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中国海南半红树植物海漆的化学成分研究

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摘　要:对生长于中国海南的半红树植物海漆(*Excoecaria agallocha* L.)的化学成分进行分离鉴定。用硅胶柱层析,凝胶柱层析和高效液相色谱对海漆的乙酸乙酯萃取物进行分离纯化,从中分离得到 15 个化合物,并运用现代波谱技术分别鉴定为:(±)-丁香脂素(**1**)、(+)-麦迪奥脂素(**2**)、(±)-buddlenol C(**3**)、*threo*-buddlenol C(**4**)、(±)-ficusesquilignan A(**5**)、(-)-(7*R*,7′*R*,7″*S*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5,5′,5″-hexamethoxy- 7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol(**6**)、salicifoliol(**7**)、臭矢菜素 C(**8**)、curcasinlignan A(**9**)、东莨菪亭(**10**)、秦皮素(**11**)、异秦皮素(**12**)、金色酰胺醇(**13**)、金色酰胺醇酯(**14**)、丁香醛(**15**)。其中化合物 **2** ~ **15** 均为首次从该种植物中分离得到。

关键词:半红树植物;海漆;化学成分;木脂素

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Chemical Constituents of Semi-Mangrove Plant *Excoecaria agallocha* L.

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Abstract: The chemical constituents of semi-mangrove *Excoecaria agallocha* L. collected at Hainan island, China were isolated by silica gel column chromatography and preparative HPLC. Fifteen compounds were finally obtained from the EtOAc extract of *E. agallocha* L. On the basis of modern spectral data, they were identified as (±)-syringaresinol (**1**), (+)-medioresinol (**2**), (±)-buddlenol C (**3**), *threo*-buddlenol C (**4**), (±)-ficusesquilignan A (**5**), (-)-(7*R*,7′*R*,7″*S*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5,5′,5″-hexamethoxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′- sesquineolignan-7″,9″-diol (**6**), salicifoliol (**7**), cleomiscosin C (**8**), curcasinlignan A (**9**), scopoletin (**10**), fraxidin (**11**), *iso*-fraxidin (**12**), aurantiamide (**13**), aurantiamide acetate (**14**), syringaldehyde (**15**). Compounds **2-15** were isolated from this plant for the first time.

Key words: semi-mangroves; *Excoecaria agallocha* L.; chemical constituent; lignan

海漆(*Excoecaria agallocha* L.)为大戟科(Euphorbiaceae)海漆属(*Excoecaria*)半红树植物[1]。海漆属植物多为灌木或乔木,全世界共约 40 余种,分布于亚洲,非洲和大洋洲的热带地区。在我国产 6 种,即海漆 *E. agallocha* L、红背桂花 *E. cochinchinensis*、绿背桂花 *E. formosana*、鸡尾木 *E. venenata*、兰屿土沉香 *E. kawakamii* 和云南土沉香 *E. acerifolia*。主要分布于东南沿海的浅滩上[2]。海漆是该属植物中唯一的半红树植物,化学成分多样,其主要次生代谢产物包括萜类、木脂素、香豆素、生物碱等。海漆药用主治体实便秘、溃疡、手足肿毒等症[3]。此外,近年来其细胞毒性和抗艾滋病病毒活性也引起了广泛关注[4]。为了从海漆中继续找寻具有药用价值的生物活性成分,本实验对产自中国海南的半红树植物海漆的化学成分进行了进一步的研究,从中分离并鉴定了 15 个化合物分别为:(±)-丁香脂素(**1**)、(+)-麦迪奥脂素(**2**)、(±)-buddlenol C(**3**)、*threo*-buddlenol C(**4**)、(±)-ficusesquilignan A(**5**)、(-)-(7*R*,7′*R*,7″*S*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5,5′,5″-hexamethoxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol(**6**)、salicifoliol(**7**)、臭矢菜素 C(**8**)、curcasinlignan A(**9**)、东莨菪亭(**10**)、秦皮素(**11**)、异秦皮素(**12**)、金色酰胺醇(**13**)、金色酰胺醇酯(**14**)、丁香醛(**15**)。结构见图 **1**。其中化合物 **2** ~ **15** 均为首次从该种植物中分离得到。

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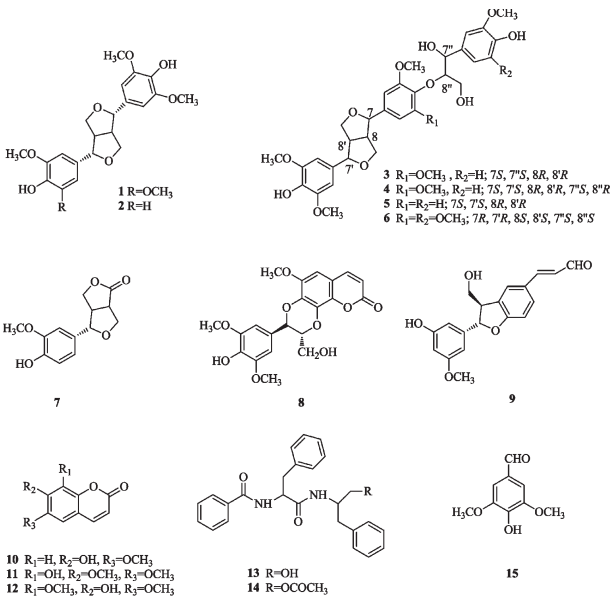

图 1　化合物 1 ~ 15 的化学结构

Fig. 1　Chemical structures of compounds **1-15**

1　仪器与材料

高效液相色谱仪(美国 Waters 公司) Waters 2695Q、2535Q 型泵和 2998 二极管阵列检测器。AVANCE III 400 型核磁共振波谱仪(瑞士 Bruker 公司),Ama Zon SL 离子阱电喷雾质谱仪(德国 Bruker Daltonics 公司),Sephadex LH-20(日本三菱化学),正相硅胶(青岛海洋化工厂),C_{18} 反相硅胶(日本 YMC 公司),YMC C_{18} 色谱柱(250 mm × 10 mm,5 μm),色谱纯乙腈、甲醇(德国 Merck 公司),分析纯丙酮、氯仿、甲醇、醋酸乙酯均重蒸。

海南半红树植物海漆的枝条于 2008 年 11 月采集于中国海南红树林湿地。由暨南大学海洋药物研究中心吴军教授鉴定为海漆(*Excoecaria agallocha* L.)。样品标本保存于暨南大学药学院海洋药物研究中心。

2　提取与分离

将干燥的海漆枝条(7 kg)粉碎后用 95% 乙醇室温提取 5 次,减压浓缩后得到粗浸膏 268.7 g。用水混悬后依次用石油醚、乙酸乙酯、正丁醇梯度萃取,得到乙酸乙酯萃取物 51.9 g。经正相硅胶(100-200 目)柱分离,以氯仿:甲醇($V_{氯仿}/V_{甲醇}$ = 100∶0、50∶1、30∶1、20∶1、10∶1、5∶1、1∶1)梯度洗脱,得到 173 个流分。利用薄层色谱和高效液相色谱分析后合并第 30-44 号流分(10 g)为 R1,第 45-51 号流分(3.6 g)为 R2。R1 经凝胶柱层析($V_{氯仿}/V_{甲醇}$ = 1∶1)脱色素和反相硅胶柱层析,丙酮-水(40∶60→100∶0)梯度洗脱得到 64 个流分。

流分 1-11 合并(701.9 mg)经反相硅胶柱色谱分离,丙酮-水(30∶70→70∶30)梯度洗脱,得到 8 个流分。流分 2、3、5、6 经高效液相色谱制备得到化合物 **1**(5 mg)、**2**(5 mg)、**3**(2 mg)、**10**(5 mg)、**11**(10 mg)、**12**(3 mg)、**15**(3 mg)。

其中流分 12-14 合并经高效液相色谱制备得到化合物 **13**(5 mg);流分 15-17 合并经高效液相色谱制备得到化合物 **14**(10 mg)。

R2 经凝胶柱层析($V_{氯仿}/V_{甲醇}$ = 1∶1)脱色素和反相硅胶柱层析,丙酮-水(30∶70→100∶0)梯度洗脱得到 50 个流分。

其中流分 3 ~ 5 合并经高效液相色谱制备得到化合物 **9**(1 mg);流分 6-8 合并经高效液相色谱制备得到化合物 **4**(5 mg)、**5**(1 mg)、**6**(2.2 mg);流分 9-12 合并经高效液相色谱制备得到化合物 **8**(1 mg);流分 24 经高效液相色谱制备得到化合物 **7**(1 mg)。

3　结构鉴定

化合物 1　无色油状物,易溶于氯仿。ESI(-)-MS *m/z* 417.21 [M-H]$^-$,分子式为 $C_{22}H_{26}O_8$。^{1}H NMR ($CDCl_3$,400 MHz) δ:6.58 (4H, s, H-2, H-2′, H-6, H-6′),5.52 (2H, s, 4, 4′-OH),4.72 (2H, d, *J* = 4.10 Hz, H-7, H-7′),3.09 (2H, m, H-8, H-8′),4.28 (2H, dd, *J* = 9.2 Hz, 7.2 Hz, H-9b, H-9b′),3.90 (12H, s, 3, 3′, 5, 5′-OCH_3),3.92 (2H, overlapped, H-9a, H-9a′);^{13}C NMR ($CDCl_3$,100 MHz) δ:132.5 (C-1, C-1′),103.1 (C-2, C-2′, C-6, C-6′),147.6 (C-3, C-3′, C-5, C-5′),134.7 (C-4, C-4′),86.5 (C-7, C-7′),54.8 (C-8, C-8′),72.2 (C-9, C-9′),56.8 (3, 3′, 5, 5′-OCH_3)。以上数据与文献[5]报道一致,因此确定化合物 **1** 为(±)-丁香脂素。

化合物 2　淡黄色颗粒,易溶于氯仿。ESI(-)-MS *m/z* 387.24 [M-H]$^-$,分子式为 $C_{21}H_{24}O_7$。^{1}H NMR ($CDCl_3$,400 MHz) δ:6.58 (2H, s, H-2′, H-6′),5.50 (1H, s, 4-OH),5.61 (1H, s, 4′-OH),4.75 (1H, d, *J* = 4.5 Hz, H-2),3.10 (2H, m, H-1, H-5),4.72 (1H, d, *J* = 4.6 Hz, H-6),4.27 (2H, m, H-4b, H-8b),6.90 (2H, m, H-2″, H-5″),6.80 (1H, dd, *J* = 1.8 Hz, 8.0 Hz, H-6″),3.90 (6H, s, 3′, 5′-

OCH_3),3.91 (3H,s,3′-OCH_3),3.88 (2H,m,H-4a,H-8a);^{13}C NMR ($CDCl_3$,100 MHz) δ:133.0 (C-1′),102.8 (C-2′,C-6′),147.3 (C-3′,C-5′),145.4 (C-4′),54.2 (C-1),54.5 (C-5),86.1 (C-2),71.7 (C-4),86.3 (C-6),72.0 (C-8),132.3 (C-1″),108.7 (C-2″),146.8 (C-3″),134.4 (C-4″),114.4 (C-5″),119.1 (C-6″),56.5 (3′,5′-OCH_3),56.1 (3″-OCH_3)。以上数据与文献[6]报道一致,因此确定化合物**2**为(+)-麦迪奥脂素。

化合物3 无色油状,易溶于氯仿。ESI(-)-MS *m/z* 613.34[M-H]$^-$,分子式为 $C_{32}H_{38}O_{12}$。^{1}H NMR ($CDCl_3$,400 MHz) δ:6.65 (2H,s,H-2,H-6),6.61 (2H,s,H-2′,H-6′),4.80 (2H,m,H-7,H-7′),3.14 (2H,m,H-8′,H-8),4.33 (2H,m,H-9a,H-9′a),6.98 (1H,s,H-2″),6.88 (1H,d,*J* = 8.1 Hz,H-5″),6.77 (1H,dd,*J* = 1.8 Hz,8.3 Hz,H-6″),5.02 (1H,brd,H-7″),4.15 (1H,m,H-8″),3.52 (1H,brd,H-9″b),3.92 (15H,s,3,5,3′,5′,3″-OCH_3),3.96 (3H,m,H-9b,H-9′b,9″a),5.61 (1H,s,4-OH),5.54 (1H,s,4″-OH),5.02 (1H,brd,H-7″);^{13}C NMR ($CDCl_3$,100 MHz) δ:137.9 (C-1),153.6 (C-3,C-5),134.36 (134.40) (C-4),86.1 (C-7),54.58 (54.62) (C-8),72.19 (72.23) (C-9),132.1 (C-1′),102.9 (C-2,C-6,C-2′,C-6′),147.3 (C-3′,C-5′),134.48 (C-4′),86.1 (C-7′),54.5 (C-8′),71.88 (71.90) (C-9′),131.4 (C-1″),108.4 (C-2″),146.7 (C-3″),145.0 (C-4″),114.3 (C-5″),119.0 (C-6″),72.63 (72.66) (C-7″),87.21 (87.25) (C-8″),60.7 (C-9″),56.5 (3,5-OCH_3),56.4 (3′,5′-OCH_3),56.1 (3″-OCH_3)。以上数据与文献[7]报道一致,因此确定化合物**3**为(±)-buddlenol C。

化合物4 无色油状,易溶于氯仿。ESI(-)-MS *m/z* 613.38[M-H]$^-$,分子式为 $C_{32}H_{38}O_{12}$。^{1}H NMR ($CDCl_3$,400 MHz) δ:6.58 (2H,s,H-2,H-6),6.62 (2H,s,H-2′,H-6′),4.75 (2H,m,H-7,H-7′),3.10 (2H,m,H-8,H-8′),4.30 (2H,m,H-9a,H-9′a),6.96 (1H,brs,H-2″),5.53 (1H,s,4″-OH),6.87 (1H,m,H-5″),6.95 (1H,m,H-6″),5.01 (1H,d,*J* = 8.7 Hz,H-7″),3.56 (1H,m,H-9″a),3.32 (1H,m,H-9″b),3.90 (15H,s,3,5,3′,5′,3″-OCH_3),3.94 (3H,m,H-8″,H-9b,H-9′b);^{13}C NMR ($CDCl_3$,100 MHz) δ:138.1 (C-1),103.0 (C-2,C-2′,C-6,C-6′),153.4 (C-3,C-5),134.6 (C-4,C-4′),86.2 (C-7),54.7 (C-8),72.3 (C-9),132.1 (C-1′,C-1″),147.4 (C-3′,C-5′),86.1 (C-7′),54.5 (C-8′),72.0 (C-9′),110.0 (C-2″),146.7 (C-3″),145.6 (C-4″),114.5 (C-5″),120.6 (C-6″),74.3 (C-7″),89.3 (C-8″),60.8 (C-9″),56.6 (3,5-OCH_3),56.5 (3′,5′-OCH_3),56.2 (3″-OCH_3)。以上数据与文献[8]报道一致,因此确定化合物**4**为 *threo*-buddlenol C。

化合物5 无色油状,易溶于氯仿。ESI(-)-MS *m/z* 583.34[M-H]$^-$,分子式为 $C_{31}H_{36}O_{11}$。^{1}H NMR ($CDCl_3$,400 MHz) δ:6.7 (2H,s,H-2,H-6),4.8 (2H,dd,*J* = 1.6 Hz,8.3 Hz,H-7,H-7′),3.1 (2H,m,H-8′,H-8),4.3 (2H,m,H-9a,H-9′a),7.0 (1H,s,H-2″),6.8 (5H,m,H-2′,H-5′,H-6′,H-5″,H-6″),5.0 (1H,m,H-7″),4.1 (1H,m,H-8″),3.5 (1H,m,H-9″b),3.91 (12H,s,3,5,3′,3″-OCH_3),3.97 (3H,m,H-9b,H-9′b,9″a);^{13}C NMR ($CDCl_3$,100 MHz) δ:138.0 (C-1),102.9 (C-2,C-6),153.6 (C-3,C-5),134.4 (C-4),86.16 (86.19) (C-7),54.63 (54.69) (C-8),72.27 (72.30) (C-9),132.9 (C-1′),108.7 (C-2′),146.8 (C-3′),145.4 (C-4′),114.4 (C-5′),119.1 (C-6′),85.8 (C-7′),54.2 (C-8′),71.67 (71.70) (C-9′),131.37 (131.40) (C-1″),108.4 (C-2″),146.7 (C-3″),145.0 (C-4″),114.3 (C-5″),118.9 (C-6″),72.63 (72.66) (C-7″),87.21 (87.26) (C-8″),60.7 (C-9″),56.4 (3,5-OCH_3),56.14 (3′-OCH_3),56.12 (3″-OCH_3)。以上数据与文献[7]报道一致,因此确定化合物**5**为(±)-ficusesquilignan A。

化合物6 白色粉末,易溶于氯仿。ESI(-)-MS *m/z* 643.40[M-H]$^-$,分子式为 $C_{33}H_{40}O_{13}$。^{1}H NMR ($CDCl_3$,400 MHz) δ:6.70 (2H,s,H-2,H-6),6.65 (2H,s,H-2′,H-6′),4.78 (2H,t,*J* = 4.6 Hz,H-7,H-7′),3.11 (2H,m,H-8,H-8′),4.30 (2H,m,H-9a,H-9′a),6.61 (2H,s,H-2″,H-6″),5.04 (1H,d,*J* = 8.8 Hz,H-7″),3.35 (1H,m,H-9″a),3.61 (1H,m,H-9″b),3.92 (6H,s,3″,5″-OCH_3),3.93 (6H,s,3′,5′-OCH_3),3.95 (6H,s,3,5-OCH_3),3.97 (3H,m,H-8″,H-9b,H-9′b);^{13}C NMR ($CDCl_3$,100 MHz) δ:138.0 (C-1),102.8 (C-2,C-2′,C-6,C-6′),153.3 (C-3,C-5),134.6 (C-4),86.1 (C-7),54.6 (C-8),72.2 (C-9),132.1 (C-1′),147.3 (C-3′,C-

5′),134.7 (C-4′),86.0 (C-7′),54.5 (C-8′),71.9 (C-9′),131.1 (C-1″),104.1 (C-2″),147.1 (C-3″,C-5″),134.5 (C-4″),102.8 (C-6″),74.5 (C-7″),89.3 (C-8″),60.8 (C-9″),56.5 (3,5,3′,5′-OCH_3),56.4 (3″,5″-OCH_3)。以上数据与文献[9]报道一致,因此确定化合物 **6** 为(-)-(7*R*,7′*R*,7″*S*,8*S*,8′*S*,8″*S*)-4′,4″-dihydroxy-3,3′,3″,5,5′,5″-hexamethoxy-7,9′:7′,9-diepoxy-4,8″-oxy-8,8′-sesquineolignan-7″,9″-diol。

化合物 7 白色粉末,易溶于氯仿。ESI(-)-MS *m/z* 249.18[M-H]$^-$,分子式为 $C_{13}H_{14}O_5$。^{1}H NMR ($CDCl_3$,400 MHz) δ:3.45 (1H,m,H-1),4.50 (1H,m,H-4a),4.33 (1H,d,*J* = 9.4 Hz,H-4b),3.12 (1H,m,H-5),4.61(1H,d,*J* = 7.1 Hz,H-6),4.37 (1H,d,*J* = 9.4 Hz,H-8a),4.19 (1H,d,*J* = 9.4 Hz,3.6 Hz,H-8b),6.90 (2H,m,H-2′,H-6′),6.80 (1H,d,*J* = 8.0 Hz,H-5′),3.91 (3H,s,3′-OCH_3),5.65 (1H,s,4′-OH);^{13}C NMR ($CDCl_3$,100 MHz) δ:48.3 (C-1),178.4 (C-2),70.0 (C-4),46.4 (C-5),86.3 (C-6),70.2 (C-8),131.2 (C-1′),108.6 (C-2′),147.2 (C-3′),146.3 (C-4′),114.7 (C-5′),119.5 (C-6′),56.4 (3′-OCH_3)。以上数据与文献[10]报道一致,因此确定化合物 **7** 为 salicifoliol。

化合物 8 白色针晶,易溶于氯仿。ESI(-)-MS *m/z* 415.23[M-H]$^-$,分子式为 $C_{21}H_{20}O_9$。^{1}H NMR ($CDCl_3$,400 MHz) δ:6.36 (1H,d,*J* = 9.5 Hz,H-3),7.66 (1H,d,*J* = 9.5 Hz,H-4),6.57 (1H,s,H-5),6.70 (2H,s,H-2′,H-6′),5.06 (1H,d,*J* = 8.28 Hz,H-7′),4.14 (1H,m,H-8′),3.61 (1H,d,*J* = 11.7 Hz,H-9′a),3.98 (1H,d,*J* = 13.0 Hz,H-9′b),3.94 (6H,s,3′,5′-OCH_3),3.92 (3H,s,6-OCH_3),2.30 (1H,brs,9′-OH),5.65 (1H,s,4′-OH);^{13}C NMR ($CDCl_3$,100 MHz) δ:161.0 (C-2),114.3 (C-3),144.0 (C-4),100.4 (C-5),146.1 (C-6),137.6 (C-7),132.3 (C-8),139.0 (C-9),111.8 (C-10),126.2 (C-1′),104.6 (C-2′,C-6′),147.5 (C-3′,C-5′),135.8 (C-4′),77.0 (C-7′),78.5 (C-8′),61.4 (C-9′),56.6 (3′,5′-OCH_3),56.5 (6-OCH_3)。以上数据与文献[11]报道一致,因此确定化合物 **8** 为臭矢菜素 C。

化合物 9 无色油状,易溶于氯仿。ESI(+)-MS *m/z* 357.17 [M+H]$^+$,分子式为 $C_{20}H_{20}O_6$。^{1}H NMR ($CDCl_3$,400 MHz) δ:6.89 (3H,s,H-2,H-4,H-6),5.64 (1H,d,*J* = 7.1 Hz,H-7),3.68 (1H,m,H-8),3.97 (2H,m,H-9),7.04 (1H,s,H-2′),7.14 (1H,s,H-6′),7.42 (1H,d,*J* = 15.9 Hz,H-7′),6.60 (1H,dd,*J* = 7.8 Hz,15.8 Hz,H-8′) ,9.64 (1H,d,*J* = 7.8 Hz,H-9′),3.87 (3H,s,3-OCH_3),3.93 (3H,s,5-OCH_3);^{13}C NMR ($CDCl_3$,100 MHz) δ:132.4 (C-1),119.7 (C-2),147.0 (C-3),114.7 (C-4),146.2 (C-5),109.0 (C-6),89.2 (C-7),53.2 (C-8),64.2 (C-9),128.4 (C-1′),112.4 (C-2′),145.1 (C-3′),151.8 (C-4′),129.3 (C-5′),118.4 (C-6′),153.2 (C-7′),126.7 (C-8′),193.8 (C-9′),56.2 (3-OCH_3),56.3 (3′-OCH_3)。以上数据与文献[12]报道一致,因此确定化合物 **9** 为 curcasinlignan A。

化合物 10 浅黄色针晶,易溶于氯仿。ESI(-)-MS *m/z* 191.08[M-H]$^-$,分子式为 $C_{10}H_8O_4$。^{1}H NMR (CD_3COCD_3,400 MHz) δ:6.18 (1H,d,*J* = 9.58 Hz,H-3),7.85 (1H,d,*J* = 9.58 Hz,H-4),6.81 (1H,s,H-5),8.79 (1H,s,7-OH),3.90 (3H,s,6-OCH_3),7.20 (1H,s,H-8);^{13}C NMR (CD_3COCD_3,100 MHz) δ:160.4 (C-2),112.4 (C-3),143.8 (C-4),109.0 (C-5),150.2 (C-6),150.9 (C-7),102.8 (C-8),145.1 (C-9),111.1 (C-10),55.8 (6-OCH_3)。以上数据与文献[13]报道一致,因此确定化合物 **10** 为东莨菪亭。

化合物 11 白色无定型粉末,易溶于氯仿,丙酮。ESI(-)-MS *m/z* 221.09[M-H]$^-$,分子式为 $C_{11}H_{10}O_5$。^{1}H NMR ($CDCl_3$,400 MHz) δ:6.3 (1H,d,*J* = 9.58 Hz,H-3),7.6 (1H,d,*J* = 9.58 Hz,H-4),6.5 (1H,s,H-5),3.9 (3H,s,6-OCH_3),4.0 (3H,s,8-OCH_3);^{13}C NMR ($CDCl_3$,100 MHz) δ:160.4 (C-2),115.5 (C-3),143.8 (C-4),100.4 (C-5),149.9 (C-6),140.0 (C-7),137.6 (C-8),138.1 (C-9),114.4 (C-10),56.4 (6-OCH_3),61.6 (7-OCH_3)。以上数据与文献[14]报道基本一致,因此确定化合物 **11** 为秦皮素。

化合物 12 黄色针状结晶,易溶于氯仿,丙酮。ESI(-)-MS *m/z* 221.15[M-H]$^-$,分子式为 $C_{11}H_{10}O_5$。^{1}H NMR (CD_3COCD_3,400 MHz) δ:6.2 (1H,d,*J* = 9.5 Hz,H-3),7.8 (1H,d,*J* = 9.5 Hz,H-4),6.9 (1H,s,H-5),3.90 (3H,s,6-OCH_3),3.96 (3H,s,8-

OCH_3);^{13}C NMR (CD_3COCD_3, 100 MHz) δ:160.0 (C-2),104.3 (C-3),144.3 (C-4),110.7 (C-4a),112.1 (C-5),145.4 (C-6),135.1 (C-7),143.9 (C-8),143.5 (C-8a),60.5 (C-9),55.9(C-10)。以上数据与文献[15]报道基本一致,因此确定化合物 **12** 为异秦皮素。

化合物 13 白色粉末,易溶于氯仿,丙酮。ESI(-)-MS *m/z* 401.31 [M-H]$^-$,分子式为 $C_{25}H_{26}O_3N_2$。^{1}H NMR ($CDCl_3$,400 MHz) δ:4.78 (1H,m,H-2),3.26 (1H,dd,*J* = 13.6 Hz,5.9 Hz,H-3a),3.04 (1H,dd,*J* = 13.6 Hz,8.8 Hz,H-3b),7.29 (5H,m,H-5,H-6,H-7,H-8,H-9),7.72 (2H,dd,*J* = 1.5 Hz,8.0 Hz,H-3′,H-7′),7.44 (2H,t,*J* = 7.8 Hz,H-4′,H-6′),7.53 (1H,m,H-5′),4.09 (1H,m,H-1″),2.78 (1H,dd,*J* = 13.8 Hz,7.5 Hz,H-2″a),2.68 (1H,dd,*J* = 13.8 Hz,7.4 Hz,H-2″b),7.08 (2H,d,*J* = 7.5 Hz,H-4″,H-8″),7.13 (3H,m,H-5″,H-6″,H-7″),3.43 (2H,m,H-9″),6.83 (1H,d,*J* = 7.6 Hz, β-NH),5.98 (1H,d,*J* = 8.2 Hz, α-NH),2.17 (1H,s,-OH);^{13}C NMR ($CDCl_3$,100 MHz) δ:170.9 (C-1),55.4 (C-2),38.8 (C-3),137.4 (C-4),128.8 (C-5,C-9),129.5 (C-6,C-8),127.3 (C-7),167.3 (C-1′),133.7 (C-2′),128.7 (C-3′,C-7′),127.2 (C-4′,C-6′),132.1 (C-5′),53.0 (C-1″),37.0 (C-2″),136.9 (C-3″),129.0 (C-4″,C-8″),129.3 (C-5″,C-7″),126.8 (C-6″),63.6 (C-9″)。以上数据与文献[16]报道一致,因此确定化合物 **13** 为金色酰胺醇。

化合物 14 白色针晶,易溶于氯仿。ESI(-)-MS *m/z* 443.18 [M-H]$^-$,分子式为 $C_{27}H_{28}O_4N_2$。^{1}H NMR ($CDCl_3$,400 MHz) δ:3.81 (1H,dd,*J* = 11.4 Hz,4.3 Hz,H-1b),3.93 (1H,dd,*J* = 11.4 Hz,5.0 Hz,H-1a),4.34 (1H,m,H-2),2.75 (1H,m,H-3),4.78 (1H,m,H-2′),3.05 (1H,dd,*J* = 13.9 Hz,8.6 Hz,H-3′a),3.22 (1H,dd,*J* = 13.8 Hz,5.8 Hz,H-3′b),6.07 (1H,d,*J* = 8.5 Hz,CH-CO-NH-CH),6.79 (1H,d,*J* = 7.8 Hz,Ar-NH),7.07 (2H,d,*J* = 7.8 Hz,H-5,H-9),7.24-7.29 (5H,overlapped,H-5′,H-6′,H-7′,H-8′,H-9′),7.11-7.18 (3H,overlapped,H-6,H-7,H-8),7.72 (2H,d,*J* = 7.3Hz,H-3″,H-7″),7.43 (2H,t,*J* = 7.7Hz,H-4″,H-6″),7.52 (1H,t,*J* = 7.4 Hz,H-5″),2.01 (3H,s,CH_3-CO);^{13}C NMR ($CDCl_3$,100 MHz) δ:64.7 (C-1),49.6 (C-2),37.6 (C-3),136.8 (C-4),129.3 (C-5,C-9),128.9 (C-6,C-8),126.9 (C-7),170.4 (C-1′),55.1 (C-2′),38.6 (C-3′),136.7 (C-4′),128.8 (C-5′,C-9′),129.4 (C-6′,C-8′),127.3 (C-7′),167.3 (C-1″),133.8 (C-2″),127.2 (C-3″,C-7″),128.7 (C-4″,C-6″),132.1 (C-5″),170.9 (CH_3-CO),20.9 (CH_3-CO)。以上数据与文献[17]报道一致,因此确定化合物 **14** 为金色酰胺酯。

化合物 15 浅黄色结晶粉末,易溶于氯仿。ESI(-)-MS *m/z* 181.10 [M-H]$^-$,分子式为 $C_9H_{10}O_4$。^{1}H NMR ($CDCl_3$,400 MHz) δ:7.14 (2H,s,H-2,H-6),3.96 (6H,s,-OCH_3),9.81 (1H,s,-CHO);^{13}C NMR ($CDCl_3$,100 MHz) δ:128.6 (C-1),106.9 (C-2,C-6),147.6 (C-3,C-5),141.0 (C-4),56.7 (-OCH_3),191.0 (-CHO)。以上数据与文献[18]报道一致,因此确定化合物 **15** 为丁香醛。

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参考文献

1 Li MY, Xiao Q, Pan JY, *et al*. Natural products from semi-mangrove flora: source, chemistry and bioactivities. *Nat Prod Rep*, 2009, 26: 281-298.

2 Flora of China Editorial of Committee of Chinese Academy of Sciences (中国科学院植物志编辑委员会). Flora of China (中国植物志). Beijing: Science Press, 1997. 44(3), 6.

3 Wang JD (王继栋), Dong ML (董美龄), Zhang W (张文), *et al*. Chemical constituents of mangrove plant *Excoecaria agallocha* L. *Nat Prod Res Dev* (天然产物研究与开发), 2006, 18: 945-947.

4 Yin BW, Shen LR, Zhang ML, *et al*. Chemical constituents of plants from the genus *Excoecaria*. *Chem Biodivers*, 2008, 5: 2356-2371.

5 Kan SQ, Chen GY, Han CR, *et al*. Chemical constituents from the roots of *Xanthium sibiricum*. *Nat Prod Res*, 2011, 25: 1243-1249.

6 Zhang Q (张强), Sun LR (孙隆儒). Study on chemical constituents *Serissa serissoides* DC. *Chin Tradit Herb Drugs* (中草药), 2006, 37: 672-673.

7 Cui YL (崔益泠), Mu Q (穆青), Hu CQ (胡昌奇). Studies on the phenylpropanoids from *Caragana rosea*. *Nat Prod Res Dev* (天然产物研究与开发), 2003, 15: 277-283.

8 Li W(李薇),Mei WL(梅文莉),Wang H(王昊),*et al*. Chemical constituents from stems of *Aquilaria sinensis* (Lour.) Gilg. *Chin J Mater Med*(中国中药杂志),2013,38:2826-2831.

9 Xiong L,Zhu CG,Li YR,*et al*. Lignans and neolignans from *Sinocalamus affinis* and their absolute configurations. *J Nat Prod*,2011,74:1188-1200.

10 Lv J(吕静),Jia LY(贾凌云),Yuan JZ(袁久志). Isolation and identification of the chemical constituents from pine needle of Pinus koraiensis Sieb. et Zucc. *J Shenyang Pharm Univ*(沈阳药科大学学报),2011,28(1):21-24.

11 Wang Y(王韵),Si-Ma SD(司马硕丹),Li JX(李继霞),*et al*. Study on chemical constituents *Eupatorium odoratum*. *Chin Tradit Herb Drugs*(中草药),2012,43:2351-2355.

12 Xu JJ,Tan NH. New lignans from *Jatropha curcas Linn*. *Z Naturforsch B*,2012,2:176-180.

13 Wang P(王培),Song QS(宋启示),Xu W(徐蔚),*et al*. Chemical constituents of the branches and leaves from *Beaumontia grandiflora*. *Chin Tradit Herb Drugs*(中草药),2009,40:1549-1551.

14 Hu HB,Zheng XD,Jian YF,*et al*. Constituents of the root of *Anemone tomentosa*. *Arch Pharm Res*,2011,34:1097-1105.

15 Ma XX(马兴霞),Luo G(罗刚),Yin XY(尹小英),*et al*. Study on chemical constituents *Chloranthus fortunei*. *Lishizhen Med Mat Re*(时珍国医国药),2014,25:272-273.

16 Zan K(咎珂),Chen XQ(陈筱清),Fu Q(付强),*et al*. Chemical ingredients isolated from the aerial parts of *Artemisia anomala*. *J Chin Pharm Sci*,2010,19:95-99.

17 Tang J(汤俊),Tewtrakul S,Wang ZT(王峥涛),*et al*. Aurantiamide acetate from stem of *Zanthoxylum Dissitum Hemsley*. *J Chin Pharm Sci*,2003,12(4):231-233.

18 Zhang X(张雪),Gao H(高昊),Wang NL(王乃利),*et al*. Phenolic components from *Dendrobium nobile*. *Chin Tradit Herb Drugs*(中草药),2006,37:652-655.

(上接第 128 页)

2 Zhang XS(张小爽),Xu XF(徐晓飞),Zhang BQ(张丙青),*et al*. Comparison of nutrition components in mushroom in different Batches. *Mod Food SciTechnol*(现代食品科技),2012,28:691-694.

3 Zhang YY,Li S,Wang XH,*et al*. Advances in lentinan:Isolation, structure, chain conformation and bioactivities. *Food Hydrocolloids*,2011,25:196-206.

4 Chen HX,Li SQ. Polysaccharides from medicinal mushrooms and their antitumor activities. *Polysaccharides*,2015,1893-1910.

5 Ren L,Perera C,Hemar Y. Antitumor activity of mushroom polysaccharides:a review. *Food Funct*,2012,3:1118-1130.

6 NY/T 1676—2008. Determination of Crude Mushroom Polysaccharides(食用菌中粗多糖含量的测定). Beijing:Agricultural Press of China,2008.

7 Zhu W(朱伟). Determination of the lentinancontent by anthrone-sulfuric acid colorimetry. *J NorthPharm*(北方药学),2011,8(8):8-9.

8 Wang GJ(王国佳),Cao H(曹红),Xing JB(邢俊波),*et al*. Determination of the lentinanmolecular weight and its content in lentinaninjection preparation by GPC. *Chin Pharm Affair*(中国药事),2013,27:1090-1094.

9 Zhang DW(张迪文),Bai Y(白雁),Xie CX(谢彩侠),*et al*. Rapid determination of specnuezhenide in Fructus*Ligustrilucidum* by near infrared spectroscopy. *Nat Prod Res Dev*(天然产物研究与开发),2015,27:1379-1384.

10 Gu ZR(顾志荣),Zhang YY(张亚亚),Ding JX(丁军霞),*et al*. Rapid determination of ferulicacid and linolicacid in *Angelica sinensis* by near-infrared diffuse reflectance spectroscopy. *Nat Prod Res Dev*(天然产物研究与开发),2015,27:849-853.

11 Lei JW(雷敬卫),Fan MY(樊明月),Guo YL(郭艳利),*et al*. Rapid determination of costunolide and dehydrocostuslactone in Radix Aucklandiae by near-infrared spectroscopy. *Nat Prod Res Dev*(天然产物研究与开发),2014,26:1062-1066.

12 Chen B(陈斌),Zou XY(邹贤勇),Zhu WJ(朱文静). Eliminating outlier samples in near-infrared model by method of PCA-mahalanobis distance. *J Jiangsu Univ*,*Nat Sci*(江苏大学学报,自科版),2008,29(4):277-279.

13 Cao DS,Liang YZ,Xu QS,*et al*. A new strategy of outlier detection for QSAR/QSPR. *J ComputChem*,2010,31:592-602.

14 Kennard RW,Stone LA. Computer aided design of experiments. *Technometrics*,2012,11(1):137-148.

15 Zheng KY(郑开逸). Studies on model optimization and model transfer methods of near infrared spectroscopy. Shanghai:East China University of Science and Technology(华东理工大学),PhD. 2013.

16 Wang M,Zheng KY,Yang GJ,*et al*. A robust near-infrared calibration model for the determination of chlorophyllconcentration in tree leaves with a calibration transfer method. *Anal Lett*,2015,48:1707-1719.

17 Zheng KY,Li QQ,Wang JJ,*et al*. Stability competitive adaptive reweighted sampling (SCARS) and its applications to multivariate calibration of NIR spectra. *ChemomIntell Lab Syst*,2012,112(6):48-54.