

质量浓度下(1 mg/mL),产生类似的抑制效果。

5 结果与讨论

从密蒙花中分离得到并鉴定了11个化合物。其中,化合物Ⅲ(芹菜素-7-O-芸香糖苷),化合物Ⅶ-1、2(cistanoside F a&b),化合物Ⅷ-1、2(campneoside I a&b)和化合物Ⅺ(songaroside A)为首次从该种以及该属(醉鱼草属)中分离得到。得到的皂苷类化合物中,songaroside A具有柴胡皂苷母核。在该属中分离得到过系列具有柴胡皂苷母核的皂苷类物质^[12],该类结构不稳定容易发生变化。比较 mimengoside A 和 songaroside A 的结构可以发现,后者为前者17位氧环开环后的产物。mimengoside A 为密蒙花中的原型皂苷,为该种植物中特征性化合物。

醛糖还原酶抑制活性筛选实验结果表明,密蒙花70%甲醇提取物显示出醛糖还原酶抑制作用,活性成分为其中含有的黄酮类物质(密蒙花苷、木犀草素-7-O-芸香糖苷),以及苯乙醇苷类物质(洋丁香苷、异洋丁香苷)和皂苷类成分(mimengoside B)。黄酮类化合物的醛糖还原酶抑制活性的报道比较多,但是苯乙醇苷类物质和皂苷类物质的相关报道比较少,这几类成分之间是否存在协同作用,还有待于研究。

拓扑异构酶Ⅳ抑制试验结果不仅验证了原有报道中密蒙花的抗菌部分,而且从抑菌机制上发现这些化合物具有环丙沙星类似的作用机制。这提示黄酮和苯乙醇苷类化合物值得深入研究,并通过构效关系的阐明,有望发现新的类型的抗菌物质。

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传社老师在活性测试方面给予的帮助。

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Chemical constituents of *Cladonia stellaris*

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Abstract: **Object** To study the chemical constituents in lichen plant of *Cladonia stellaris*. **Methods** *C. stellaris* was extracted with petroleum ether, separated and purified by column chromatography and preparative TLC on silica gel. All the compounds were identified on the basis of spectral analysis. **Results** Six compounds were obtained. Their structures were characterized as usnic acid (I), evinic acid (II), perlatolic acid (III), olivetoric acid (IV), 2-hydroxyl-4-methoxyl-6-pentyl benzoic acid (V) and 2, 4-dihy-

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droxyl benzoic acid (V), respectively. **Conclusion** Compounds II and IV were isolated from *C. stellaris* for the first time.

Key words: *Cladonia stellaris* (Opiz.) Pouzar. et Vezda; evinic acid; olivetoric acid

太白花化学成分的研究

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摘要:目的 研究地衣植物太白花(又称雀石蕊) *Cladonia stellaris* 的化学成分。方法 太白花经石油醚提取, 采用硅胶柱色谱和硅胶制备 TLC 分离纯化, 波谱分析鉴定结构。结果 从太白花的石油醚部分得到 6 个化合物, 分别鉴定为: 松萝酸(I)、去甲环萝酸(II)、珠光酸(III)、漂红梅衣酸(IV)、2-羟基-4-甲氧基-6-正戊基苯甲酸(V)和 2,4-二羟基-6-正戊基苯甲酸(VI)。结论 化合物 II 和 IV 为首次从太白花中分离得到。

关键词: 太白花; 去甲环萝酸; 漂红梅衣酸

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Cladonia stellaris (Opiz.) Pouzar et Vezda is a kind of important lichen plant. It has been used for medicinal purposes in many countries over the ages in the treatment of pulmonary tuberculosis and as antiviral and antimicrobial agents^[1~3]. Previous phytochemical studies on *C. stellaris* revealed the presence of several plant secondary metabolites, e. g. usnic acid, atranoyin, perlatolic acid, 2-hydroxyl-4-methoxyl-6-pentyl benzoic acid, and 2,4-dihydroxyl-pentyl benzoic acid and so on^[4,5]. In this paper, the isolation and the structural identification of six compounds were reported, they are usnic acid (I), evinic acid (II), perlatolic acid (III), olivetoric acid (IV), 2-hydroxyl-4-methoxyl-6-pentyl benzoic acid (V) and 2,4-dihydroxyl-6-pentyl benzoic acid (VI), of which evinic acid (II) and olivetoric acid (IV) were isolated from this lichen plant for the first time.

1 Experiment

1.1 General: Melting points were determined on a MP-J3 micromelting point apparatus and uncorrected. HR-FAN-MS mass spectra were recorded in an Autospec-3000 instrument, NMR spectra were recorded on a Bruker AM-400 Instrument.

1.2 Plant material: The plant material of *C. stellaris* was collected in Qinling Mountain, Shaanxi Province, China, in August 2001. A voucher specimen was deposited in the Herbarium of Department of Biology, Shaanxi Normal University.

1.3 Extraction and isolation: The air-dried materials (5.0 kg) were powdered and extracted with

petroleum ether (3×25 L). The petroleum ether extract (100 g) was crystallized with CH₃COCH₃ to give yellow needles. Yellow needles were purified by crystallization method using CH₃COCH₃ as solvent to give compound I (40 g). Half of the mother liquor fraction (25 g) was subjected to column chromatography on silic gel (600 g) and eluted with a gradient solvent system from petroleum ether-EtOAc (10:1) to petroleum ether-EtOAc-HCOOH (5:1:0.05) to give fractions II-IV, respectively. Fraction II (1.5 g) was subjected to preparative TLC (CHCl₃-MeOH-HCCOH = 10:0.1:0.05) to give compound I (800 mg), II (10 mg), and III (46 mg), orderly. Fraction III was purified using EtOAc to give compound IV (8 mg). Fraction IV (220 mg) was subjected to preparative TLC (petroleum ether-EtOAc-MeOH = 5:2:0.1) to give compound V (100 mg) and VI (86 mg).

2 Identification

Compound I (usnic acid)^[6]: C₁₈H₁₆O₇, yellow needles, mp 202-204 °C. $[\alpha]_D^{20} = +472.1^\circ$ (c, 0.32, CHCl₃). HR-FAB-MS m/z : 345.0831 [M+H]⁺. EI-MS (70 eV) m/z : 344 [M]⁺, 260, 233, 217, 149, 83, 69, 55, 43. ¹H-NMR (400 MHz, CDCl₃) δ : 18.81 (1H, s, OH-3), 13.30 (1H, s, OH-7), 11.02 (1H, s, OH-9), 5.97 (1H, s, H-4), 2.67 (3H, s, COCH₃-6), 2.65 (3H, s, COCH₃-2), 2.10 (3H, s, CH₃-8), 1.75 (3H, s, CH₃-9b). ¹³C-NMR (100 MHz) δ : 198.03 s (C-1), 105.21 s (C-2), 201.73 s (COCH₃-2),

27.84 q (COCH₃-2), 191.68 s (C-3), 98.30 d (C-4), 179.33 s (C-4a), 101.50 s (C-6), 200.28 s (COCH₃-6), 31.22 q (COCH₃-6), 155.21 s (C-6a), 163.86 s (C-7), 109.29 s (C-8), 7.54 q (CH₃-8), 157.48 s (C-9), 103.92 s (C-9a), 59.05 s (C-9b), 32.09 q (CH₃-9b).

Compound II (evinic acid)^[7]: C₁₇H₁₆O₇, colorless needles, mp 169–170 °C. HR-FAB-MS *m/z*: 332.091 2 [M+H]⁺. EI-MS (70 eV) *m/z*: 332

[M]⁺, 314 [M-H₂O]⁺, 182, 168, 165, 150, 136, 122. ¹H-NMR (400 MHz, CDCl₃) δ: 11.35 (1H, s, OH-2), 11.30 (1H, s, OH-2'), 6.74 (1H, d, *J*=2.4 Hz, H-5'), 6.63 (1H, d, *J*=2.4 Hz, H-3'), 6.39 (1H, d, *J*=2.4 Hz, H-3), 6.36 (1H, d, *J*=2.4 Hz, H-5), 2.10 (2×3H, s, 2×ArCH₃). ¹³C-NMR (100 MHz) spectral data are seen in Table 1.

Compound III (perlatolic acid)^[8]: C₂₅H₃₂O₇,

Table 1 ¹³C-NMR data for compounds II–VI

Atom	II	III	IV	V	VI
C-1	108.68	108.94	104.70	103.22	103.52
C-2	166.05	166.55	168.01	166.65	167.05
C-3	98.67	99.02	101.01	98.84	100.44
C-4	165.44	165.25	166.03	164.94	159.98
C-5	109.22	108.68	113.24	111.12	113.08
C-6	149.65	149.97	141.93	149.58	149.96
C-7	169.59	169.40	170.00	175.14	175.22
C-1'	110.97	111.44	111.43		
C-2'	164.83	164.92	165.56		
C-3'	103.52	103.63	103.80		
C-4'	154.90	154.96	154.39		
C-5'	116.08	116.13	116.14		
C-6'	147.91	148.44	149.06		
C-7'	174.42	174.94	174.80		
R ₁	20.12	37.21 30.87 13.98	32.01 22.56 14.00	52.09 31.59 14.00	208.11 23.75 31.83
R ₂	20.04	36.50 29.69 13.98	31.91 22.42 22.40	36.46 14.02	29.66
R ₃	56.00	55.40		55.36	

colorless needles, mp 118–120 °C. HR-FAB-MS *m/z*: 445.215 5 [M+H]⁺. EI-MS (70 eV) *m/z*: 426 [M-H₂O]⁺, 238, 224, 220, 206, 182, 164, 150, 135. ¹H-NMR (400 MHz, CDCl₃) δ: 11.37 (1H, s, OH-2), 11.30 (1H, s, OH-2'), 6.77 (1H, d, *J*=2.4 Hz, H-5'), 6.65 (1H, d, *J*=2.4 Hz, H-3'), 6.41 (1H, d, *J*=2.4 Hz, H-3), 6.38 (1H, d, *J*=2.4 Hz, H-5), 3.02, 2.98 (2×2H, t, *J*=8 Hz, 2×ArCH₂), 1.65 (4H, m, 2×ArCH₂CH₂), 1.35 (8H, m, 2×Ar(CH₂)₂-CH₂CH₂), 0.91, 0.85 (2×3H, t, *J*=7.3 Hz, 2×Ar(CH₂)₄CH₃). ¹³C-NMR (100 MHz) spectral data are seen in Table 1.

Compound IV (olivetic acid)^[8]: C₂₆H₃₂O₈, white powder, mp 147–148 °C. HR-FAB-MS *m/z*: 473.204 8 [M+H]⁺. EI-MS (70 eV) *m/z*: 249, 224, 206, 192, 177, 169, 150, 135, 124,

121. ¹H-NMR (400 MHz, CDCl₃) δ: 11.29 (3H, brs, 3×OH), 7.09 (1H, s, H-5'), 6.82 (2H, s, H-3', H-5), 6.80 (1H, s, H-3), 4.08 (2H, s, ArCH₂CO), 2.73 (2H, t, *J*=7.8 Hz, ArCH₂), 2.41 (4H, t, ArCH₂CH₂CH₂CH₂Ar), 1.20 (4H, m, 2×ArCH₂COCH₂CH₂CH₂CH₂), 0.89 (3H, t, *J*=7.0 Hz, Ar(CH₂)₄CH₃), 0.85 (3H, t, *J*=7.0 Hz, ArCH₂CO(CH₂)₄CH₃). ¹³C-NMR (100 MHz) spectral data are seen in Table 1.

Compound V (2-hydroxyl-4-methoxyl-6-pentyl benzoic acid)^[5,8]: C₁₃H₁₈O₄, colorless needles, 6.37 mp 102–104 °C. HR-FAB-MS *m/z*: 239.104 7 [M+H]⁺. EI-MS (70 eV) *m/z*: 238 [M]⁺, 220 [M-H₂O]⁺, 192 [220-CO], 182, 164, 138, 135. ¹H-NMR (400 MHz, CDCl₃) δ: 11.59 (1H, s, OH), 6.37, 6.35 (2H, s, H-3, H-5), 3.84 (3H, s, OCH₃), 2.94 (2H, t, *J*=8 Hz,

ArCH₂), 1.62 (2H, m, ArCH₂CH₂), 1.35 (4H, m, Ar(CH₂)₂CH₂CH₂), 0.91 (3H, t, $J=7.0$ Hz, Ar(CH₂)₄CH₃). ¹³C-NMR (100 MHz) spectral data are seen in Table 1.

Compound VI (2, 4-dihydroxyl-6-pentyl benzoic acid)^[5,8]: C₁₂H₁₆O₄, white powder, mp 114–116 °C. HR-FAB-MS m/z : 225.115 2 [M+H]⁺. EI-MS (70 eV) m/z : 224 [M]⁺, 206 [M–H₂O]⁺, 178 [206–CO], 168, 163, 150, 135, 122. ¹H-NMR (400 MHz, CDCl₃) δ : 10.30 (2H, brs, 2×OH), 6.21, 6.33 (2H, s, H-3, H-5), 2.92 (2H, t, $J=8$ Hz, ArCH₂), 1.61 (2H, m, ArCH₂CH₂), 1.35 (4H, m, Ar(CH₂)₂CH₂CH₂), 0.88 (3H, t, $J=7.0$ Hz, Ar(CH₂)₄CH₃). ¹³C-NMR (100 MHz) spectral data are seen in Table 1.

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当归与日本当归挥发油中化学组份的比较

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当归与日本当归均为伞形科当归属植物, 当归为 *Angelica sinensis* (Oliver) Diels 的干燥根茎, 日本当归为东当归 *A. acutiloba* (Sieb. et Zucc.) Kitag 的干燥根茎。

国产当归有秦归、云归、川归之分, 传统认为栽培在甘肃岷县海拔2 000 m以上者质量最佳, 称为道地药材。如果生长在海拔低于1 700 m以下, 质量就难以达到优质标准, 这是目前当归次品较多的主要原因。日本当归主产于日本, 早在20世纪70年代, 此种就在中国吉林省延吉市引种成功, 朝鲜族常用, 并称之为东当归^[1]。为便于区别与论述, 本实验称之为和当归, 因为是日本原产药材, 即不能混称当归, 也不宜用东当归, 应按日本民族的俗称较为妥当。国产当归和日本当归(和当归)分别被《中华人民共和国药典》^[2]和《日本药局方》^[3]收载。值得特别提出的是《日本药局方》规定: 和当归具有补血调经、活血止痛、润肠通便的作用, 与中国当归的功能主治相一致, 并且与其他中药一样, 作为汉方制剂中的原

料, 制成制剂, 销往本国及世界各地, 这就是目前洋中药大量在我国市场上销售, 导致中药贸易逆差的主要原因之一。但中日两国所用的方剂相同, 而配伍的药材确是两种同属不同种的药材, 故有必要与国产当归进行研究比较。

当归含有挥发油、阿魏酸、棕榈酸等多种化学成分^[4]。其中挥发油是有效成分之一, 具有镇静大脑、兴奋和麻痹延髓中枢的作用, 并可弛缓子宫肌肉。临床用于治疗月经不调、痛经等症^[5]。但由于当归挥发油含有较多的脂肪酸类成分, 给分离鉴定带来较多困难, 在以往的报道中所分离的成分不过40种^[6]。本实验采用气相色谱—质谱—计算机联用的方法, 分别对秦当归、云当归、和当归中挥发油成分进行分析比较; 将所得质谱图与标准图对照共鉴定64个化合物。

1 实验部分

1.1 样品来源: 所用生药样品分别采集或购自的产地见表1。各样品经本所胡世林研究员鉴定。