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四合木化学成分的分离与鉴定

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摘　要:为了明确四合木乙醇提取物的化学成分,采用硅胶柱色谱对四合木乙醇提取物进行分离,然后经核磁共振数据鉴定其结构式。分离鉴定了 8 个化合物,分别为 3,4-二羟基苯甲醛(**1**),儿茶素(**2**)、表没食子儿茶素(**3**)、没食子儿茶素(**4**),3β-咖啡酰基-古柯二醇(**5**),roseosid (**6**),槲皮素(**7**),槲皮素-3-*O*-β-D-葡萄糖苷(**8**)。化合物 **1** ~ **8** 为首次该植物中分得。

关键词:四合木;化学成分;分离;鉴定

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Isolation and Identification of Chemical Constituents from *Tetraena Mongolica* Maxim

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Abstract: For researching the chemical constituents of the CH_3CH_2OH extracts from *Tetraena mongolica* Maxim, the silica gel column chromatography was used to isolate the chemical constituents of *Tetraena mongolica* Maxim. The obtained compounds were characterized by NMR data to identify their structure. Eight conpounds were obtained and identified the CH_3CH_2OH extracts from *Tetraena mongolica* Maxim, namely 3,4-dihydroxy benzaldehyde (**1**), catechin (**2**), gallocatechin (**3**), epigallocatechin (**4**), 3β-caffeoyl-erythrodiol (**5**), roseosid (**6**), quercetin (**7**), quercetin-3-*O*-β-D-glucoside (**8**). Compounds **1-8** were isolated from this plant for the first time.

Key words: *Tetraena mongolica* Maxim.; chemical constituents; isolation; identification

四合木(*Tetraena mongolica* Maxim)系蒺藜科四合木属强旱生落叶小灌木,是中国特有孑遗单种属植物,草原化荒漠的群种之一[1]。其主要分布于内蒙古鄂尔多斯,是国家二级保护植物、内蒙一级保护植物,不仅在维持荒漠生态系统的功能方面有重要的作用,而且对于研究环境演化、植物区系、生物进化、生物多样性和全球变化等有着重大的学术价值和诊断意义。现代研究[2,3]表明,四合木甲醇提取物具有较强的杀线虫活性,并其中分离得到化合物有黄酮、三萜、甾体、酚类及有机酸[4-7]。四合木由于繁殖速度缓慢、羊的啃吃、当地居民的砍伐及环境污染而面临着濒危。为了该植物生源地的保护、栽培及合理利用提供有力依据,本实验所用四合木采集于内蒙古鄂尔多斯鄂多克旗,并对其乙醇提取物进行了全面系统的研究,从中分离得到 20 个化合物,其中 8 个为首次从该植物分离得到。本文报道 8 个首分化合物的结构信息。

1　实验材料

Bruker AVAIVCE Ⅲ—500 型核磁共振谱仪(布鲁克公司);氘代试剂为 Cambridge Isotope Laboratories, InC;日本岛津液相色谱仪(LC-20Ap 输液泵,SPD—20AP 检测器,CBM-20A 工作站);AUW220D 型电子天平(日本岛津);HH-S26S 型水浴锅(金坛市大地自动化仪器厂);RE52-2 型旋转蒸发器(上海泸西分析仪器厂);KQ-100 型系列超声波冲洗器(昆山市超声仪器有限公司);硅胶(青岛海洋化工厂,200 ~ 300 目);柱色谱试剂均为分析纯。四合木采集于内蒙古鄂尔多斯,由内蒙古民族大学蒙医药学院蒙药生药学教研室主任布和巴特尔教授鉴定为蒺藜科四合木属四合木 *Tetraena mongolica* Maxim 的地上部分。四合木标本(No. 20140722)保存于内蒙

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2 提取与分离

四合木 1.0 kg,加 95% 乙醇(10 L)回流提取 3 次,每次 3 h。合并提取液回收乙醇,加水适量,搅拌成混悬液,依次用石油醚、氯仿、乙酸乙酯和正丁醇萃取。氯仿萃取物 12 g,加少量硅胶拌样,晾干后上硅胶色谱柱,依次用不同比例氯仿和丙酮混合液洗脱,分离得到化合物 **1** (12 mg),**2** (9 mg),**3** (18 mg)和 **4** (27 mg);乙酸乙酯萃取物 20 g,加少量硅胶拌样,晾干后上硅胶色谱柱,依次用不同比例氯仿和甲醇混合液洗脱,分离得到化合物 **5** (21 mg),**6** (18 mg),**7** (10 mg)和 **8** (14 mg)。

3 结构鉴定

化合物 1 白色结晶(氯仿);mp:125 ~ 128 ℃,易溶于石油醚、氯仿等亲脂性有机溶剂。^{1}H NMR ($CDCl_3$, 500 MHz) δ (H):9.71 (1H, s),7.32 (1H, dd, J = 7.5, 1.5 Hz),7.33 (1H, d, J = 1.5 Hz),6.94 (1H, d, J = 7.5 Hz);^{13}C NMR ($CDCl_3$, 125 MHz) δ (C):129.4 (C-1),113.9 (C-2),145.8 (C-3),152.3 (C-4),114.8 (C-5),125.0 (C-6),-CHO (191.7)。以上数据并与文献[8]报告 3,4-二羟基苯甲醛的一致。

化合物 2 浅黄色胶状固体(甲醇);mp:175 ~ 178 ℃,易溶于氯仿、乙酸乙酯等有机溶剂。^{1}H NMR ($CDCl_3$, 500 MHz) δ (H):5.97 (1H, d, J = 1.5 Hz, H-6),5.89 (1H, d, J = 1.5 Hz, H-8),6.87 (1H, d, J = 1.5 Hz, H-2′),6.79 (1H, d, J = 8.0 Hz, H-5′),6.75 (1H, dd, J = 8.0, 1.5 Hz, H-6′),4.60 (1H, d, J = 7.5 Hz, H-2),4.01 (1H, dd, J = 8.0, 7.5 Hz, H-3),2.87 (1H, dd, J = 16.5, 5.0 Hz, H-4a),2.55 (1H, dd, J = 16.5, 8.0 Hz, H-4b);^{13}C NMR ($CDCl_3$, 125 MHz) δ (C):80.6 (C-2),66.6 (C-3),26.3 (C-4),154.7 (C-5),94.2 (C-6),155.6 (C-7),93.4 (C-8),155.4 (C-9),98.7 (C-10),130.0 (C-1′),113.1 (C-2′),144.1 (C-3′),144.0 (C-4′),113.9 (C-5′),117.9 (C-6′)。以上数据与文献报道一致[9,10],故鉴定化合物 **2** 为儿茶素。

化合物 3 浅黄色胶状固体;mp:208 ~ 211 ℃,易溶于氯仿、乙酸乙酯等有机溶剂。^{1}H NMR ($CDCl_3$, 500 MHz) δ (H):5.98 (1H, s, H-6),5.91 (1H, s, H-8),6.45 (2H, s, H-2′,6′),4.60 (1H, brs, H-2),4.15 (1H, brs, H-3),2.86 (1H, dd, J = 16.0, 4.0 Hz, H-4a),2.58 (1H, dd, J = 16.0, 2.0 Hz, H-4b);^{13}C NMR ($CDCl_3$, 125 MHz) δ (C):78.4 (C-2),66.2 (C-3),27.8 (C-4),155.4 (C-5),95.2 (C-6),156.5 (C-7),94.7 (C-8),155.9 (C-9),99.6 (C-10),130.2 (C-1′),105.8 (C-2′, 6′),145.3 (C-3′,5′),132.2 (C-4′)。以上数据与文献报道一致[9-10],故鉴定化合物 **3** 为表没食子儿茶素。

化合物 4 浅黄色胶状固体;mp:197 ~ 201 ℃,易溶于氯仿、乙酸乙酯等有机溶剂。^{1}H NMR ($CDCl_3$, 500 MHz) δ (H):5.96 (1H, s, H-6),5.91 (1H, s, H-8),6.57 (2H, s, H-2′,6′),4.63 (1H, d, J = 7.0 Hz, H-2),4.03 (1H, dd, J = 8.0, 7.0 Hz, H-3),2.85 (1H, dd, J = 16.0, 4.5 Hz, H-4a),2.54 (1H, dd, J = 16.0, 8.0 Hz, H-4b);^{13}C NMR ($CDCl_3$, 125 MHz) δ (C):81.4 (C-2),67.4 (C-3),26.6 (C-4),155.5 (C-5),95.1 (C-6),156.6 (C-7),94.3 (C-8),156.0 (C-9),99.5 (C-10),130.2 (C-1′),105.9 (C-2′,6′),145.5 (C-3′,5′),132.6 (C-4′)。以上数据与文献报道一致[9-10],故鉴定化合物 **4** 为没食子儿茶素。

化合物 5 白色无定形粉末(氯仿);mp:268 ~ 271 ℃,易溶于石油醚、氯仿等亲脂性有机溶剂。^{1}H NMR ($CDCl_3$, 500 MHz) δ (H):0.89 (3H, s, CH_3-30),0.91 (3H, s, CH_3-29),1.19 (3H, s, CH_3-27),0.96 (3H, s, H-26),0.95 (3H, s, CH_3-25),0.81 (3H, s, CH_3-24),1.02 (3H, s, CH_3-23),7.46 (1H, d, J = 16.0 Hz, H-7′),6.25 (1H, d, J = 16.0 Hz, H-8′),7.05 (1H, d, J = 2.0 Hz, H-2′),6.76 (1H, d, J = 8.0 Hz, H-5′),6.99 (1H, dd, J = 8.0, 2.0 Hz, H-6′);^{13}C NMR ($CDCl_3$, 125 MHz) δ (C):38.2 (C-1),23.8 (C-2),80.2 (C-3),37.9 (C-4),54.9 (C-5),18.3 (C-6),32.5 (C-7),39.9 (C-8),47.3 (C-9),36.8 (C-10),23.5 (C-11),121.8 (C-12),144.9 (C-13),41.7 (C-14),25.6 (C-15),22.1 (C-16),36.9 (C-17),42.3 (C-18),34.3 (C-19),31.2 (C-20),46.8 (C-21),31.4 (C-22),28.3 (C-23),16.9 (C-24),15.7 (C-25),17.2 (C-26),26.1 (C-27),69.77.9 (C-28),33.5 (C-29),24.0 (C-30),125.9 (C-1′),115.3 (C-2′),148.8 (C-3′),146.0 (C-4′),116.2 (C-5′),121.7 (C-6′),145.3 (C-7′),114.9 (C-8′),166.8 (C-9′)。以上数据并与文献[11,12]报告的 3β-咖啡酰基-古柯二醇一致。

化合物 6 白色针状结晶(甲醇);mp:168 ~ 170 ℃,易溶于甲醇、乙醇和乙酸乙酯等有机溶剂。^{1}H NMR (MeOD,500 MHz) δ (H):1.06 (3H,s,CH_3-3),1.05 (3H,s,CH_3-3),1.94 (3H,s,CH_3-5),2.54 (1H,d,*J* = 17.0 Hz,H-2a),2.16 (1H,d,*J* = 17.0 Hz,H-2b),5.89 (1H,s,H-6),4.36 (1H,d,*J* =7.5 Hz,H-1′),3.38 (1H,m,H-2′),3.19 (1H,t,*J* =8.0 Hz,H-3′),3.28 (1H,m,H-4′),3.25 (1H,m,H-5′),3.98 (1H,d,*J* = 7.5 Hz,H-6′a),3.65 (1H,m,H-6′b);^{13}C NMR (MeOD,125 MHz) δ (C):199.8 (C-1),49.2 (C-2),41.0 (C-3),78.6 (C-4),165.8 (C-5),125.8 (C-6),130.1 (C-7),133.9 (C-8),19.8 (C-9),22.0 (2-CH_3),23.3 (2-CH_3),18.2 (5-CH_3),101.3 (C-1′),76.6 (C-2′),73.8 (C-3′),70.2 (C-4′),76.7 (C-5′),61.4 (C-6′)。以上数据并与文献[13]报告的 roseosid 一致。

化合物 7 黄色针状结晶(甲醇);mp:313 ~ 315 ℃,易溶于甲醇、乙醇等有机溶剂。^{1}H NMR (MeOD,500 MHz) δ (H):6.07(1H,d,*J* = 2.0 Hz,H-6),6.28 (1H,d, *J* = 2.0 Hz,H-8),7.62 (1H,d,*J* = 2.0 Hz,H-2′),6.78 (1H,d,*J* = 8.5 Hz,H-5′),7.53 (1H,dd,*J* = 8.5 Hz,*J* = 2.0 Hz,H-6′);^{13}C NMR (MeOD,125 MHz) δ (C):157.2 (C-2),135.2 (C-3),175.2 (C-4),161.5 (C-5),96.3 (C-6),163.4 (C-7),95.6(C-8),155.9 (C-9),104.4 (C-10),130.2 (C-1′),113.4 (C-2′),144.3 (C-3′),145.2 (C-4′) 115.4 (C-5′),124.5 (C-6′)。以上数据与文献[14]基本一致,鉴定为槲皮素。

化合物 8 黄色粉末(甲醇);mp:326 ~ 329 ℃,易溶于甲醇、乙醇等有机溶剂。^{1}H NMR (MeOD,500 MHz) δ (H):δ 6.19 (1H,d,*J* = 2.0 Hz,H-6),6.38 (1H,d,*J* = 2.0 Hz,H-8),7.73 (1H,d,*J* = 2.0Hz,H-2′),6.88 (1H,d,*J* = 8.5 Hz,H-5′),7.60 (1H,dd,*J* = 8.5,2.0 Hz,H-6′),5.12 (1H,d,*J* = 7.5 Hz,H-1″),3.33 (1H,m,H-2″),3.15 (1H,t,*J* =8.0 Hz,H-3″),3.31 (1H,m,H-4″),3.27 (1H,m,H-5″),4.02 (1H,d,*J* = 7.5 Hz,H-6″a),3.78 (1H,m,H-6″b);^{13}C NMR (MeOD,125 MHz) δ (C):157.0 (C-2),134.2 (C-3),178.0 (C-4),161.6 (C-5),98.5 (C-6),164.6 (C-7),93.3 (C-8),157.6 (C-9),104.3 (C-10),121.7 (C-1′),114.6 (C-2′),144.5 (C-3′),148.4 (C-4′),116.2 (C-5′),121.8 (C-6′),102.9 (C-1″),76.7 (C-2″),74.3 (C-3″),69.8 (C-4″),76.9 (C-5″),61.2 (C-6″)。将核磁数据进行归属后与文献[15]对照基本一致,鉴定为槲皮素-3-*O*-β-D-葡萄糖苷。

4 讨论

本文采用各种色谱技术对四合木不同溶剂提取物进行了系统的化学成分研究。结果从中分离鉴定了 20 个化合物,其中 8 个首次从该植物中分离得到。8 个首分化合物中化合物 **1 ~ 4** 分离于氯仿提取物,而化合物 **5 ~ 8** 分离于乙酸乙酯提取物。化合物 **2 ~ 4**,**7**,**8** 均为黄酮类化合物,黄酮类化合物可能是四合木的主要化学成分之一。

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