

五花血藤化学成分的研究

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摘要: 目的 对五花血藤(*Sargentodoxa cuneata*)的藤茎部分进行化学成分研究。方法 五花血藤藤茎的 95% 乙醇提取物加水溶解后, 分别用石油醚、醋酸乙酯和正丁醇萃取。正丁醇萃取物应用多种色谱柱及仪器进行分离纯化, 并运用理化性质、核磁数据和光谱学数据等方法鉴定化合物的结构。结果 从五花血藤藤茎中分离鉴定了 12 个化合物, 分别为: 毛柳苷(1)、3,4-二羟基苯乙醇葡萄糖苷(2)、N-(对羟基苯乙基)阿魏酸酰胺(3)、eugenyl β -rutinoside(4)、原绿酸(5)、齐墩果酸(6)、(-)-表儿茶素(7)、2-苯乙基- β -D-呋喃芹糖基-(1''-6')- β -D-吡喃葡萄糖苷(8)、 β -谷甾醇(9)、胡萝卜苷(10)、3,4-二羟基苯乙醇(11)、豆甾醇(12)。结论 化合物 5、6、11 为首次从该植物中分离得到。

关键词: 五花血藤; 毛柳苷; 3,4-二羟基苯乙醇葡萄糖苷; 齐墩果酸; β -谷甾醇

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五花血藤又名大血藤、血藤、红皮藤、千年健、大活血、红藤、活血藤、血灌肠、大血通、五花血通、红血藤等。系木通科植物五花血藤 *Sargentodoxa cuneata* (Oliv.) Rehd. Et Wils. 的茎。生于山坡疏林、溪边; 有栽培。主产于湖北、四川、江西、河南、江苏; 安徽、浙江亦产。其藤茎具有清热解毒、活血通经及祛风湿等功效, 用以治疗肠痈痛经、跌打扑痛。在近几十年的临床应用中, 五花血藤主要与其它中草药配伍, 用于治疗盆腔炎、子宫内膜异位症、阑尾脓肿等疾病, 据文献报道, 在民间五花血藤用于治疗骨癌, 并具有抗肿瘤活性。本实验从五花血藤 95% 乙醇提取物的正丁醇层和乙酸乙酯萃取物中分离得到 5 个化合物, 分别鉴定为: 毛柳苷(1)、3,4-二羟基苯乙醇葡萄糖苷(2)、N-(对羟基苯乙基)阿魏酸酰胺(3)、eugenyl β -rutinoside(4)、原绿酸(5)、齐墩果酸。研究表明, 化合物 5 为首次从该化合物中分离得到。

1 仪器与材料

德国 Bruker Avance III 600 MHz 核磁共振仪 (TMS 为内标, δ 为 ppm, J 为 Hz); 高分辨傅里叶变

换离子回旋质谱仪 (布鲁克/德国); 中压制备系统 (瑞典 Biotage 公司); 循环半制备色谱仪 (日本岛津公司); Polarimeter Type AA-55 型数字式旋光仪; Sephadex LH-20 (Pharmacia 公司产品); C18 反相填料 (北京慧得易科技有限责任公司分装); 薄层色谱和正相柱色谱硅胶 (青岛海洋化工); 薄层硅胶 GF254 (烟台市化学工业研究所); 石油醚、氯仿、丙酮、乙酸乙酯、甲醇等有机溶剂均为工业纯经重蒸后使用。

五花血藤 *Sargentodoxa cuneata* 样品来自于中国科学院昆明植物研究所。

2 提取和分离

取五花血藤颈部切片药材 (5kg), 用 95% 的乙醇加热回流提取 3 次, 每次 2h。滤过合并滤液, 减压浓缩至浸膏状。加水 (约 1L) 溶解后, 分别用石油醚、醋酸乙酯和正丁醇萃取。石油醚、乙酸乙酯和正丁醇层萃取物浸膏分别约为 37.7g, 26.6g, 183.4g。其中正丁醇萃取部分经硅胶柱色谱分离 (石油醚-丙酮, 氯仿-甲醇系统梯度洗脱), 粗分为 10 个馏分。选取其中第 4 馏分再经硅胶柱色谱分离 (石油醚/乙酸乙酯: 1:6),

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得到 4 个馏分。对第 3 个馏分使用 Sephadex LH-20 柱色谱分离,中压液相柱色谱分离,SFC 柱色谱分离(SFC)柱色谱分离,HPLC 分离,重结晶等方法分离纯化,分别得到毛柳苷(1)、3,4-二羟基苯乙醇葡萄糖苷(2)、N-(对羟基苯乙基)阿魏酸酰胺(3)、eugenyl β -rutinoside(4)、原绿酸(5)。

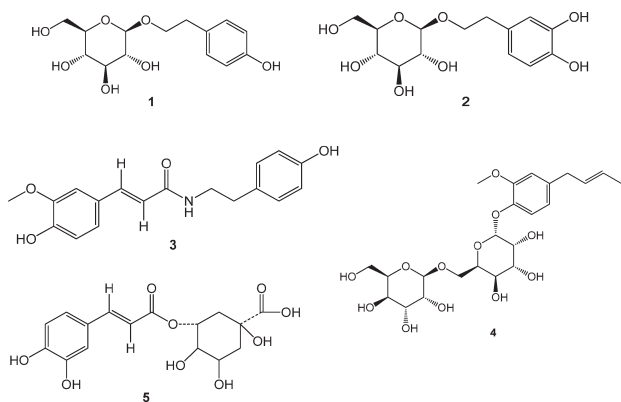


图 1 化合物 1-5 的化学结构

3 结构鉴定

化合物 1 白色粉末($C_{14}H_{20}O_7$);UV(H_2O) λ_{max} (log ϵ):203 (4.23),280 (3.31);IR (KBr) ν_{max} :3380 (OH), 2929, 2882, 1613, 1517, 1450, 1374, 1236, 1163, 1077 (C-O), 830, 633, 552;ESI-MS m/z :299.2 [M-H]⁻,323.2 [M+Na]⁺; ¹H-NMR(CD_3OD ,600MHz) δ :7.08 (2H,d, J =8.4Hz,H-2,6),6.70~6.75 (2H,m,H-3,5),2.80~2.90 (2H,m,H-7),3.67~3.75 (2H,m,H-8),4.32 (1H,d, J =8.0Hz,H-1'-Glc),3.19~3.24 (1H,m,H-2'),3.29 (1H,ddd, J =3.1,5.8,9.6Hz,H-3'),3.32~3.35 (1H,m,H-4'),4.05 (1H,td, J =6.9,8.8Hz,H-5'),3.89 (1H,dd, J =1.9,11.9Hz,H-6'); ¹³C-NMR(CD_3OD ,151Hz) δ :155.3(C-1),114.8(C-2,6),129.4(C-3,5),129.6(C-4),35.0(C-7),70.7(C-8),102.9(C-1'-Glc),73.7(C-2'),76.5(C-3'),70.2(C-4'),76.6(C-5'),61.3(C-6')以上数据与文献报道[1]一致,故鉴定化合物 1 为毛柳苷。

化合物 2 白色粉末($C_{14}H_{20}O_8$);UV(H_2O) λ_{max} (log ϵ):220 (4.48),280 (4.06);IR (KBr) ν_{max} :3379 (OH), 2926, 1610, 1523, 1449, 1372, 1282, 1077, 1030 (C-O), 632;ESI-MS(m/z):334[M+H₂O]⁺,339[M+Na]⁺,335[M+H₂O+H]⁺; ¹H-NMR(CD_3OD ,600MHz) δ :6.71 (1H,d, J =1.9Hz,H-2),6.69 (1H,d,

J =8.0Hz,H-5), 6.57 (1H,dd, J =1.9,8.0Hz,H-6), 4.04 (1H,td, J =6.8,8.8Hz,H-8),3.66~3.74 (2H,m,H-8),2.76~2.85 (2H,m,H-7),4.31 (1H,d, J =7.8,H-1'-Glc),3.88 (1H,dd, J =1.9,11.9Hz,H-6-Glc),3.30~3.37 (2H,overlap,H-2,3-Glc), 3.28 (1H,dd, J =1.8,5.4Hz,H-5-Glc),3.20 (1H,dd, J =8.0,9.0Hz,H-4-Glc); ¹³C-NMR(CD_3OD ,151MHz) δ :130.1(C-1),114.8(C-2),144.7(C-3),143.2(C-4),115.7(C-5),119.8(C-6),70.6(C-8),35.2(C-7),103.0(C-1'-Glc),73.7(C-2'),76.5(C-3'),70.2(C-4'),76.6(C-5'),61.3(C-6')。以上数据与文献报道[2-3]一致,故鉴定化合物 52 为 3,4-二羟基苯乙醇葡萄糖苷。

化合物 3 无色针晶($C_{18}H_{19}O_{14}N$);UV(MeOH) λ_{max} (log ϵ):221 (3.31),285 (3.16),320 (3.27);IR (KBr) ν_{max} :3264 (OH),3016,2934,1651 (C=O),1592,1513,1450,1425,1253,1004 (C-O),820,766,574;ESI-MS m/z :472.1 [M-H]⁻,496.2 [M+Na]⁺; ¹H-NMR(CD_3OD ,600MHz) δ :7.11 (1H,d, J =1.5Hz,H-2), 7.02 (1H,dd, J =1.6,8.2Hz,H-6), 6.80 (1H,d, J =8.1Hz,H-5),7.45 (1H,d, J =15.7Hz,H-7),6.42 (1H,d, J =15.7Hz,H-8),7.05 (2H,d, J =8.4Hz,H-2',6'), 6.73 (2H,d, J =8.4Hz,H-3'',5'), 2.75 (2H,t, J =7.4Hz,H-7'), 3.47 (2H,d, J =7.4Hz,H-8'), 3.87 (3H,s,-OMe); ¹³C-NMR(CD_3OD ,151MHz) δ :126.7(C-1),110.1(C-2),147.6(C-3),148.2(C-4),114.7(C-5),121.6(C-6),140.5(C-7),117.3(C-8),167.8(C-9),129.7(C-1'),129.3(C-2',6'),115.0(C-3',5'),155.3(C-4'),34.3(C-7'),41.1(C-8'),55.3(-OMe)。以上数据与文献报道[4]一致,故鉴定化合物 3 为 N-(对羟基苯乙基)阿魏酸酰胺。

化合物 4 无定形粉末($C_{23}H_{34}O_{12}$);ESI-MS m/z :495[M+Na]⁺; ¹H-NMR(CD_3OD ,600MHz) δ :6.83 (1H,brs,H-3),6.75 (1H,d, J =8.2Hz,H-5),7.05 (1H,d, J =8.2Hz,H-6),3.34 (2H,m,H-7),5.96 (1H,m,H-8), 5.04 (2H,t, J =16.9,6.2Hz,H-9), 4.08 (1H,d, J =7.6Hz,H-1'), 3.48 (1H,m,H-2'), 3.47 (1H,m,H-3'), 3.38 (1H,m,H-4'), 3.34 (1H,m,H-5'), 3.99 (1H,d, J =10.4Hz,H-6'), 3.60 (1H,d,H-6'), 4.70 (1H,brs,H-1'), 3.81 (1H,m,H-2''), 3.68 (1H,m,H-3''), 3.34 (1H,m,H-4''), 3.64 (1H,dd, J =

6.4, 9.6 Hz, H-5''), 1.20 (3H, d, $J=6.0$ Hz, H-6''); ^{13}C -NMR (CD_3OD , 151 MHz) δ : 144.9 (C-1), 149.6 (C-2), 114.4 (C-3), 135.3 (C-4), 120.8 (C-5), 117.2 (C-6), 39.3 (C-7), 137.6 (C-8), 113.0 (C-9), 16.5 (C-10), 101.8 (C-1'), 100.8 (C-1''), 73.6 (C-2'), 75.6 (C-3'), 70.8 (C-4'), 76.6 (C-5'), 66.4 (C-6'), 71.0 (C-2''), 72.7 (C-3''), 73.6 (C-4''), 68.4 (C-5''), 62.9 (C-6''), 55.4 (-OCH₃)。以上数据与文献[5]报道的一致,故鉴定该化合物 4 为 eugenyl β -rutinoside。

化合物 5 淡黄色粉末 ($\text{C}_{16}\text{H}_{18}\text{O}_9$); ESI-MS (m/z): 354 $[\text{M}+\text{H}_2\text{O}]^+$; UV (MeOH) λ_{max} ($\log \epsilon$): 218 (4.09), 245 (3.94), 296 (4.03), 329 (4.17); IR (KBr) ν_{max} : 3393 (OH), 2956, 1733 (C=O), 1693 (C=O), 1632 (C=C), 1600, 1520, 1445, 1276, 1180, 1110, 1080, 1002 (C-O), 813, 773, 605; ^1H -NMR (CD_3OD , 600 MHz) δ : 7.03 (1H, d, $J=1.9$ Hz, H-2), 6.77 (1H, d, $J=8.1$ Hz, H-5), 6.90 (1H, dd, $J=1.9, 8.0$ Hz, H-6), 7.50 (1H, d, $J=15.6$ Hz, H-7), 6.01 (1H, d, $J=15.6$ Hz, H-8), 2.18 (2H, m, H-2'), 5.25 (1H, m, H-3'), 3.70 (1H, dd, $J=2.9, 7.2$ Hz, H-4'), 4.10 (1H, m, H-5'), 2.09 (1H, m, H-6'), 2.20 (1H, m, H-6'); ^{13}C -NMR (CD_3OD , 151 MHz) δ : 127.3 (C-1), 115.0 (C-2), 147.1 (C-3), 149.5 (C-4), 116.3 (C-5), 123.0 (C-6), 146.8 (C-7), 114.9 (C-8), 168.1 (C-9), 75.6 (C-1'), 38.0 (C-2'), 72.0 (C-3'), 72.4 (C-4'), 70.2 (C-5'), 37.9 (C-6'), 175.3 (-COOH)。以上数据与文献报道[6-8]一致,故

鉴定化合物 5 为原绿酸。

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Study on the Chemical Constituents of *Sargentodoxa cuneata*

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ABSTRACT: **Objective** To study the chemical constituents of *Sargentodoxa cuneata*. **Methods** *Sargentodoxa cuneata* was extracted with 95% ethanol, and the extract was extracted with petroleum ether, ethyl acetate, n-butanol alcohol respectively. The compounds of n-butyl alcohol extract were isolated by various columns and instruments, and were identified through the use of physical and chemical properties, NMR data and spectroscopy data. **Results** Twelve compounds were isolated, and identified as salidroside (1), 3, 4-dihydroxy-phenethyl- β -D-glucopyranoside (2), 7-(4-hydroxy-3-methoxyphenyl)-N-[7'-(4'-hydroxyphenyl)ethyl]-(E)-8-propenamide (3), eugenyl β -rutinoside (4), Chlorogenic acid (5), oleanolic acid (6), (-)-epicatechin (7), 2-Phenylethyl- β -D-apiofuranosyl-(1'' $\rightarrow$ 6')- β -D-glucopyranoside (8), β -sitosterol (9), daucosterol (10), 3, 4-dihydroxy-benzaldehyde (11), stigasterol (12). **Conclusion** Chlorogenic acid, oleanolic acid, 3, 4-dihydroxy-benzaldehyde were the first cerebrosides isolated from *Sargentodoxa cuneata*.

KEY WORDS: *Sargentodoxa cuneata*; salidroside; 3, 4-dihydroxy-phenethyl- β -D-glucopyranoside; oleanolic acid; β -sitosterol