海州常山茎的化学成分研究

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摘 要 采用多种柱色谱方法对大青属 *Clerodendrum* Linn. 植物海州常山 *Clerodendrum trichotomum* Thunb. 茎的乙醇提取液进行分离纯化,运用波谱学方法鉴定了 13 个化合物,分别为木栓酮(friedelin,**1**),白桦脂酸(betulinic acid,**2**),蒲公英萜醇(taraxerol,**3**),3-羟基-30-去甲基-20-酮基-28-羽扇豆酸(3-hydroxy-30-nor-20-oxo-28-lupanoic acid,platanic acid,**4**),金合欢素(acacetin,**5**),5,7-二羟基 3′,4′-二甲氧基黄酮(5,7-dihydroxy 3′,4′-dimethoxyflavone,**6**),β-谷甾醇(β-sitosterol,**7**),豆甾醇(stigmasterol,**8**),胡萝卜苷(daucosterol,**9**),豆甾醇-3-*O*-葡萄糖苷(stigmasterol-3-*O*-glucopyranoside,**10**),异香草醛(isovanillin,**11**),邻苯二甲酸二丁酯(dibutyl phthalate,**12**)和丁香醛(syringaldehyde,**13**)。化合物 **4**,**6**,**11** ~ **13** 均为首次从该属植物中分离得到,化合物 **4**,**6**,**10** ~ **13** 为首次从该物种中分离得到。

关键词 海州常山;化学成分;分离;结构鉴定

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Chemical constituents from the stems of *Clerodendrum trichotomum* Thunb.

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Abstract Thirteen compounds were isolated and purified from the ethanol extract of *Clerodendrum trichotomum* Thunb. by various chromatographic methods. Their structures were identified as friedelin (**1**), betulinic acid (**2**), taraxerol (**3**), platanic acid (**4**), acacetin (**5**), 5, 7-dihydroxy 3′, 4′-dimethoxyflavone (**6**), β-sitosterol (**7**), stigmasterol (**8**), daucosterol (**9**), stigmasterol-3-*O*-glucopyranoside (**10**), isovanillin (**11**), dibutyl phthalate (**12**) and syringaldehyde (**13**). Compounds **4**, **6**, **11**−**13** were isolated from genus *Clerodendrum* Linn. for the first time. Compounds **4**, **6**, **10**−**13** were isolated from *Clerodendrum trichotomum* Thunb. for the first time.

Key words *Clerodendrum trichotomum* Thunb.; chemical constituents; isolation; structural identification

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海州常山为大青属 *Clerodendrum* Linn. 植物,落叶灌木或小乔木,又名臭梧桐、泡火桐、后庭花、香楸、地梧桐、矮桐子等。分布于我国华北、华东、中南、西南等地,朝鲜、日本以及菲律宾北部也有分布[1]。其味苦、微辛,性平,具有祛风除湿、平肝降压、解毒杀虫的功效。主治风湿痹痛,半身不遂,高血压病,偏头痛,疟疾,痢疾等[2]。目前,从海州常山中分离得到的化学成分类型主要有苯丙素类[3-6]、黄酮类[7]、二萜[8-9]、三萜[10]和甾体化合物[11]。现代药理学研究发现海州常山具有抗氧化[3]、抗 HIV 病毒[4]、抗哮喘[5]、降压[6]、细胞毒[9,11]及抗炎[12]等多种生物活性。海州常山在民间应用广泛,根、茎、叶、花、果皆可入药,且可治疗多种疾病,但目前研究的部位多以叶、根居多,茎部位研究较少。为了更好地开发海州常山的药用价值,阐明其药效物质基础,笔者对海州常山茎化学成分进行了系统的研究。继笔者从海州常山茎中分离得到二萜[13]、蒽醌和木脂素[14]后,本实验报道分离并鉴定 13 个化合物,包括 4 个三萜:木栓酮(friedelin,**1**),白桦脂酸(betulinic acid,**2**),蒲公英萜醇(taraxerol,**3**)和 3-羟基-30-去甲基-20-酮基-28-羽扇豆酸(3-hydroxy-30-nor-20-oxo-28-lupanoic acid, platanic acid, **4**);2 个黄酮:金合欢素(acacetin,**5**)和 5,7-二羟基 3′,4′-二甲氧基黄酮(5,7-dihydroxy 3′,4′-dimethoxyflavone,**6**);4 个甾体:β-谷甾醇(β-sitosterol,**7**),豆甾醇(stigmasterol,**8**),胡萝卜苷(daucosterol,**9**)和豆甾醇-3-*O*-葡萄糖苷(stigmasterol-3-*O*-glucopyranoside,**10**);3 个其他类型化合物:异香草醛(isovanillin,**11**),邻苯二甲酸二丁酯(dibutyl phthalate,**12**)和丁香醛(syringaldehyde,**13**)。其中化合物 **4**,**6**,**11** ~ **13** 均为首次从该属植物中分离得到,化合物 **4**,**6**,**10** ~ **13** 为首次从该物种中分离得到。

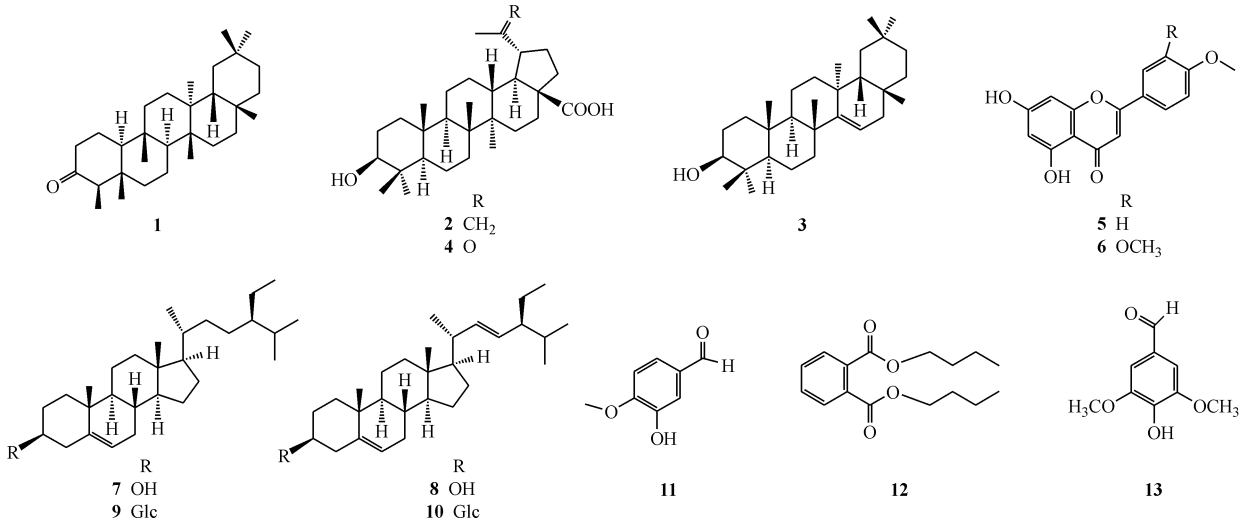

Figure 1　Structures of compounds **1**−**13** from the stems of *Clerodendrum trichotomum* Thunb.

1　材　料

X-4 型数字显示双目显微熔点测定仪(温度未校正,北京泰克仪器有限公司制造);Bruker Avance-300 和 Bruker Avance-500 核磁共振仪;Agilent HP-100 型质谱仪;Sephadex LH-20 为 Pharmacia 产品;薄层色谱、柱色谱用硅胶均为青岛海洋化工集团产品;其余试剂均为分析纯试剂。

海州常山药材 2012 年 11 月采自江苏省南京市,经江苏省中国科学院植物研究所姚淦研究员鉴定为马鞭草科大青属植物海州常山 *Clerodendron trichotomum* Thunb. 的干燥茎,凭证标本(标本编号 No. CT20121116)保存在中国药科大学中药学院天然药物化学教研室。

2　提取与分离

海州常山干燥茎 15 kg,铡细,粉碎,用 85% 的乙醇回流提取 3 次,浓缩至无醇味后加适量水混悬,依次用石油醚、乙酸乙酯和正丁醇萃取。乙酸乙酯部位 70 g 经硅胶柱色谱,以石油醚-乙酸乙酯(60∶1→0∶100)梯度洗脱,减压蒸馏,得到 5 个组分 f1 ~ f5。将 f1 组分用硅胶柱色谱梯度洗脱(石油醚-乙酸乙酯系统),经反复硅胶柱色谱、ODS 柱色谱、凝胶柱色谱、制备薄层色谱、重结晶等多种分

离纯化手段,从中分离得到化合物 **1**(266.6 mg),化合物 **2**(50.6 mg),化合物 **3**(56.7 mg),化合物 **7**(28.2 mg),化合物 **8**(20.2 mg),化合物 **11**(48.7 mg)和化合物 **12**(221.9 mg)。将 f3 组分经硅胶柱色谱梯度洗脱(二氯甲烷-甲醇系统),经反复硅胶柱色谱、ODS 柱色谱、凝胶柱色谱、制备薄层色谱、重结晶等多种分离纯化手段,从中分离得到化合物 **4**(11.3 mg),化合物 **5**(6.9 mg),化合物 **6**(3.4 mg)和化合物 **13**(8.4 mg)。将 f5 组分经硅胶柱色谱梯度洗脱(二氯甲烷-甲醇系统),用以上分离方法得到化合物 **9**(548.2 mg)和化合物 **10**(516.2 mg)。

3 结构鉴定

化合物 **1** 白色针状结晶,溶于二氯甲烷、三氯甲烷。Liebermann-Burchard 反应阳性。EI-MS *m/z*:426[M]$^+$,分子式 $C_{30}H_{50}O$。^{1}H NMR($CDCl_3$,300 MHz) δ:1.20(3H,s,28-H),1.07(3H,s,27-H),1.03(3H,s,26-H),1.02(3H,s,30-H),0.97(3H,s,29-H),0.90(3H,d,J = 6.7 Hz,23-H),0.89(3H,s,25-H)和 0.74(3H,s,24-H)。^{13}C NMR($CDCl_3$,75 MHz) δ:22.3(C-1),41.5(C-2),213.1(C-3),58.2(C-4),42.1(C-5),41.3(C-6),18.2(C-7),53.1(C-8),37.4(C-9),59.5(C-10),35.6(C-11),30.5(C-12),39.7(C-13),38.3(C-14),32.4(C-15),36.0(C-16),30.0(C-17),42.8(C-18),35.3(C-19),28.2(C-20),32.8(C-21),39.2(C-22),6.8(C-23),14.6(C-24),17.9(C-25),20.2(C-26),18.6(C-27),32.1(C-28),35.0(C-29),31.8(C-30)。对照波谱数据与文献[15]报道一致,鉴定该化合物为木栓酮(friedelin)。

化合物 **2** 白色针状结晶,易溶于二氯甲烷、三氯甲烷等。Liebermann-Burchard 反应阳性。ESI-MS *m/z*:455[M - H]$^-$,分子式 $C_{30}H_{48}O_3$。^{1}H NMR($CDCl_3$,300 MHz) δ:4.74(1H,br.s,H-29a),4.61(1H,br.s,H-29b),3.19(1H,m,H-3),3.00(1H,m,H-19),1.69(3H,s,H-30),0.98(3H,s,H-27),0.97(3H,s,H-23),0.94(3H,s,H-25),0.83(3H,s,H-26),0.76(3H,s,H-24)。^{13}C NMR($CDCl_3$,75 MHz) δ:38.7(C-1),27.4(C-2),79.0(C-3),38.9(C-4),55.4(C-5),18.3(C-6),34.4(C-7),40.7(C-8),50.6(C-9),37.2(C-10),20.9(C-11),25.5(C-12),38.4(C-13),42.5(C-14),30.6(C-15),32.2(C-16),56.3(C-17),46.9(C-18),49.3(C-19),150.4(C-20),29.7(C-21),37.0(C-22),28.0(C-23),15.3(C-24),16.0(C-25),16.1(C-26),14.7(C-27),177.6(C-28),109.7(C-29),19.4(C-30)。对照波谱数据与文献[16]报道一致,鉴定该化合物为白桦脂酸(betulinic acid)。

化合物 **3** 白色粉末,易溶于二氯甲烷、三氯甲烷等。Liebermann-Burchard 反应阳性。^{1}H NMR($CDCl_3$,300 MHz) δ:5.53(1H,dd,J = 8.2,3.3 Hz,15-H),3.19(1H,dd,J = 10.2,5.0 Hz,3-H),1.09(3H,s,H-27),0.98(3H,s,H-23),0.95(3H,s,H-25),0.93(3H,s,H-26),0.91(3H,s,H-29),0.91(3H,s,H-30),0.82(3H,s,H-28),0.80(3H,s,H-24)。^{13}C NMR($CDCl_3$,75 MHz) δ:37.8(C-1),27.2(C-2),79.1(C-3),39.0(C-4),55.5(C-5),18.8(C-6),35.1(C-7),38.8(C-8),48.8(C-9),38.0(C-10),17.5(C-11),35.8(C-12),37.7(C-13),158.1(C-14),116.9(C-15),36.7(C-16),38.0(C-17),49.3(C-18),41.3(C-19),28.8(C-20),33.7(C-21),33.1(C-22),28.0(C-23),15.4(C-24),15.4(C-25),29.9(C-26),25.9(C-27),29.8(C-28),33.3(C-29),21.3(C-30)。对照波谱数据与文献[17]报道一致,鉴定该化合物为蒲公英萜醇(taraxerol)。

化合物 **4** 白色粒状结晶,易溶于二氯甲烷、三氯甲烷等。Liebermann-Burchard 反应阳性。ESI-MS *m/z*:457[M - H]$^-$,分子式 $C_{29}H_{46}O_4$。^{1}H NMR($CDCl_3$,300 MHz) δ:2.19(3H,s,H-23),1.02(3H,s,H-27),0.98(3H,s,H-24),0.93(3H,s,H-26),0.84(3H,s,H-25),0.77(3H,s,H-23)。^{13}C NMR($CDCl_3$,75 MHz) δ:38.7(C-1),27.3(C-2),78.9(C-3),38.8(C-4),55.3(C-5),18.2(C-6),34.2(C-7),40.6(C-8),50.3(C-9),37.2(C-10),20.8(C-11),27.2(C-12),37.5(C-13),42.2(C-14),28.3(C-15),31.5(C-16),36.2(C-17),49.2(C-18),51.2(C-19),212.2(C-20),29.7(C-21),36.7(C-22),15.3(C-23),28.0(C-24),16.1(C-25),16.0(C-26),14.7(C-27),181.2(C-28),30.1(C-29)。对照波谱数据与文献[18 - 19]报道一致,鉴定该化合物为 3-羟基-30-去甲基-20-酮基-28-羽扇豆酸(3-hydroxy-30-nor-20-oxo-28-lupanoic acid,platanic acid)。

化合物 **5** 浅黄色粉末,不溶于二氯甲烷和甲醇,易溶于 DMSO 等。与 $FeCl_3$ 溶液、$AlCl_3$ 呈阳性

反应。ESI-MS m/z :313 [M - H]$^-$,分子式 $C_{17}H_{14}O_6$。^{1}H NMR (DMSO-d_6, 500 MHz) δ: 12.92 (1H,s,5-OH),10.81(1H,s,7-OH),7.68(1H,dd, J = 8.5,2.0 Hz,H-6′),7.57(1H,d,J = 2.1 Hz,H-2′),7.13(1H,d,J = 8.6 Hz,H-5′),6.96(1H,s,H-3),6.53(1H,d,J = 2.0 Hz,H-8),6.21(1H,d,J = 2.0 Hz,H-6),3.88(3H,s,3′-OCH_3),3.86(3H,s,4′-OCH_3)。波谱数据与文献[20]报道一致,鉴定该化合物为 5,7-二羟基 3′,4′-二甲氧基黄酮(5,7-dihydroxy 3′,4′-dimethoxyflavone)。

化合物 **6**　浅黄色针状结晶,不溶于二氯甲烷和甲醇,易溶于 DMSO 等。与 $FeCl_3$ 溶液、$AlCl_3$ 呈阳性反应。ESI-MS m/z: 283 [M - H]$^-$,分子式 $C_{16}H_{12}O_5$。^{1}H NMR (DMSO-d_6, 300 MHz) δ: 12.92 (1H,s,5-OH),10.81(1H,s,7-OH),8.03(2H,d, J = 8.3 Hz,H-2′,6′),7.10(2H,d,J = 8.3 Hz,H-3′,5′),6.86(1H,s,H-3),6.50(1H,s,H-8),6.20 (1H,s,H-6),3.86(3H,s,4′-OCH_3)。波谱数据与文献[21]报道一致,鉴定该化合物为金合欢素(acacetin)。

化合物 **7**　白色针状结晶,易溶于二氯甲烷、三氯甲烷等。ESI-MS m/z:413 [M - H]$^-$,分子式 $C_{29}H_{50}O$。Liebermann-Burchard 反应阳性,TLC 与 β-谷甾醇对照品一致,且混合熔点不下降,故该化合物鉴定为 β-谷甾醇(β-sitosterol)。

化合物 **8**　白色针晶,易溶于二氯甲烷、三氯甲烷等。EI-MS m/z: 412 [M]$^+$, 分子式 $C_{29}H_{48}O$。^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.36 (1H, d, J = 5.1 Hz, H-6), 5.15 (1H, dd, J = 15.7, 6.0 Hz,H-22),5.06(1H,dd,J = 15.7,5.8 Hz,H-23), 3.53(1H,t,J = 4.5 Hz,H-3),0.94(3H,d,J = 6.8 Hz,21-CH_3), 0.86 (3H, t, J = 7.2 Hz, 29-CH_3), 0.84(3H,d,J = 7.0 Hz,26-CH_3),0.83(3H,d,J = 7.0 Hz,27-CH_3),0.81(3H,s,19-CH_3),0.69(3H, s,18-CH_3)。^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.2 (C-1),31.7 (C-2),71.8 (C-3),39.7 (C-4),140.8 (C-5),121.7 (C-6),31.7 (C-7),31.9 (C-8),50.2 (C-9),37.3 (C-10),21.5 (C-11),39.8 (C-12),42.3 (C-13),55.9 (C-14),24.3 (C-15),29.4 (C-16), 56.9(C-17),12.3(C-18),19.8(C-19),40.2(C-20), 21.3(C-21),137.2(C-22),130.1(C-23),52.0(C-24),31.9(C-25),18.6(C-26),21.2(C-27),25.7(C-28),12.4(C-29)。以上波谱数据与文献报道[22]基本一致。且样品与对照品混合测熔点不下降,故鉴定该化合物为豆甾醇(stigmasterol)。

化合物 **9**　白色粉末,不溶于二氯甲烷、三氯甲烷和甲醇等,易溶于吡啶。Liebermann-Burchard 反应阳性,Molish 反应阳性。与胡萝卜苷对照品共薄层对照,R_f 及显色行为均一致,且与对照品混合后熔点不下降,故鉴定该化合物为胡萝卜苷(daucosterol)。

化合物 **10**　白色粉末,不溶于二氯甲烷、三氯甲烷和甲醇等,易溶于吡啶。Liebermann-Burchard 反应阳性,Molish 反应阳性。ESI-MS m/z:575 [M + H]$^+$,分子式 $C_{35}H_{58}O_6$。^{1}H NMR (300 MHz, C_5D_5N) δ: 5.32(1H,s,H-6),5.16(1H,d,J = 8.4 Hz,H-22), 4.97(1H,d,J = 8.4 Hz,H-23),3.61(1H,m,H-3), 1.03(3H,d,J = 6.5 Hz,21-CH_3),1.01(3H,t,J = 7.1 Hz,29-CH_3),0.94(3H,d,J = 7.0 Hz,26-CH_3),0.91 (3H,d,J = 6.9 Hz,27-CH_3),0.75(3H,s,19-CH_3), 0.56(3H,s,18-CH_3)。^{13}C NMR (75 MHz, C_5D_5N) δ: 39.4 (C-1), 29.3 (C-2), 78.6 (C-3), 39.3 (C-4), 140.9 (C-5), 121.9 (C-6), 31.2 (C-7), 31.0 (C-8), 49.8 (C-9), 36.9 (C-10), 22.4 (C-11), 40.0 (C-12), 42.5 (C-13), 56.3 (C-14), 24.6 (C-15), 29.1 (C-16), 56.0 (C-17), 11.6 (C-18), 19.4 (C-19), 40.4 (C-20), 23.6 (C-21), 137.6 (C-22), 130.3 (C-23), 50.4 (C-24), 32.0 (C-25), 20.8 (C-26), 19.3 (C-27), 25.5 (C-28), 11.5 (C-29), 102.6 (C-1′), 75.3 (C-2′), 78.6 (C-3′), 71.7 (C-4′), 78.1 (C-5′), 62.9 (C-6′)。与文献[23]数据基本一致,确定为豆甾醇-3-*O*-葡萄糖苷。

化合物 **11**　黄色胶状固体,易溶于二氯甲烷、三氯甲烷等。三氯化铁-铁氰化钾显色反应呈阳性。ESI-MS m/z: 151 [M - H]$^-$,分子式 $C_8H_8O_3$。^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.80 (1H, s, 1-CHO), 6.49 (1H, br. s, 3-OH), 7.42 (1H, br. s, 2-H), 7.40 (1H, br. s, 6-H), 7.02 (1H, d, J = 8.5 Hz, 5-H), 3.93 (3H, s, 4-OCH_3)。^{13}C NMR ($CDCl_3$, 75 MHz) δ: 129.8 (C-1), 108.9 (C-2), 147.2 (C-3), 151.8 (C-4), 114.4 (C-5), 127.5 (C-6), 190.9 (1-CHO), 56.0 (4-OCH_3)。对照波谱数据与文献[24]报道一致,鉴定该化合物为异香草醛(isovanillin)。

化合物 **12**　黄色油状液体,易溶于二氯甲烷、三氯甲烷等。ESI-MS m/z:301 [M + Na]$^+$,分子式 $C_{16}H_{22}O_4$。^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.71 (2H, dd, J = 5.6, 3.4 Hz, H-3 和 H-6), 7.51 (2H, m, H-4 和

H-5),4.30(4H,t,J = 6.7 Hz,H_2-8 和 H_2-8′),1.72(4H,m,H_2-9 和 H_2-9′),1.43(4H,m,H_2-10 和 H_2-10′),0.95(6H,t,J = 7.4 Hz,H_3-11 和 H_3-11′)。^{13}C NMR($CDCl_3$,75 MHz) δ:130.8(C-1,2),128.8(C-3,6),132.3(C-4,5),167.6(C-7,7′),65.5(C-8,8′),30.5(C-9,9′),19.1(C-10,10′),13.6(C-11,11′)。对照波谱数据与文献[25]报道一致,鉴定该化合物为邻苯二甲酸二丁酯(dibutyl phthalate)。

化合物 **13** 棕黄色粉末,易溶于二氯甲烷、三氯甲烷,不溶于甲醇。ESI-MS m/z:183[M + H]$^+$,分子式 $C_9H_{10}O_4$。^{1}H NMR($CDCl_3$,300 MHz) δ:9.82(1H,s,1-CHO),7.15(2H,s,H-2,6),6.09(1H,s,4-OH),3.97(6H,s,H-3,5-OCH_3)。^{13}C NMR($CDCl_3$,75 MHz) δ:128.4(C-1),106.8(C-2,6),147.4(C-3,5),140.9(C-4),190.6(1-CHO),56.5(C-3,5-OCH_3)。对照波谱数据与文献[26]报道一致,鉴定该化合物为丁香醛(syringaldehyde)。

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