猪牙皂的化学成分

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摘 要 采用大孔树脂、硅胶、凝胶、MCI、反相高效液相色谱等各种柱色谱技术和现代波谱学方法,结合物理化学性质,从猪牙皂(Fructus Gleditsiae Abnormalis)醇提物中分离并鉴定了 12 个化合物,分别为:gleditsioside A(**1**)、gleditsioside B(**2**)、gleditsioside H(**3**)、gleditsioside I(**4**)、gleditsioside J(**5**)、gleditsioside K(**6**)、gleditsia saponins C′(**7**)、柽柳素-7-*O*-*β*-D-葡萄糖苷(**8**)、新橙皮苷(**9**)、金圣草素-7-*O*-新橙皮糖苷(**10**)、丁香脂素-*O*-*β*-D-吡喃葡萄糖苷(**11**)、鹅掌揪苷(**12**)。其中化合物 **8** ~ **12** 为首次从该属植物中分离得到。

关键词 猪牙皂;分离;化学成分;结构鉴定

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Chemical constituents of Fructus Gleditsiae Abnormalis

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Abstract Twelve compounds were isolated from the ethanol extract of Fructus Gleditsiae Abnormalis by macroporous resin, silica gel, Sephadex LH-20, MCI and ODS column chromatographies. Their structures were identified on the basis of physicochemical properties and spectral data as gleditsioside A(**1**), gleditsioside B(**2**), gleditsioside H(**3**), gleditsioside I(**4**), gleditsioside J(**5**), gleditsioside K(**6**), gleditsia saponins C′(**7**), tamarixetin-7-*O*-*β*-D-glucopyranoside(**8**), neohesperidin(**9**), chrysoeirol-7-*O*-neohesperidoside(**10**); syringaresinol- *O*-*β*-D-glucopyranoside(**11**), liriodendrin(**12**). Compounds **8-12** were firstly isolated from this genus.

Key words Fructus Gleditsiae Abnormalis; isolation; chemical constituents; structural identification

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猪牙皂(Fructus Gleditsiae Abnormalis)系豆科苏木亚科皂荚属(*Gleditisia* Linn)植物皂荚(*Gleditsia sinensis* Lam.)所结之短小、弯曲而无种子的荚[1],主产于山东、河南、四川等省[2]。其性辛、咸、温,归肺、大肠经,具去痰开窍、消肿散结之功效,用于中风口噤,昏迷不醒,癫痫痰盛,关窍不通,喉痹痰阻,顽痰喘咳,咯痰不爽,大便燥结;外治痈肿,作为一种传统中药被《中华人民共和国药典》(2010 年版)收载[3]。现代研究表明猪牙皂具抗炎、抗肿瘤、抗过敏、改善心肌缺血等活性[4-7],其

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主要化学成分为三萜皂苷[8-10]。笔者曾以碱水解的次生皂苷 prosapogenin 2b 为指标成分,建立猪牙皂药材质量标准[11]。为继续探索该药材中微量及非三萜皂苷类成分,本研究对其开展更深入的化学成分研究。从其醇提取物中分离并鉴定出 12 个化合物,包括 7 个三萜皂苷:gleditsioside A(**1**)、gleditsioside B(**2**)、gleditsioside H(**3**)、gleditsioside I(**4**)、gleditsioside J(**5**)、gleditsioside K(**6**)、gleditsia saponins C′(**7**);3 个黄酮和 2 个木脂素:柽柳素-7-*O*-*β*-D-葡萄糖苷(**8**)、新橙皮苷(**9**)、金圣草素-7-*O*-新橙皮糖苷(**10**)、丁香脂素-*O*-*β*-D-吡喃葡萄糖苷(**11**)、鹅掌揪苷(**12**)。其中化合物 **8** ~ **12** 为首次从该属植物中分离得到。

1　材　料

1.1　仪器与试剂

X-4 数字显示双目显微熔点测定仪(温度计未校正);Bruker AV-500 和 AV-300 型核磁共振仪(德国 Bruker 公司);Agilent 1100 Series LC/MSD Trap 质谱仪(美国 Agilent 公司)。柱色谱硅胶(青岛海洋化工厂);薄层色谱硅胶 GF_{254}(烟台化工研究所);MCI HP-20(日本三菱化学公司);Sephadex LH-20(美国 Pharmacia 公司);ODS(德国 Merck 公司);D101 大孔树脂(天津市海光化工有限公司)。所用试剂均为市售分析纯。

1.2　药　材

猪牙皂药材于 2010 年 3 月购买,产地为安徽,经中国药科大学秦民坚教授鉴定为猪牙皂(Fructus Gleditisiae Abnormalis),标本(No. 20100401)保存于中国药科大学天然药物化学教研室。

2　提取与分离

猪牙皂 50 kg,70% 乙醇回流提取 3 次,每次 2 h,合并提取液,减压回收得醇提浸膏。将浸膏加水混悬,上样于 D 101 大孔树脂,依次用水、30%、60%、90% 乙醇洗脱得到 Fr. 1 ~ 3。Fr. 1(50 g)上样于 MCI 色谱柱,依次用 30%、60%、90% 甲醇洗脱,得到 Fr. 1a ~ 1c。Fr. 1a 经硅胶柱色谱,以氯仿-甲醇(10∶1 → 1∶1)梯度洗脱,得化合物 **10**(13 mg)、**12**(11 mg)。Fr. 1b 经 ODS 柱色谱,依次用 50% ~90% 甲醇-水梯度洗脱,其中 50% ~60% 甲醇水洗脱部分合并为流分 1 ~ 8,经 ODS 柱以 50% 甲醇-水等度洗脱,得到化合物 **3**(95 mg);而 70% ~80% 甲醇水洗脱部分合并为流分 9 ~ 16,经 ODS 柱色谱以 70% 甲醇-水等度洗脱,再经反复 Sephadex LH-20 柱色谱以甲醇洗脱,得到化合物 **4**(110 mg)、**5**(14 mg)、**7**(60 mg);最后 90% 甲醇-水洗脱部分合并为流分 17 ~ 22,经硅胶柱色谱以氯仿-甲醇(15∶1→1∶1)梯度洗脱,再经 Sephadex LH-20 柱色谱以氯仿-甲醇(1∶1)洗脱,得到化合物 **8**(11 mg)、**9**(15 mg)、**11**(12 mg)。Fr. 2 经反复 ODS 柱色谱,以不同比例的甲醇-水系统梯度或等度洗脱得化合物 **1**(130 mg)、**2**(22 mg)、**6**(15 mg)。

3　结构鉴定

化合物 **1**　白色固体(甲醇),mp:205 ~ 206 ℃,浓硫酸香草醛反应显紫红色,Liebermann-Burchard 和 Molish 反应均阳性。ESI-MS *m/z*:1 643$[M+Na]^+$。^{1}H NMR(500 MHz, C_5D_5N) δ:7. 02(1H, t, *J* = 7. 8 Hz, MT H-3), 6. 34(1H, br. s, C_{28}-Rha-H-1), 6. 12(1H, d, *J* = 7. 1 Hz, C_{28}-Glc′-H-1), 6. 10(1H, dd, *J* = 18. 0, 10. 6 Hz, MT H-7), 5. 53(1H, br. d, *J* = 17. 5 Hz, MT H-8a), 5. 43(1H, br. s, H-12), 5. 17(1H, br d, *J* = 11. 2 Hz, MT H-8b), 5. 16(1H, d, *J* = 7. 2 Hz, C_{28}-Xyl″-H-1), 5. 12(1H, d, *J* = 5. 1 Hz, C_3-Ara-H-1), 5. 04(1H, d, *J* = 6. 7 Hz, C_{28}-Xyl′-H-1), 4. 95(1H, d, *J* = 6. 8 Hz, C_3-Xyl-H-1), 4. 86(1H, d, *J* = 7. 6 Hz, C_3-Glc-H-1), 3. 50(1H, dd, *J* = 3. 8, 12. 0 Hz, H-3), 2. 40(1H, m, MT H-4a), 2. 35(1H, m, MT H-4b), 1. 86(3H, s, MT Me-9), 1. 72(1H, d, *J* = 5. 9 Hz, C_{28}-Rha-Me), 1. 44(3H, s, MT Me-10), 1. 33, 1. 30, 1. 04, 0. 96, 0. 94, 0. 87, 0. 84(each 3H, s, Me-23, 27, 26, 24, 30, 25, 29)。^{13}C NMR(125 MHz, C_5D_5N)见表 1、表 2。以上波谱数据与文献[9]对照一致,确定化合物 **1** 为 gleditsioside A。

化合物 **2**　白色粉末(甲醇),mp:203 ~ 204 ℃,浓硫酸香草醛反应显紫红色,Liebermann-Burchard 和 Molish 反应均阳性。ESI-MS *m/z*:1 659$[M+Na]^+$。^{1}H NMR(500 MHz, C_5D_5N) δ:7. 21(1H, t, *J* = 7. 3 Hz, MT H-3), 6. 34(1H, br. s, C_{28}-Rha-H-1), 6. 10(1H, d, *J* = 7. 8 Hz, C_{28}-Glc′-H-1), 6. 08(1H, dd, *J* = 17. 3, 10. 7 Hz, MT H-7), 5. 51(1H, dd, *J* = 17. 3, 1. 9 Hz, MT H-8a), 5. 45(1H, br. t, H-12), 5. 16(1H, d, *J* = 7. 5 Hz, C_{28}-Xyl″-H-1), 5. 13(1H, dd, *J* = 10. 6, 1. 9 Hz, MT H-8b), 5. 12(d, *J* = 5. 3 Hz, C_3-Ara-H-1), 5. 05(1H, d, *J* = 7. 0 Hz, C_{28}-Xyl′-H-1), 4. 95(d, *J* = 6. 8 Hz, C_3-Xyl-H-1), 4. 86(1H, d, *J* = 7. 7 Hz, C_3-Glc-H-1), 4. 71(2H, br. s, MT H-9), 3. 50(1H, dd, *J* = 11. 2, 4. 3 Hz, H-3), 2. 68(1H, m, MT H-4a), 2. 60(1H, m, MT H-4b), 1. 75(1H, d, *J* = 6. 0 Hz, C_{28}-Rha-CH_3), 1. 42(3H, s, MT H-10), 1. 34, 1. 31, 1. 05, 0. 96, 0. 94, 0. 88, 0. 84(each 3H, s, Me-23, 27, 26, 24, 30, 25,

29)。^{13}C NMR(125 MHz,C_5D_5N)见表1、2。以上波谱数据与文献[9]对照一致,确定化合物**2**为gleditsioside B。

化合物**3** 白色粉末(甲醇),mp:250 ~ 251 ℃,浓硫酸香草醛反应显蓝紫色,Liebermann-Burchard和Molish反应均阳性。ESI-MS *m/z*:1 623[M + Na]$^+$。^{1}H NMR(500 MHz,C_5D_5N) δ:6.34(1H,br. s,C_{28}-Rha-H-1),6.09(1H,d,*J* = 7.8 Hz,C_{28}-Glc′-H-1),5.36(1H,br. s,H-12),5.36(1H,br. s,C_{28}-Rha′-H-1),5.14(1H,d,*J* = 7.4 Hz,C_{28}-Xyl″-H-1),5.12(1H,d,*J* = 4.6 Hz,C_3-Ara-H-1),5.03(1H,d,*J* = 6.4 Hz,C_{28}-Xyl′-H-1),4.94(1H,d,*J* = 6.7 Hz,C_3-Xyl-H-1),4.84(1H,d,*J* = 7.5 Hz,C_3-Glc-H-1),3.47(1H,m,H-3),1.33,1.29,1.07,0.95,0.95,0.85,0.83(each 3H,s,Me-23,27,26,24,30,25,29)。^{13}C NMR(125 MHz,C_5D_5N)见表1、2。以上波谱数据与文献[8]报道一致,确定化合物**3**为gleditsioside H。

化合物**4** 白色粉末(甲醇),mp:255 ~ 256 ℃,浓硫酸香草醛反应显蓝紫色,Liebermann-Burchard和Molish反应均阳性。ESI-MS *m/z*:1 477[M + Na]$^+$。^{1}H NMR(500 MHz,C_5D_5N) δ:6.41(1H,br. s,C_{28}-Rha-H-1),6.18(1H,d,*J* = 7.9 Hz,C_{28}-Glc′-H-1),5.39(1H,br. t,H-12),5.16(1H,d,*J* = 7.5 Hz,C_{28}-Xyl″-H-1),5.13(1H,d,*J* = 5.2 Hz,C_3-Ara-H-1),5.05(1H,d,*J* = 7.3 Hz,C_{28}-Xyl′-H-1),4.96(1H,d,*J* = 6.9 Hz,C_3-Xyl-H-1),4.86(1H,d,*J* = 7.8 Hz,C_3-Glc-H-1),3.50(1H,dd,*J* = 11.8,4.2 Hz,H-3),1.77(1H,d,*J* = 6.2 Hz,C_{28}-Rha-CH_3),1.33,1.31,1.06,0.95,0.84,0.83,0.82(each 3H,s,Me-23,27,26,24,30,25,29)。^{13}C NMR(125 MHz,C_5D_5N)见表1、2。以上波谱数据与文献[8]报道的一致,确定化合物**4**为gleditsioside I。

化合物**5** 白色粉末(甲醇),浓硫酸香草醛反应显蓝紫色,Liebermann-Burchard和Molish反应均阳性。ESI-MS *m/z*:1 655[M + Na]$^+$。^{1}H NMR(500 MHz,C_5D_5N) δ:6.48(1H,b. s,C_{28}-Rha-H-1),6.14(1H,d,*J* = 7.5 Hz,C_{28}-Glc′-H-1),5.39(1H,br. s,H-12),5.17(1H,d,*J* = 7.3 Hz,C_{28}-Gal-H-1),5.16(1H,d,*J* = 4.9 Hz,C_3-Ara-H-1),5.14(1H,br. t,H-16),5.13(1H,d,*J* = 5.1 Hz,C_{28}-Xyl″-H-1),5.08(1H,d,*J* = 7.5 Hz,C_{28}-Xyl′-H-1),4.99(1H,d,*J* = 7.0 Hz,C_3-Xyl-H-1),4.86(1H,d,*J* = 8.0 Hz,C_3-Glc-H-1),3.34(1H,m,H-3),1.67(3H,d,*J* = 6.1 Hz,C_{28}-Rha-6),1.82,1.29,1.06,0.95,0.89,0.88,0.87(each 3H,s,Me-27,23,30,26,24,29,25)。^{13}C NMR(125 MHz,C_5D_5N)见表1、2。以上波谱数据与文献[8]对照一致,确定化合物**5**为gleditsioside J。

化合物**6** 白色粉末(甲醇),浓硫酸香草醛反应显蓝紫色,Liebermann-Burchard和Molish反应均阳性。ESI-MS *m/z*:1 625[M + Na]$^+$。^{1}H NMR(500 MHz,C_5D_5N) δ:6.48(1H,br. s,C_{28}-Rha-H-1),6.08(1H,d,*J* = 8.3 Hz,C_{28}-Glc′-H-1),5.19(1H,d,*J* = 7.0 Hz,C_{28}-Xyl‴-H-1),5.56(1H,br. s,H-12),5.14(1H,d,*J* = 4.7 Hz,C_3-Ara-H-1),5.13(1H,d,*J* = 6.5 Hz,C_{28}-Xyl″-H-1),5.14(1H,m,H-16),5.12(1H,d,*J* = 7.0 Hz,C_{28}-Xyl′-H-1),4.95(1H,d,*J* = 7.0 Hz,C_3-Xyl-H-1),4.86(1H,d,*J* = 7.7 Hz,C_3-Glc-H-1),3.57(1H,m,H-3),1.80,1.26,1.08,0.95,0.89,0.88,0.87(each 3H,s,Me-27,23,30,26,24,29,25)。^{13}C NMR(125 MHz,C_5D_5N)见表1、2。以上波谱数据与文献[8]对照一致,确定化合物**6**为gleditsioside K。

化合物**7** 白色粉末(甲醇),mp:234 ~ 235 ℃,[α] = -18°(*c* 0.10,MeOH),浓硫酸香草醛反应显蓝紫色,Liebermann-Burchard和Molish反应均阳性。ESI-MS *m/z*:1 639[M + Na]$^+$。^{1}H NMR(500 MHz,C_5D_5N) δ:6.37(1H,br. s,C_{28}-Rha-H-1),6.14(1H,d,*J* = 7.8 Hz,C_{28}-Glc′-H-1),5.60(1H,br. s,H-12),5.42(1H,br. s,C_{28}-Rha′-H-1),5.20(1H,d,*J* = 7.0 Hz,C_{28}-Xyl″-H-1),5.18(1H,d,*J* = 5.0 Hz,C_3-Ara-H-1);5.17(1H,m,H-16),5.16(1H,d,*J* = 7.5 Hz,C_{28}-Xyl′-H-1),5.01(1H,d,*J* = 6.5 Hz,C_3-Xyl-H-1),4.90(1H,d,*J* = 7.2 Hz,C_3-Glc-H-1),3.48(1H,m,H-3),1.87、1.34、1.14、1.14、1.02、1.00、0.95(each 3H,s,Me-27,23,30,26,24,29,25)。^{13}C NMR(125 MHz,C_5D_5N)见表1、2。以上波谱数据与文献[8]报道一致,确定化合物**7**为gleditsia saponins C′。

Table 1 ^{13}C NMR data for the aglycone moieties of compounds **1-7** (125 MHz in C_5D_5N)

Position	1	2	3	4	5	6	7
1	38.9	38.9	38.9	38.9	38.9	38.9	39.0
2	26.8	26.8	26.8	26.8	26.8	26.8	26.8
3	88.6	88.6	88.7	88.6	88.6	88.7	88.9
4	39.6	39.6	39.6	39.6	39.6	39.6	39.6
5	56.0	56.0	56.0	56.0	55.9	56.0	56.1
6	18.7	18.7	18.7	18.6	18.5	18.6	18.7
7	33.3	33.3	33.2	33.1	33.1	33.5	33.5
8	40.0	40.0	40.0	40.0	40.0	40.1	40.1
9	48.1	48.1	47.3	48.1	47.1	47.2	47.2
10	37.1	37.1	37.1	37.1	37.1	37.1	37.1
11	23.9	24.0	23.8	23.9	23.9	23.9	23.9
12	122.9	122.9	122.8	122.9	122.8	122.5	122.6
13	144.0	144.0	144.1	144.0	144.0	144.4	144.4
14	42.3	42.3	42.3	42.3	42.2	42.1	42.2
15	28.4	28.5	28.6	28.5	28.5	36.2	36.0
16	23.4	23.4	23.3	23.5	74.6	74.1	74.0
17	47.2	47.2	48.1	47.1	48.0	49.2	49.5
18	42.0	41.9	41.9	42.1	42.0	41.5	41.5
19	46.3	46.3	46.4	46.3	46.2	47.3	47.5
20	30.8	30.8	30.8	30.7	30.7	30.7	30.8
21	34.1	34.0	34.1	34.0	34.0	35.9	36.0
22	32.5	32.5	32.5	32.4	32.3	31.8	31.9
23	28.2	28.2	28.2	28.2	28.2	28.3	28.3
24	17.1	17.1	17.1	17.1	17.1	17.1	17.1
25	15.7	15.7	15.7	15.7	15.7	15.8	15.9
26	17.6	17.6	17.5	17.5	17.5	17.5	17.6
27	26.1	26.1	26.0	26.1	26.0	27.1	27.2
28	176.5	176.5	176.6	176.4	176.4	175.8	176.0
29	33.2	33.2	33.2	33.3	33.3	33.1	33.2
30	23.9	23.9	23.8	23.8	23.7	24.5	24.7

Table 2 ^{13}C NMR data for the sugar moieties of compounds **1-7**(125 MHz in C_5D_5N)

Position	**1**	**2**	**3**	**4**	**5**	**6**	**7**
C_3-Glc	C_5D_5N						
1	106.7	106.7	106.7	106.7	106.7	106.8	106.8
2	75.7	75.8	75.7	75.7	75.7	75.7	75.7
3	78.4	78.4	78.4	78.4	78.4	78.4	78.4
4	72.3	72.2	72.2	72.3	72.2	72.2	72.2
5	76.2	76.2	76.2	76.3	76.2	76.1	76.1
6	69.6	69.6	69.6	69.6	69.6	69.5	69.6
Ara							
1	102.4	102.4	102.4	102.4	102.4	102.3	102.3
2	80.6	80.6	80.6	80.6	80.6	80.5	80.5
3	72.7	72.7	72.6	72.5	72.6	72.6	72.5
4	67.5	67.5	67.5	67.5	67.5	67.5	67.4
5	64.4	67.3	64.3	64.4	64.4	64.3	64.3
Xyl							
1	106.4	106.4	106.3	106.4	106.5	106.2	106.3
2	75.5	75.5	75.4	75.5	75.5	75.4	75.4
3	77.9	77.9	77.9	77.9	77.8	77.8	77.9
4	70.9	70.8	70.8	70.9	70.8	70.8	70.9
5	67.3	67.3	67.3	67.3	67.3	67.3	67.3
C_{28}-Glc′							
1	94.6	94.6	94.6	94.8	94.6	94.7	94.7
2	76.8	76.7	76.5	76.5	77.1	76.7	76.5
3	79.0	79.0	79.1	79.4	79.0	79.0	79.1
4	71.3	71.5	71.1	71.3	71.3	71.2	71.2
5	75.8	75.7	77.6	78.8	78.9	78.9	77.6
6	64.3	64.4	66.5	62.2	62.1	62.0	66.7
Rha							
1	101.5	101.4	101.4	101.3	100.4	100.1	101.4
2	71.7	71.6	71.6	71.7	81.2	81.4	71.8
3	72.5	72.5	72.6	72.7	72.2	72.2	72.6
4	85.0	85.0	85.1	85.1	84.5	82.8	83.8
5	68.3	68.1	68.2	68.2	68.0	68.1	68.4
6	18.6	18.6	18.6	18.7	18.7	18.6	18.6
Xyl′							
1	106.8	106.8	106.9	106.9	106.4	106.0	106.3
2	75.1	75.0	75.0	75.0	75.2	75.1	75.0
3	87.3	87.3	87.3	87.4	87.2	87.3	87.5
4	68.9	68.9	68.9	68.9	68.9	69.0	69.0
5	66.9	66.9	66.9	66.9	66.8	66.7	66.9
Xyl″							
1	105.9	105.9	105.9	105.9	105.9	105.7	106.1
2	75.2	75.2	75.1	75.2	75.2	75.2	75.1
3	78.1	78.1	78.0	78.1	78.0	78.1	78.1
4	70.8	70.8	70.8	70.8	70.9	70.8	70.9
5	67.3	67.3	67.3	67.4	67.3	67.3	67.4
	Monoterpenoid	Monoterpenoid	Rha′	Gal	Xyl‴	Rha′	
1	168.0	167.7	101.8	107.7	107.6	101.9	
2	127.7	133.0	72.1	73.4	78.1	72.1	
3	143.5	146.6	72.6	75.1	78.9	72.7	
4	24.0	24.0	73.9	70.1	70.2	74.0	
5	41.5	41.9	69.6	77.1	67.3	69.7	
6	72.1	72.2	18.7	62.1	18.7		
7	146.6	146.5					
8	111.7	111.8					
9	12.5	56.3					
10	28.6	28.6					

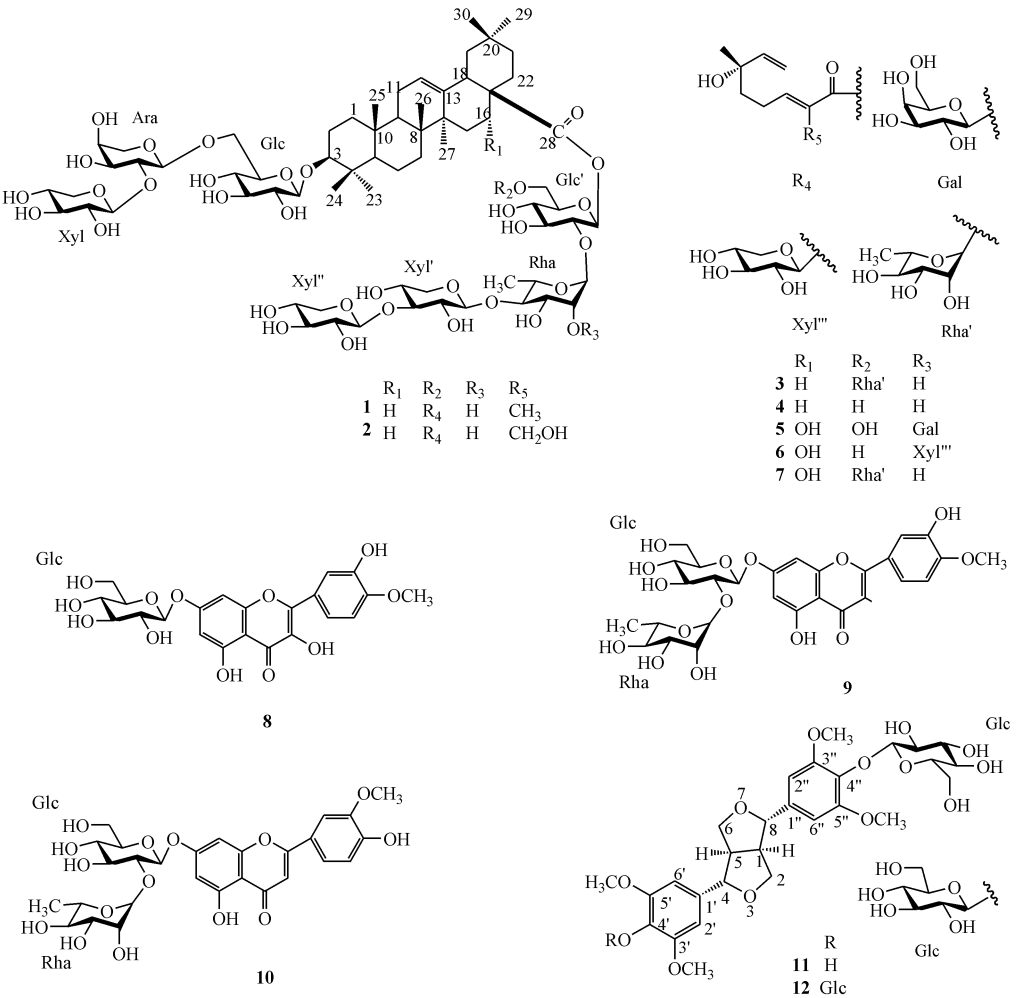

Figure 1 Chemical structures of compounds **1-12** from the ethanol extract of Fructus Gleditsiae Abnormalis

化合物 **8** 黄色粉末(甲醇),mp 206 ~ 208 ℃,盐酸-镁粉反应和 Molish 反应均阳性,浓硫酸-香草醛显黄色。ESI-MS *m/z*:479[M + H]$^+$。^{1}H NMR(300 MHz,DMSO-d_6) δ:12.48(1H,s,5-OH),9.72(2H,s,3,3′-OH),7.77(1H,dd,*J* = 2.0,9.6 Hz,H-6′),7.72(1H,d,*J* = 2.0 Hz,H-2′),6.95(1H,d,*J* = 8.5 Hz,H-5′),6.85(1H,d,*J* = 2.0 Hz,H-8),6.43(1H,d,*J* = 2.0 Hz,H-6),5.05(1H,d,*J* = 7.2 Hz,Glc-H-1);3.87(3H,s,OCH_3)。^{13}C NMR(75 MHz,DMSO-d_6) δ:172.0(C-4),162.7(C-7),160.4(C-5),155.7(C-9),149.1(C-4′),147.4(C-2,3′),134.6(C-3),122.1(C-1′,6′),115.5(C-2′),111.7(C-5′),104.6(C-10),100.0(Glc-1),98.5(C-6),94.7(C-8),77.3(Glc-3),76.5(Glc-5),73.1(Glc-2),69.6(Glc-4),60.6(Glc-6),55.8(-OCH_3)。以上波谱数据与文献[12]报道一致,确定化合物 **8** 为柽柳素-7-*O*-β-D-吡喃葡萄糖苷(tamarixetin-7-*O*-β-D-glucopyranoside)。

化合物 **9** 黄色结晶(甲醇),mp:239 ~ 243 ℃,盐酸-镁粉反应和 Molish 反应均阳性,浓硫酸-香草醛显橙红色。ESI-MS *m/z*:611[M + H]$^+$。^{1}H NMR(300 MHz,DMSO-d_6) δ:12.05(1H,s,5-OH),9.15(1H,4′-OH),7.11(1H,br. s,H-2′),6.92(1H,br. d,*J* = 8.2 Hz,H-6′),6.79(1H,d,*J* = 8.1 Hz,H-5′),6.13(1H,d,*J* = 2.1 Hz,H-8),6.08(1H,d,*J* = 2.1 Hz,H-6),5.51(1H,m,H-2),5.15(1H,d,*J* = 7.2 Hz,Glc-H-1),5.12(1H,br. s,Rha-H-1),3.79(3H,s,OCH_3),3.16(1H,m,H-3),2.74(1H,dd,*J* = 15.0,3.0 Hz,H-3),1.15(3H,d,*J* = 6.2 Hz,Rha-H-6)。^{13}C NMR(75 MHz,DMSO-d_6) δ:197.3(C-4),164.7(C-7),162.9(C-5,9),147.5(C-4′),147.0(C-3′),129.2(C-1′),119.6(C-6′),115.2(C-2′),111.3(C-5′),103.3(C-10),100.3(Rha-C-1),97.4(Glc-C-1),96.3(C-6),95.1(C-8),78.7(C-2),77.1(Glc-C-3,5),76.7(Glc-C-2),71.8(Rha-C-4),70.3(Rha-C-2,3),69.6(Glc-C-4),68.2(Rha-C-5),60.4(Glc-C-6),55.7(OCH_3),42.2(C-3),18.0(Rha-C-6)。以上波谱数据与文献[13]报道一致,确定化合物 **9** 为新橙皮苷(neohesperidin)。

化合物 **10** 黄色结晶(甲醇),mp > 300 ℃,盐酸-镁粉

反应和 Molish 反应均阳性,浓硫酸-香草醛显橙黄色。ESI-MS m/z:609[M + H]$^+$。^{1}H NMR(300 MHz, DMSO-d_6) δ: 12.96(1H,s,5-OH),10.00(1H,s,4′-OH),7.57(2H,br. s,H-2′,6′),6.99(1H,s,H-3),6.95(1H,d,J = 8.9 Hz,H-5′),6.83(1H,d,J = 1.8 Hz,H-8),6.37(1H,d,J = 1.9 Hz,H-6),5.22(1H,d,J = 7.4 Hz,Glc-H-1),5.12(1H,br. s,Rha-H-1),3.86(3H,s,OCH_3),1.20(3H,d,J = 6.2 Hz,Rha-H-6)。^{13}C NMR(75 MHz,DMSO-d_6) δ:182.0(C-4),164.1(C-7),162.5(C-2),161.1(C-9),156.9(C-5),150.9(C-3′),148.0(C-4′),121.3(C-6′),120.4(C-1′),115.7(C-5′),110.3(C-2′),105.4(C-3),103.5(C-10),100.4(Rha-C-1),99.5(Glc-C-1),98.0(C-6),94.6(C-8),77.2(Glc-C-2),76.3(Glc-C-3,5),71.8(Glc-C-4),70.5(Rha-C-4),70.4(Rha-C-3),69.7(Rha-C-2),68.3(Rha-C-5),60.5(Glc-C-6),55.8(OCH_3),18.0(Rha-C-6)。以上与文献[14]报道的数据一致,确定化合物 **10** 为金圣草素-7-*O*-新橙皮糖苷(chrysoeirol-7-*O*-neohesperidoside)。

化合物 **11**　白色粉末(甲醇),mp:261 ~ 262 ℃,浓硫酸香草醛反应显紫红色,Molish 反应呈阳性。ESI-MS m/z:603[M + Na]$^+$。^{1}H NMR(500 MHz,C_5D_5N) δ:6.95(2H,s,H-2′,2″),6.92(2H,s,H-6′,6″),4.95(1H,d,J = 8.5 Hz,Glc-H-1),4.32(2H,q,J = 5.3 Hz,H-4b,8b),3.91(2H,m,H-4a,8a),3.82(6H,s,-OCH_3),3.78(6H,s,-OCH_3),3.20(2H,m,H-1,5)。^{13}C NMR(125 MHz,C_5D_5N) δ:154.0(C-3′,5′),149.3(C-3″),138.4(C-4′),137.4(C-4″),132.1(C-1′,1″),105.1(C-2′,6′),104.9(C-2″,6″),104.3(Glc-C-1),86.5(C-2),86.3(C-6),78.7(Glc-C-5),78.4(Glc-C-3),76.1(Glc-C-2),72.2(C-4),72.1(C-8),71.7(Glc-C-4),62.6(Glc-C-6),56.7(2 ×-OCH_3),56.5(2 ×-OCH_3),54.9(C-1),54.8(C-5)。以上波谱数据与文献[15]报道一致,确定化合物 **11** 为丁香脂素-*O*-β-D-吡喃葡萄糖苷(syringaresinol-*O*-β-D-glucopyranoside)。

化合物 **12**　白色粉末(甲醇),mp:176 ~ 178 ℃,浓硫酸香草醛反应显紫红色,Molish 反应呈阳性。ESI-MS m/z:765[M + Na]$^+$。^{1}H NMR(500 MHz,C_5D_5N) δ:6.95(4H,br. s,H-2′,2″,6′,6″),5.82(2H,d,J = 6.9 Hz,H-2,6),4.96(2H,d,J = 6.0 Hz,Glc-H-1,1′),4.04(2H,br. s,H-8b,8′b),3.96(2H,br. s,H-8a,8′a),3.82(12H,s,OCH_3),3.18(2H,br. s,H-1,5)。^{13}C NMR(125 MHz,C_5D_5N) δ:154.0(C-3′,3″,5′,5″),138.3(C-4′,4″),105.1(Glc-C-1,1′),105.0(C-2′,2″,6′,6″),86.2(C-2,6),78.7(Glc-C-3,3′),78.4(Glc-C-5,5′),76.1(Glc-C-2,2′),72.3(C-4,8),71.7(Glc-C-4,4′),62.7(Glc-C-6,6′),56.8(OCH_3),54.8(C-1,5)。以上数据与文献[16]报道一致,确定化合物 **12** 为鹅掌楸苷(liriodendrin)。

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