藏药翁布的黄酮类化学成分研究

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摘要:从藏药翁布(*Myricaria germanica*)的60%丙酮提取物中分离得到了11个黄酮类化合物,利用光谱、波谱分析法鉴定其结构分别为:3,5,4'-三羟基-7,3'-二甲氧基黄酮(1),3,5,4'-三羟基-7-甲氧基黄酮(2),3,5,3',4'-四羟基-7-甲氧基黄酮(3),3,5,7-三羟基-4'-甲氧基黄酮(4),槲柳素(5),山柰酚(6),槲皮素-3-O-β-D-葡萄糖苷(7),5,7,4'-三羟基-3-O-β-D-葡萄糖醛酸(8),5,7,3',4'-四羟基-3-O-β-D-葡萄糖醛酸(9),槲皮苷(10)和阿福豆苷(11)。上述化合物均为首次从该植物中分离得到,其中化合物4、5、7~11为首次从水柏枝属植物中分离得到。

关键词:水柏枝属;藏药翁布;化学成分;黄酮

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Flavonoids from the Twigs of the Tibetan Medicine *Myricaria germanica*LA Xiao-qin¹, ZENG Yang^{1,2*}, XU Min³, ZHANG Ying-jun³

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Abstract: Eleven flavonoids were isolated from the 60% aq. acetone extract of the air-dried twigs of *Myricaria germanica* (Tamaricaceae), a famous Tibetan medicine. Their structures were elucidated by spectroscopic analysis and identified as 3,5,4'-trihydroxy-7,3'-dimethoxyflavone (1), 3,5,4'-trihydroxy-7-methoxyflavone (2), rhamnetin (3), 3,5,7-trihydroxy-4'-methoxyflavone (4), tamarixetin (5), kaempferol (6), quercetin-3-O-β-D-glucoside (7), kaempferol-3-O-β-D-glucuronic acid (8), quercetin-3-O-β-D-glucuronic acid (9), quercetin (10), and afzelin (11), respectively. All compounds were obtained from *M. germanica* for the first time, and compounds 4, 5, 7-11 were obtained from the genus *Myricaria* for the first time.

Key words: *Myricaria*; *Myricaria germanica*; chemical constituents; flavone

藏药翁布(*Myricaria germanica* auct. non Linn. Desv.)是槲柳科(Tamaricaceae)水柏枝属(*Myricaria*)植物,生长于海拔2000~2900 m的环境。灌木,茎直立,具多数分枝,枝红棕色,叶线形,总状花序,花期6~7月,蒴果。药用部位为嫩枝,青绿色,其性平,味涩微苦,治黄水病、内腔毒热、发散透疹,用于瘟疫、血热、中毒热证,麻疹不透及咽喉肿痛等症^[1]。据报道,水柏枝属植物的化学成分研究主要集中于宽苞水柏枝(*M. bracteata*)、三春水柏枝(*M. paniculata*)、小花水柏枝(*M. wardii*)三种植物,分离

鉴定的化学成分包括黄酮类、简单酚类、萜类。藏药翁布具有抑菌、抑制炎症、抗疲劳和抗氧化等作用,但对其化学成分的研究报道很少,仅2000年Jetter从*M. germanica*中分离得到四种不同的长链链烷二醇^[2]。

为阐明其药效物质基础,本文对采自青海民和县古鄯的藏药翁布的化学成分进行深入研究,从其嫩枝的60%丙酮提取物中分离得到11个黄酮类化合物,经详细的波谱分析及对照文献,分别鉴定为3,5,4'-三羟基-7,3'-二甲氧基黄酮(1)^[3],3,5,4'-三羟基-7-甲氧基黄酮(2)^[4],3,5,3',4'-四羟基-7-甲氧基黄酮(3)^[5],3,5,7-三羟基-4'-甲氧基黄酮(4)^[6],槲柳素(5)^[7],山柰酚(6)^[8],槲皮素-3-O-β-D-葡萄糖苷(7)^[9],5,7,4'-三羟基-3-O-β-D-葡萄糖

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醛酸(8)^[10]、5,7,3'-*A'*-四羟基-3-*O*- β -D-葡萄糖醛酸(9)^[10]、槲皮苷(10)^[11]和阿福豆苷(11)^[12](图1)。所有化合物均为首次从藏药翁布中分离得到,其中化合物4、5和7~11为首次从水柏枝属植物中分离得到。

图1 化合物1~11的化学结构

Fig. 1 The chemical structures of 1-11

1 仪器与材料

Bruker AM-400 和 500 MHz 核磁共振仪; Auto Spec-3000 型质谱仪; Bruker Tensor 27 型红外光谱仪(KBr 压片); Shimadzu UV-2401 PC 紫外光谱仪; JASCO-4020 型高分辨旋光光谱仪; 硅胶 H 板(薄层用) 柱色谱用硅胶(200~300目)为青岛海洋化工厂出品; 显色剂为5%的硫酸乙醇溶液和5%茴香醛溶液; 其他试剂为工业试剂重蒸。

藏药翁布的嫩枝采自青海民和县古鄯, 由青海师范大学生命与地理科学学院马继雄副教授鉴定为 *Myricaria germanica*。

2 提取分离

藏药翁布干燥嫩枝(12 kg)以60%丙酮室温浸提3次,每次7天,合并提取液,并减压浓缩去除有机溶剂后,用乙酸乙酯萃取5次,合并萃取液,得乙酸乙酯萃取物147.0 g。水层部分(1.5 kg)经 Diaion HP20SS 柱层析,以水-甲醇(1:0~0:1)进行梯度洗脱得到6个部分(Fr. 1-6)。Fr. 4(20.8 g)经 Sephadex LH-20 柱层析,以水-甲醇(1:0~0:1)进行梯度洗脱得到6个部分(Fr. A-F)。其中,Fr. C(3.4 g)经重结晶,以及硅胶(氯仿-甲醇,9:1~6:4), MCI-gel CHP20P(水-甲醇,1:0~0:1)反复柱层析,得到化合物1(98 mg) 2(65 mg) 3(70 mg)和8(50 mg)。Fr. D(3.8 g)经 Sephadex LH-20(水-甲醇,1:0~0:1) MCI-gel CHP20P(水-甲醇,10:0~5:5)柱层析,得到化合物4(50 mg)。Fr. E(4.6 g)经 MCI-

gel CHP20P(水-甲醇,1:0~0:1)和硅胶(氯仿-甲醇,9:1~7:3)反复柱层析,得到化合物6(94 mg)和7(65 mg)。Fr. 2(130 g)和 Fr. 3(140 g)分别经 Sephadex LH-20(水-甲醇,1:0~0:1), MCI-gel CHP20P 和硅胶(氯仿-甲醇,10:0~6:4)反复柱层析,分别得到化合物9(150 mg)和5(20 mg)。乙酸乙酯部分(147 g)经 Sephadex LH-20(水-甲醇,1:0~0:1) MCI-gel CHP20P(水-甲醇,5:5~0:10)柱层析,以及重结晶,得到化合物10(101 mg)和化合物11(414 mg)。

3 结构鉴定

化合物1 黄色粉末, IR(KBr) cm^{-1} : 3401(OH), 1650(C=O), 1605, 1562, 1520(Ar)。EI-MS m/z : 330 [M]⁺; ¹H NMR(DMSO-*d*₆, 500 MHz): δ 6.34(1H, d, J = 1.8 Hz, H-6), 6.74(1H, d, J = 1.8 Hz, H-8), 7.67(1H, s, H-2'), 6.88(1H, d, J = 8.4 Hz, H-5'), 7.73(1H, d, J = 8.4 Hz, H-6'), 3.84(3H, s), 3.85(3H, s); ¹³C NMR(DMSO-*d*₆, 100 MHz): δ 147.4(s, C-2), 136.4(s, C-3), 176.0(s, C-4), 156.1(s, C-5), 97.5(d, C-6), 164.9(s, C-7), 92.1(d, C-8), 160.2(s, C-9), 104.0(s, C-10), 121.9(s, C-1'), 111.7(d, C-2'), 147.0(s, C-3'), 148.8(s, C-4'), 115.5(d, C-5'), 121.9(d, C-6'), 55.8(q, OCH₃-7), 56.0(q, OCH₃-3')。以上数据与文献^[3]中3,5,4'-三羟基-7,3'-二甲氧基黄酮(3,5,4'-trihydroxy-7,3'-dimethoxyflavone)的数据一致。

化合物2 黄色粉末, IR(KBr) cm^{-1} : 3400(OH), 1655(C=O), 1605, 1560, 1520(Ar)。EI-MS m/z : 300 [M]⁺; ¹H NMR(DMSO-*d*₆, 500 MHz): δ 6.34(1H, d, J = 1.9 Hz, H-6), 6.72(1H, d, J = 2.2 Hz, H-8), 6.84(2H, d, J = 8.4 Hz, H-3', 5'), 8.12(2H, d, J = 8.6 Hz, H-2', 6')。 ¹³C NMR(DMSO-*d*₆, 100 MHz): δ 147.1(s, C-2), 136.0(s, C-3), 176.0(s, C-4), 156.1(s, C-5), 97.4(d, C-6), 164.9(s, C-7), 92.0(d, C-8), 160.4(s, C-9), 104.0(s, C-10), 121.7(s, C-1'), 130.8(d, C-2'), 115.4(d, C-3', 5'), 159.4(s, C-4'), 130.5(d, C-6') 56.0(q, OCH₃-7)。以上数据与文献^[4]中3,5,4'-三羟基-7-甲氧基黄酮(3,5,4'-trihydroxy-7-methoxyflavone)的数据一致。

化合物3 黄色粉末, IR(KBr) cm^{-1} : 3300(OH), 1655(C=O), 1655, 1610, 1560, 1515(Ar),

1250 823(-OCH₃)。EI-MS m/z : 316 [M]⁺。¹H NMR (DMSO-*d*₆ 400 MHz): δ 6.33(1H, d, J = 1.8 Hz, H-6), 6.66(1H, d, J = 1.8 Hz, H-8), 7.60(1H, s, H-2'), 6.81(1H, dd, J = 8.3, 2.0 Hz, H-5'), 7.63(1H, dd, J = 8.4, 2.0 Hz, H-6'), 3.84(3H, s); ¹³C NMR (DMSO-*d*₆ 100 MHz): δ 147.4(s, C-2), 136.2(s, C-3), 176.2(s, C-4), 156.1(s, C-5), 97.4(d, C-6), 164.7(s, C-7), 92.0(d, C-8), 160.2(s, C-9), 104.1(s, C-10), 121.6(s, C-1'), 115.2(d, C-2'), 145.0(s, C-3'), 147.8(s, C-4'), 115.6(d, C-5'), 121.8(d, C-6'), 56.0(q, OCH₃-7)。以上数据与文献^[5]中 3,5,3',4'-四羟基-7-甲氧基黄酮(rhamnetin)的数据一致。

化合物 4 黄色粉末, ¹H NMR (DMSO-*d*₆ 500 MHz): δ 6.19(1H, d, J = 2.0 Hz, H-6), 6.45(1H, d, J = 2.0 Hz, H-8), 8.08(2H, d, J = 9.0 Hz, H-2', 6'), 6.87(2H, d, J = 9.0 Hz, H-3', 5'), 3.82(3H, s); ¹³C NMR (DMSO-*d*₆ 100 MHz): δ 146.0(s, C-2), 135.9(s, C-3), 175.7(s, C-4), 160.5(s, C-5), 98.1(d, C-6), 163.8(s, C-7), 93.4(d, C-8), 156.0(s, C-9), 103.0(s, C-10), 123.1(s, C-1'), 129.2(d, C-2', 6'), 113.9(d, C-3', 5'), 160.2(s, C-4'), 55.3(q, OCH₃-4')。以上数据与文献^[6]3,5,7-三羟基-4'-甲氧基黄酮(3,5,7-trihydroxy-4'-methoxyflavone)的数据一致。

化合物 5 黄色粉末, ¹H NMR (DMSO-*d*₆ 400 MHz): δ 6.18(1H, d, J = 2.0 Hz, H-6), 6.42(1H, d, J = 2.0 Hz, H-8), 7.74(1H, d, J = 2.2 Hz, H-2'), 7.64(1H, dd, J = 8.4, 2.0 Hz, H-6'), 6.92(1H, d, J = 8.0 Hz, H-5'), 3.82(3H, s); ¹³C NMR (DMSO-*d*₆ 100 MHz): δ 147.2(s, C-2), 136.2(s, C-3), 175.9(s, C-4), 156.3(s, C-5), 97.1(d, C-6), 163.8(s, C-7), 93.4(d, C-8), 160.1(s, C-9), 104.0(s, C-10), 122.1(s, C-1'), 114.6(d, C-2'), 147.0(s, C-3'), 149.2(s, C-4'), 111.8(d, C-5'), 120.1(d, C-6'), 55.3(q, OCH₃-4')。以上数据与文献^[7]中柽柳素(tamarixetin)的数据一致。

化合物 6 黄色粉末, IR (KBr) cm⁻¹: 3390 (OH), 1665 (C=O), 1615, 1506, 1455。EI-MS m/z : 286 [M]⁺ (100), 285 (22), 258 (18), 153 (24), 134 (22), 125 (15), 93 (67), 69 (10); ¹H NMR (DMSO-*d*₆ 400 MHz): δ 6.17(1H, d, J = 1.8 Hz, H-6), 6.41(1H, d, J = 1.8 Hz, H-8), 8.07(2H, d, J = 8.7 Hz, H-

2', 6') 6.84(2H, d, J = 8.8 Hz, H-3', 5'); ¹³C NMR (DMSO-*d*₆ 100 MHz): δ 146.8(s, C-2), 135.4(s, C-3), 176.2(s, C-4), 156.1(s, C-5), 98.3(d, C-6), 164.0(s, C-7), 93.5(d, C-8), 160.5(s, C-9), 103.1(s, C-10), 121.6(s, C-1'), 129.4(d, C-2'), 115.4(d, C-3'), 159.3(s, C-4'), 115.6(d, C-5'), 129.8(d, C-6')。以上数据与文献^[8]中山奈酚(kaempferol)的数据一致。

化合物 7 黄色粉末, ¹H NMR (DMSO-*d*₆ 500 MHz): δ 6.18(1H, s, H-6), 6.39(1H, s, H-8), 7.56(2H, d, J = 9.0 Hz, H-2', 6'), 6.82(2H, d, J = 8.5 Hz, H-5'), 5.45(1H, d, J = 7.0 Hz, glc-H1), 3.20 ~ 3.39(4H, m, glc-H_{2,3,4,5}), 3.95(1H, dd, J = 2.4 Hz, glc-H_{6 α}), 3.75(1H, J = 5.4, 18.0 Hz, glc-H_{6 β}); ¹³C NMR (DMSO-*d*₆ 125 MHz): δ 156.2(s, C-2), 133.4(s, C-3), 177.4(s, C-4), 161.3(s, C-5), 98.7(d, C-6), 164.2(s, C-7), 93.5(d, C-8), 156.4(s, C-9), 104.0(s, C-10), 121.2(s, C-1'), 115.2(d, C-2'), 144.8(s, C-3'), 148.5(s, C-4'), 116.2(d, C-5'), 121.6(d, C-6'), 101.0(d, C-1''), 74.1(d, C-2''), 77.6(d, C-3''), 70.0(d, C-4''), 76.5(d, C-5''), 61.0(t, C-6'')。以上数据与文献^[9]中槲皮素-3-O- β -D-葡萄糖苷(quercetin-3-O- β -D-glucoside)的数据一致。

化合物 8 黄色粉末, EI-MS m/z : 462 [M]⁺。¹H NMR (DMSO-*d*₆ 400 MHz): δ 5.95(1H, s, H-6), 6.15(1H, s, H-8), 8.01(2H, d, J = 8.5 Hz, H-2', 6'), 6.82(2H, d, J = 8.7 Hz, H-3', 5'), 5.15(d, J = 5.4 Hz, gluA-H1); ¹³C NMR (DMSO-*d*₆ 100 MHz): δ 156.8(s, C-2), 133.5(s, C-3), 176.9(s, C-4), 160.9(s, C-5), 99.9(d, C-6), 168.2(s, C-7), 94.4(d, C-8), 160.2(s, C-9), 102.3(s, C-10), 120.7(s, C-1'), 131.0(d, C-2', 6'), 115.2(d, C-3', 5'), 155.8(s, C-4'), 101.9(d, C-1''), 73.8(d, C-2''), 76.4(d, C-3''), 72.0(d, C-4''), 74.2(d, C-5''), 172.4(s, C-6'')。以上数据与文献^[10]中 5,7,4'-三羟基-3-O- β -D-葡萄糖醛酸(kaempferol-3-O- β -D-glucuronic acid)的数据一致。

化合物 9 黄色粉末, EI-MS m/z : 478 [M]⁺。¹H NMR (DMSO-*d*₆ 400 MHz): δ 6.20(1H, s, H-6), 6.39(1H, s, H-8), 7.60(1H, d, J = 2.0 Hz, H-2', 6'), 6.82(2H, d, J = 8.0 Hz, H-5'), 5.25(1H, d, J = 5.4 Hz, gluA-H1); ¹³C NMR (DMSO-*d*₆ 100 MHz): δ 156.3(s, C-2), 133.1(s, C-3), 177.2(s, C-4),

161.2 (s, C-5), 98.9 (d, C-6), 164.3 (s, C-7), 93.7 (d, C-8), 156.3 (s, C-9), 104.0 (s, C-10), 121.8 (s, C-1'), 115.3 (d, C-2'), 148.7 (s, C-3'), 145.1 (s, C-4'), 16.1 (d, C-5'), 120.9 (d, C-6'), 101.1 (d, C-1''), 73.9 (d, C-2''), 76.1 (d, C-3''), 71.4 (d, C-4''), 75.9 (d, C-5''), 169.9 (s, C-6'')。以上数据与文献^[10]中 5,7,3',4'-四羟基-3-O-β-D-葡萄糖醛酸 (quercetin-3-O-β-D-glucuronic acid) 的数据一致。

化合物 10 黄色粉末, ¹H NMR (DMSO-*d*₆, 400 MHz): δ 6.19 (1H, d, *J* = 2.0 Hz, H-6), 6.39 (1H, d, *J* = 2.0 Hz, H-8), 7.44 (1H, d, *J* = 2.0 Hz, H-2'), 6.86 (1H, d, *J* = 8.1 Hz, H-5'), 7.28 (1H, dd, *J* = 8.4 Hz, 2.1 Hz, H-6'), 5.23 (1H, d, *J* = 1.0 Hz, Rha-1), 0.80 (3H, d, *J* = 7.0 Hz, Rha-Me); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ 157.8 (s, C-2), 135.5 (s, C-3), 178.9 (s, C-4), 161.9 (s, C-5), 99.6 (d, C-6), 165.2 (s, C-7), 94.4 (d, C-8), 158.2 (s, C-9), 105.3 (s, C-10), 120.7 (s, C-1'), 116.5 (d, C-2'), 145.2 (s, C-3'), 149.8 (s, C-4'), 116.0 (d, C-5'), 122.1 (d, C-6'), 102.9 (d, C-1''), 71.8 (d, C-2''), 71.4 (d, C-3''), 72.0 (d, C-4''), 71.2 (d, C-5''), 17.4 (q, Me)。以上数据与文献^[11]中槲皮苷 (quercetrin) 的数据一致。

化合物 11 黄色粉末, ¹H NMR (DMSO-*d*₆, 400 MHz): δ 6.19 (1H, s, H-6), 6.40 (1H, s, H-8), 6.90 (1H, d, *J* = 8.7 Hz, H-2', H-6'), 7.75 (1H, d, *J* = 8.7 Hz, H-3', H-5'), 5.27 (1H, d, *J* = 1.0 Hz, Rha-1), 0.78 (3H, d, *J* = 5.9 Hz, Rha-Me); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ 156.5 (s, C-2), 134.2 (s, C-3), 177.7 (s, C-4), 161.3 (s, C-5), 98.7 (d, C-6), 164.2 (s, C-7), 93.8 (d, C-8), 160.0 (s, C-9), 104.2 (s, C-10), 120.5 (s, C-1'), 130.6 (d, C-2', C-6'), 115.4 (d, C-3', C-5'), 147.3 (s, C-4'), 101.8 (d, C-1''), 70.3 (d, C-2''), 70.7 (d, C-3''), 71.1 (d, C-4''), 70.1 (d, C-5''), 17.5 (q, Me)。以上数据与文献^[12]中阿福豆苷 (afzelin) 的数据一致。

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