-26 都具有相同朝向; 同理, H-8 和 Me-25,27 以及 Me-28 和 Me-27,29 的 ROE 相关表明 Me-25, H-8, Me-27, Me-28 和 Me-29 拥有相同朝向, 因此, 化合物1被鉴定为乔木萜烷型的三萜, 结构如图1所示。

化合物2为白色针状晶体(甲醇); ESI-MS m/z 457 [$M + H$] $^+$, 479 [$M + Na$] $^+$, 935 [$2M + Na$] $^+$; 其 1H - ^{13}C NMR 以及 ESI-MS 都表明该化合物为 rubiarbonone D^[11]。然而, 我们测得化合物2比旋光为 +9.2 ($c 0.03, \text{CHCl}_3$), 与 rubiarbonone D (+94.4 ($c 0.03, \text{CHCl}_3$))相差较大, 因此我们猜测化合物2为一对对映体。最后, 我们得到化合物2的X射线(Ga K α , $\lambda = 1.34139$)单晶衍射(Flack parameter, -0.029(8))数据(图2), 证明了化合物2就是 rubiarbonone D, 并且确定该化合物的绝对构型为 5R,7S,8S,10S,13R,14S,17S,18S,19R,21S。化合物1和2是来源于同一植物中具有相似分子骨架的化学成分, 非常有可能有相同的生物合成途径。除此以外, 即便从不同属植物得到的乔木萜烷型三萜, 如从茜草科(Rubiaceae)紫参(*Rubia yunnanensis* Diels)^[12]中分离得到 rubianols A-E 以及从棕榈科(Palmae)槟榔(*Areca catechu* L.)^[13]中分离得到的乔木萜烷三帖, 在 C-5, C-8, C-10, C-13, C-14, C-17 和 C-21 都有相同手性碳。因此, 化合物1和2在相同手性碳位置非常可能具有相同绝对构型。最终, 我们将化合物1的绝对构型确定为 3S,5R,7S,8S,

10S,13R,14S,17S,21S。

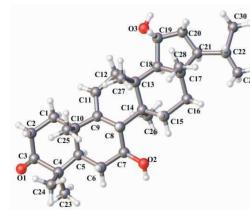


图2 化合物2的椭球图

Fig. 2 ORTEP drawing of compound 2

化合物1 白色无定形粉末; [a]_D²⁵ -14.3 ($c 0.11, \text{MeOH}$); HR-ESIMS [$M + H$] $^+$ m/z 455.3517 (calcd for $C_{30}H_{47}O_3$, 455.3520); UV (MeOH) λ_{max} ($\log \varepsilon$) 235 (2.30) nm; CD ($c 2.42 \text{ mM}, \text{MeOH}$) λ_{max} ($\Delta\varepsilon$) 244 (-2.01), 276 (-0.04), 327 (-0.71) nm; IR (KBr) ν_{max} 3438, 2965, 2918, 2875, 2858, 1690, 1656, 1387, 1033 cm^{-1} 。 1H - ^{13}C NMR 见表1。

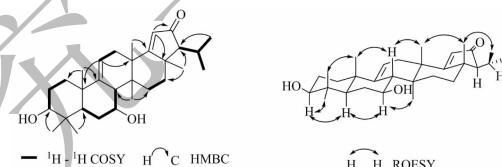


图3 化合物1的关键 COSY, HMBC 和 ROESY 相关

Fig. 3 Key COSY, HMBC and ROESY correlations of compound 1

化合物2 白色针状晶体(甲醇); mp. 231 ~ 232 °C; [a]_D²⁵ +9.2 ($c 0.03, \text{CHCl}_3$) [文献值: +94.4 ($c 0.03, \text{CHCl}_3$)]^[11]; CD ($c 2.41 \text{ mM}, \text{MeOH}$) λ_{max} ($\Delta\varepsilon$) 300 (-0.25) nm; ESI-MS: m/z 457 [$M + H$] $^+$, 479 [$M + Na$] $^+$, 935 [$2M + Na$] $^+$; 1H NMR (400 MHz, CDCl_3) δ_H : 5.36 (1H, d, $J = 4.9$ Hz, H-11), 4.23 (1H, td, $J = 8.9, 2.3$ Hz, H-19), 3.80 (1H, t, $J = 9.8$ Hz, H-7), 2.76 (1H, td, $J = 14.9, 4.9$ Hz, H-2b), 2.39 (1H, br d, $J = 14.9$ Hz, H-2a), 2.15 (1H, br d, $J = 9.8$ Hz, H-8a), 2.04 (1H, m, H-1b), 2.01 (1H, m, H-15a), 1.99 (1H, m, H-12a), 1.89 (1H, m, H-20b), 1.87 (1H, m, H-6a), 1.85 (1H, m, H-12b), 1.74 (1H, m, H-1a), 1.73 (1H, m, H-6b), 1.71 (1H, m, H-20a), 1.65 (1H, m, H-15b), 1.63 (2H, m, H-16b, H-18), 1.53 (1H, br d, $J = 12.3$ Hz, H-16a), 1.43 (1H, m, H-22), 1.35 (1H, m, H-5), 1.30 (1H, m, H-21), 1.28 (3H, s, H-25), 1.08 (6H, s, H-23, H-24), 0.98 (3H, s, H-26), 0.95 (3H, s, H-27), 0.89 (3H, d, $J = 6.5$ Hz, H-29), 0.83 (3H, d, $J = 6.5$ Hz, H-30), 0.82 (3H, s, H-28); ^{13}C NMR (150

MHz, CDCl₃) δ_{C} : 216.2 (s, C-3), 144.9 (s, C-9), 118.2 (d, C-11), 71.7 (d, C-7), 71.4 (d, C-19), 59.3 (d, C-18), 57.2 (d, C-21), 49.1 (d, C-5), 48.9 (d, C-8), 47.3 (s, C-4), 43.9 (s, C-17), 41.0 (t, C-20), 39.45 (s, C-14), 39.0 (s, C-10), 37.7 (s, C-13), 37.0

(t, C-1), 36.9 (t, C-12), 36.4 (t, C-16), 34.9 (t, C-2), 33.7 (t, C-6), 31.9 (t, C-15), 30.3 (d, C-22), 25.0 (q, C-23), 22.9 (q, C-30), 22.0 (q, C-24), 21.9 (q, C-29), 21.1 (q, C-25), 16.8 (q, C-27), 16.7 (q, C-26), 15.5 (q, C-28)。

表 1 化合物 1 的核磁数据
Table 1 NMR data of compound 1

编号 Position	δ_{H} (J in Hz)	δ_{C}	编号 Position	δ_{H} (J in Hz)	δ_{C}
1 α	1.74 m		16 α	1.82 ddd(14.5, 10.3, 6.8)	35.3
1 β	1.46 ddd(13.5, 12.7, 3.4)	36.2	16 β	1.75 ddd(11.7, 10.3, 3.6)	47.6
2 α	1.79 m	27.8	17		191.5
2 β	1.69 m		18		126.4
3	3.24 dd(11.4, 3.2)	78.6	19	5.74 s	209.1
4		38.8	20	2.02 d(9.2)	68.5
5	0.94 dd(13.1, 2.3)	48.3	21		26.1
6 α	1.64 ddd(13.1, 13.1, 10.7)	33.3	22	2.01 m	28.0
6 β	1.92 ddd(13.1, 5.3, 2.3)		23	1.00 s	15.4
7	3.68 ddd(10.9, 10.7, 5.3)	72.6	24	0.85 s	21.5
8	2.16 br d(10.9)	48.2	25	1.10 s	
9		145.8	26	0.82 s	18.0
10		39.4	27	1.16 s	21.1
11	5.44 dd(6.8, 3.3)	116.2	28	1.31 s	24.9
12 α	2.20 dd(17.1, 3.3)	34.5	29	1.08 d(6.4)	23.1
12 β	1.88 dd(17.1, 6.8)		30	1.21 d(6.4)	20.8
13		41.1			
14		39.4			
15 α	1.85 ddd(11.7, 10.6, 6.8)	30.1			
15 β	2.42 ddd(14.5, 10.6, 3.6)				

注:¹H 和¹³C 数据分别于 600 MHz 和 150 MHz 核磁条件下于 CDCl₃ 中测得。

Note: Data were measured in CDCl₃ at 600 MHz for ¹H and at 150 MHz for ¹³C.

化合物 3 白色无定形粉末; [a]_D²⁵ + 2.7 (c 0.11, MeOH); ¹H NMR (CDCl₃, 400 MHz) δ_{H} : 5.96 (1H, dd, J = 10.5, 1.3 Hz, H-11), 5.57 (1H, dd, J = 10.5, 3.0 Hz, H-12), 2.65 (1H, m, H-2a), 2.43 (1H, m, H-2b), 2.16 (1H, m, H-16a), 2.09 (1H, m, H-1a), 2.05 (1H, m, H-9), 1.81 (1H, m, H-19), 1.76 (1H, m, H-15a), 1.72 (2H, m, H-22), 1.67 (1H, br s, H-18), 1.64 (2H, m, H-6), 1.60 (2H, m, H-7), 1.55 (2H, m, H-21), 1.44 (1H, m, H-1b), 1.43 (1H, m, H-16b), 1.23 (1H, m, H-15b), 1.18 (3H, s, H-27), 1.10 (6H, s, H-23, 26), 1.06 (3H, s, H-25), 1.05 (3H, s, H-24), 1.00 (3H, d, J = 6.5 Hz, H-29), 0.95 (3H, d, J = 6.5 Hz, H-30), 0.89 (2H, m, H-5, 20); ¹³C NMR (CDCl₃, 150 MHz) δ_{C} : 216.7 (s, C-3), 179.8 (s, C-28), 132.8 (d, C-11), 129.4 (d, C-12), 89.4 (s, C-13), 60.6 (d, C-18), 54.7 (d, C-5), 52.4

(d, C-9), 47.6 (s, C-4), 45.0 (s, C-17), 42.5 (s, C-14), 41.6 (s, C-8), 40.3 (d, C-20), 39.1 (t, C-1), 38.3 (d, C-19), 36.2 (s, C-10), 33.9 (t, C-2), 31.3 (t, C-22), 30.9 (t, C-7), 30.6 (t, C-21), 26.0 (q, C-23), 25.5 (t, C-15), 22.8 (t, C-16), 20.8 (q, C-24), 19.3 (q, C-25), 18.9 (q, C-26), 18.5 (q, C-30), 17.8 (q, C-29), 17.2 (t, C-6), 16.0 (q, C-27); ESI-MS: m/z 453 [M + H]⁺, 475 [M + Na]⁺, 927 [2M + Na]⁺。以上数据与文献^[14]报道基本一致, 故鉴定该化合物为 camarolide。

化合物 4 白色无定形粉末; [a]_D²⁵ + 15.1 (c 1.0, MeOH); ¹H NMR (CDCl₃, 400 MHz) δ_{H} : 5.27 (1H, t, J = 3.5 Hz, H-12), 3.41 (1H, t, J = 2.7 Hz, H-3), 2.82 (1H, dd, J = 13.5, 4.5 Hz, H-18), 1.68 (1H, m, H-9), 1.26 (1H, dd, J = 12.8, 3.5 Hz, H-5), 1.14 (3H, s, H-27), 0.94 (3H, s, H-25), 0.92 (6H, s,

H-23,30),0.90(3H,s,H-29),0.83(3H,s,H-24),0.75(3H,s,H-26);¹³C NMR(150 MHz,CDCl₃) δ_{C} : 183.3(s,C-28),143.7(s,C-13),122.8(d,C-12),76.3(d,C-3),49.1(d,C-5),47.6(d,C-9),46.7(s,C-17),46.0(t,C-19),41.8(s,C-14),41.1(d,C-18),39.6(s,C-8),37.5(s,C-4),37.3(s,C-10),34.0(t,C-21),33.2(q,C-29),33.0(t,C-22),32.6(t,C-1,7),30.8(s,C-20),28.4(q,C-23),27.8(t,C-15),26.2(q,C-27),25.3(t,C-2),23.7(q,C-30),23.5(t,C-16),23.1(t,C-11),22.4(q,C-24),18.4(t,C-6),17.3(q,C-26),15.3(q,C-25);ESI-MS:*m/z* 479 [M+Na]⁺,935 [2M+Na]⁺。以上数据与文献^[15]报道基本一致,故鉴定该化合物为表齐墩果酸。

化合物5 白色无定形粉末;[*a*]_D²⁵+85.5(*c* 0.4,MeOH);¹H NMR(CDCl₃,400 MHz): δ_{H} : 5.30(1H,br d,2.2,H-12),2.84(1H,dd,*J*=12.2,4.5 Hz,H-18),2.54(1H,m,H-2),2.37(1H,m,H-2),1.13(3H,s,H-27),1.07(3H,s,H-23),1.04(6H,s,H-24,30),0.92(3H,s,H-29),0.79(3H,s,H-26);¹³C NMR(150 MHz,CDCl₃) δ_{C} : 217.3(s,C-3),183.0(s,C-28),143.8(s,C-13),122.6(d,C-12),55.5(d,C-5),47.6(s,C-4),46.7(C-9,17),46.0(t,C-19),41.9(s,C-14),41.2(d,C-18),39.4(s,C-8),39.3(t,C-1),36.9(s,C-10),34.3(t,C-2),34.0(t,C-21),33.2(q,C-29),32.5(t,C-22),32.3(t,C-7),30.8(s,C-20),27.8(t,C-15),26.6(q,C-23),26.0(q,C-27),23.7(t,C-16),23.6(q,C-30),23.1(t,C-11),21.6(q,C-24),19.7(t,C-6),17.1(q,C-26),15.2(q,C-25);ESI-MS:*m/z* 477 [M+Na]⁺。以上数据与文献^[15]报道基本一致,故鉴定该化合物为齐墩果酮酸。

化合物6 无色胶状物;[*a*]_D²⁵+31.2(*c* 0.11,CHCl₃);¹H NMR(CDCl₃,400 MHz) δ_{H} : 6.61(1H,d,*J*=9.0 Hz,H-7),6.30(1H,d,*J*=9.0 Hz,H-6),5.44(1H,d,,*J*=7.2 Hz,H-11),5.24,(1H,m,H-23),5.19(1H,m,H-22),4.00(1H,m,H-3),1.10(3H,s,H-19),1.01(3H,d,*J*=6.5 Hz,H-21),0.93(3H,d,*J*=6.5 Hz,H-28),0.84(3H,d,*J*=6.5 Hz,H-26),0.82(3H,d,*J*=6.5 Hz,H-27),0.74(3H,s,H-18);¹³C NMR(CDCl₃,150 MHz) δ_{C} : 142.5(s,C-9),135.4(d,C-6),135.1(d,C-22),132.4(d,C-23),130.7(d,C-7),119.7(d,C-11),82.7(s,C-5),78.3(s,C-8),66.3(d,C-3),55.9(d,C-17),48.2(d,C-14),43.6(s,C-13),42.8(d,C-24),41.2(t,

C-12),39.9(d,C-20),38.0(t,C-4),36.1(s,C-10),33.1(d,C-25),32.6(t,C-1),30.6(t,C-2),28.6(t,C-16),25.5(q,C-19),20.9(t,C-15),20.7(q,C-21),19.9(q,C-26),19.6(q,C-27),19.5(q,C-28),13.0(q,C-18);ESI-MS *m/z* 449 [M+Na]⁺,875 [2M+Na]⁺。以上数据与文献^[16]报道基本一致,故鉴定该化合物为5,8-epidioxy-(3 β ,5 α ,8 α ,22E)-ergosta-6,9(11),22-trien-3-ol。

化合物7 白色粉末;[*a*]_D²⁵+90.8(*c* 0.38,CHCl₃);¹H NMR(CDCl₃,400 MHz) δ_{H} : 6.91(2H,s,H-2,2'),6.90(2H,d,*J*=8.5 Hz,H-5,5'),6.85(2H,d,*J*=8.5 Hz,H-6,6'),4.76(2H,d,*J*=2.5 Hz,H-7,7'),4.26(2H,t,*J*=8.5 Hz,H-9a,9a'),3.99(2H,br s,H-9b,9b'),3.90(6H,s,3,3'-OCH₃),3.88(6H,s,4,4'-OCH₃),3.12(2H,s,H-8,8');¹³C NMR(150 MHz,CDCl₃) δ_{C} : 149.1(s,C-3,3'),148.7(s,C-4,4'),133.6(s,C-1,1'),118.3(d,C-6,6'),111.2(d,C-2,2'),109.0(d,C-5,5'),85.1(d,C-7,7'),71.8(t,C-9,9'),56.0(q,3,3'-OCH₃),55.9(q,4,4'-OCH₃),54.3(d,C-8,8');ESI-MS *m/z* 409 [M+Na]⁺,795 [2M+Na]⁺。以上数据与文献报道基本一致^[17],故鉴定该化合物为桉脂素。

以上化合物的详细结构鉴定数据原始图谱可从本刊官网免费下载(www.trcw.ac.cn)。

4 结论

本研究首次对短角湿生冷水花的化学成分进行了研究,从中分离并鉴定了七个化合物。其中,化合物**1**和**2**为乔木萜烷型三萜化合物。乔木萜烷型和羊齿烷型三萜都属于hopane型三萜,这类三萜化合物被认为是许多原核生物的必须成分,广泛存在于地质沉积物中^[18]。在植物界,目前仅在茜草科(Rubiaceae)^[11,12]、禾本科(Poaceae)^[19]以及石竹科(Caryophyllaceae)^[20]等少数科属植物中被发现,本文为首次报导荨麻科植物中分离得到乔木萜烷型三萜化合物。

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