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叶轮木的化学成分研究

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摘 要 从叶轮木的乙醇提取物中分离鉴定了10个已知化合物,经波谱分析确定其结构分别为:油酮酸(1)、豆甾醇-4-烯-3,6-二酮(2)、β-谷甾醇(3)、胡萝卜苷(4)、5,6-二羟基-3,3′,4′,7,8-五甲氧基黄酮(5)、没食子酸甲酯(6)、香草醛(7)、东莨菪内酯(8)、硬脂酸(9)、二十八碳醇(10)。以上化合物均为首次从该属植物中分离得到。

关键词 叶轮木;化学成分

STUDY ON THE CHEMICAL CONSTITUENTS OF *OSTODES PANICULATA*

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Abstract Ten compounds were isolated from the twig of *Ostodes paniculata*. On the basis of spectroscopic methods, their structures were elucidated as acetylaleuritolic acid (1), stigma-4-en-3, 6-dione (2), β-sitosterol (3), daucosterol (4), 5, 6-dihydroxy-3, 3′, 4′, 7, 8- pentamethoxyflavone (5), methyl gallate (6), vanillin (7), scopoletin (8), stearic acid (9) and octacosanol (10). All these compounds were firstly isolated from this species.

Key words *Ostodes paniculata*; chemical constituens

叶轮木(*Ostodes paniculata* O.P.Bl.)为大戟科(Euphorbiaceae)叶轮木属(*Ostodes* Bl.)植物,南亚次大陆、中南半岛、马来半岛、印度尼西亚(爪哇)有分布,我国主产于海南、云南、广东、广西及西藏东南部。同属植物约12种,我国产3种,叶轮木(*O. Paniculata*)、云南叶轮木(*O. Katharinae*)和绒毛叶轮木(*O. Kuangii*)[1]。1982年Handa SS曾从该种植物的茎枝和果实中提取分离得到两个具有抗癌活性的化学成分—12-*O*-undecadienoylphorbol-13-acetate和Ostodin[2]。另外,曾有报道过其乙醇提取物有提高实验性狗低血压和对肠痉挛有镇痉的作用[3]。我们对叶轮木的枝条部分进行了化学成分的研究,从其乙醇提取物中分离鉴定了10个已知化合物。

1 实验部分

1.1 实验仪器和材料

熔点用四川大学科仪厂生产的XRC-1型显微熔点仪测定,温度未校正;旋光用SEPA-300仪测定;红外在Bio-Rad FTS-135红外光谱仪上测定;紫外在UV-210A紫外光谱仪上测定;^{1}H, ^{13}C NMR谱用Bruker AM-400 MHz和DRX-500 MHz核磁共振

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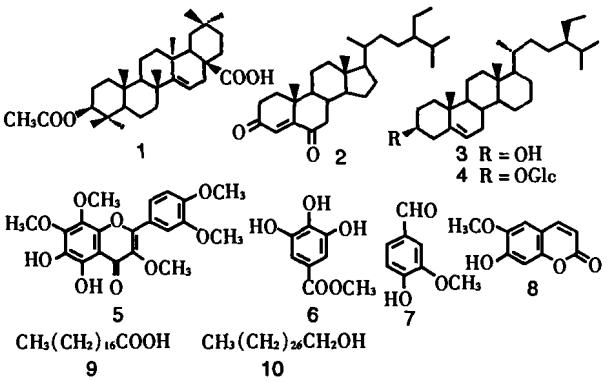

仪测定,TMS 为内标;质谱用 VG Auto Spec-3000 型质谱仪测定。薄层色谱硅胶和柱色谱硅胶均购自青岛海洋化工厂。

1.2 提取分离

叶轮木(*O. Paniculata*)枝条于2001年11月采集自云南省西双版纳州,标本由中国科学院西双版纳热带植物园崔景云老师鉴定。将叶轮木枝条干料(8 kg)粉碎,用工业乙醇加热回流提取三次,浓缩,加适量水稀释,用乙酸乙酯萃取三次。乙酸乙酯层浓缩近干,称重 98 g,加甲醇与氯仿溶解完全,加入适量硅胶拌样,自然凉干。将乙酸乙酯层过常压硅胶柱层析,以石油醚-乙酸乙酯溶剂系统梯度洗脱,得8个组分。组分2(16 g)经反复硅胶柱色谱,用石油醚-乙酸乙酯(from 12:1 to 8:2)洗脱,得10(8 mg)、3(2.8 g)、9(24 mg)、1(14 mg)。组分3(13 g)经反复硅胶柱色谱,用石油醚-乙酸乙酯(from 9:1 to 7:3)洗脱,得7(9 mg)、2(11 mg)、8(15 mg)、6(12 mg),组分3(8 g)经反复硅胶柱色谱,用氯仿-丙酮(from 9:1 to 8:2)洗脱,得5(4 mg)。从组分5(20 g)中析出4(3.5 g)。

2 鉴 定

油酮酸(1) 无色结晶(氯仿-丙酮);mp.301-302 ℃;$[\alpha]_D$+23.1 (*c*,0.6 in $CHCl_3$);$C_{32}H_{50}O_4$;^{1}H NMR (500 MHz,$CDCl_3$) δ_H: 5.48 (1H,dd,J=8.1,4.0 Hz,H-15),4.40 (1H,dd,J=10.2,6.0 Hz,H-3),2.30 (1H,m,H-16a),1.89 (1H,m,H-16b),2.25 (1H,d,J=10.8 Hz,H-18),1.98 (3H,s,*Me*CO),1.41 (1H,m,H-9),0.7-1.0 (3H×7,s,Me-23,24,25,26,27,29,30);^{13}C NMR (125 MHz,$CDCl_3$) (C: 37.8 (t,C-1),23.5 (t,C-2),81.0 (d,C-3),37.8 (s,C-4),55.7 (d,C-5),18.8 (t,C-6),40.9 (t,C-7),39.1 (s,C-8),49.2 (d,C-9),38.0 (s,C-10),17.4 (t,C-11),33.4 (t,C-12),37.4 (d,C-13),160.6 (s,C-14),116.6 (d,C-15),31.5 (t,C-16),51.4 (s,C-17),41.6 (d,C-18),35.5 (t,C-19),29.3 (s,C-20),33.8 (t,C-21),30.8 (t,C-22),28.0 (q,C-23),16.6 (q,C-24),15.6 (q,C-25),26.2 (q,C-26),22.5 (q,C-27),184.0 (s,C-28),32.0 (q,C-29),28.7 (q,C-30); EIMS *m/z* 498 [M]$^+$ (7),452 (10),368 (27),329 (10),269 (13),234 (100),189(64). ^{1}H NMR 和^{13}C NMR 数据与文献报道[4]一致。

豆甾醇-4-烯-3,6-二酮(2) 白色粉末;$C_{29}H_{46}O_2$; mp.160-164 ℃; $[\alpha]_D$-60.5 (*c*, 0.99 in $CHCl_3$); UV (MeOH) λ_{max} 249.5 nm; IR (KBr) υ_{max} 3024,2958,2873,1688,1603,1466,1380,1246 cm^{-1};^{1}H NMR (400 MHz,$CDCl_3$) δ_H: 6.14 (1H,s,H-4),0.72 (3H,s,Me-18),1.14 (3H,s,Me-19),0.80 (3H,d,J=6.5 Hz,Me-21),0.84 (3H,d,J=6.6 Hz,Me-26),0.80 (3H,d,J=6.6 Hz,Me-27),0.82 (3H,t,J=7.3 Hz,Me-29); ^{13}C NMR (100 MHz,$CDCl_3$) δ_C: 35.5 (t,C-1),34.0 (t,C-2),201.9 (s,C-3),125.4 (d,C-4),160.9 (s,C-5),199.2 (s,C-6),46.8 (t,C-7),39.1 (d,C-8),51.0 (d,C-9),34.2 (s,C-10),20.9 (t,C-11),39.8 (t,C-12),42.7 (s,C-13),55.9 (d,C-14),24.0 (t,C-15),30.0 (t,C-16),56.5 (d,C-17),11.8 (q,C-18),17.5 (q,C-19),36.2 (d,C-20),18.7 (q,C-21),34.0 (t,C-22),26.1 (t,C-23),45.8 (d,C-24),29.1 (d,C-25),19.8 (q,C-26),19.0 (q,C-27),23.0 (t,C-28),11.9 (q,C-29); EIMS *m/z* 426 [M]$^+$ (100),411 (15),398 (40),384 (16),285 (32),275 (21),243 (21),137 (47). ^{1}H NMR 和^{13}C NMR 数据与文献报道[5]一致。

β-谷甾醇(3) 无色针晶(氯仿);与β-谷甾醇标准品进行 TLC 对照,多种展开系统下 R_f 值均一致。

胡萝卜苷(4) 白色无定形粉末;与胡萝卜苷标准品进行 TLC 对照,多种展开系统下 R_f 值均一致。

5,6-二羟基-3,3′,4′,7,8-五甲氧基黄酮(5) 黄色结晶;$C_{20}H_{20}O_9$; ^{1}H NMR (400 MHz,C_5D_5N) δ_H: 7.60(1H,d,J=2.5 Hz,H-2′),6.84 (1H,d,J=9 Hz,H-5′),7.70(1H,dd, J=9,2.5 Hz,H-6′),3.87,3.72,3.95,3.92,3.88 (s,5(OMe);^{13}C NMR

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(100 MHz,C_5D_5N) δ_C: 151.4 (s,C-2),138.0 (s,C-3),180.0 (s,C-4),151.9 (s,C-5),131.5 (s,C-6),158.0 (s,C-7),118.5 (s,C-8),155.9 (s,C-9),105.7 (s,C-10),122.1 (s,C-1′),110.7 (d,C-2′),148.0 (s,C-3′),150.8 (s,C-4′),110.3 (d,C-5′),121.5 (d,C-6′); EI-MS m/z 404[M]$^+$(8),388 (88),374 (66),358 (100),345 (7),331 (10),315 (7),300 (4),287 (10). ^{1}H NMR 和^{13}C NMR 数据与文献报道[6]一致。

没食子酸甲酯(6) 白色粉末; $C_8H_8O_5$; UV (甲醇)λ_{max} 215.5,267.0 nm; IR (KBr) υ_{max} 3500,3178,1710,1608,1520,1466,1318,1280,1115,765 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ_H: 7.08 (2H,s,H-2,6),4.05 (3H,s,$COOCH_3$); ^{13}C NMR (100 MHz,CD_3OD) δ_C: 121.5 (s,C-1),109.4 (d,C-2,6),146.7 (s,C-3,5),139.5 (s,C-4),168.3 (s,$COOCH_3$),52.1 (q,-$COOCH_3$); EIMS m/z 184 [M]$^+$(100),169 (20),153 (36),125 (18),107 (8),79 (24). ^{1}H NMR 和^{13}C NMR 数据与文献报道[7]一致。

香草醛(7) 无色针状结晶; $C_8H_8O_3$; mp.81～83 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 6.89 (1H,dd,J = 3.8,8.5 Hz,H-6),6.53 (1H,d,J = 8.5 Hz,H-5),4.20 (1H,s,H-2),9.29 (1H,s,CHO),3.43 (3H,s,OCH_3); ^{13}C NMR (125 MHz,$CDCl_3$) δ_C: 128.3 (s,C-1),109.4 (d,C-2),147.7 (s,C-3),152.7 (s,C-4),114.7 (d,C-5),126.2 (d,C-6),190.3 (s,CHO),55.2 (q,OCH_3); EIMS m/z 152[M]$^+$(100),137[M-CH_3]$^+$(8),109 (16),95 (4),81 (32),65 (7),57 (4). ^{1}H NMR 和^{13}C NMR 数据与文献报道[8]一致。

东莨菪内酯(8) 无色针晶(丙酮); UV (MeOH) λ_{max}: 228, 252, 257, 346, 383 nm; IR (KBr) υ_{max} 3334, 2948, 1704, 1629, 1608, 1511, 1454, 1434, 1375, 1291, 1263, 1220, 1190, 1141, 1017, 922, 859 cm^{-1}; ^{1}H NMR (400 MHz, CD_3COCD_3) δ_H:7.84 (1H,d,J=9.4 Hz,H-4),7.19 (1H,s,H-5),6.79 (1H,s,H-8),6.17 (1H,d,J = 9.4 Hz,H-3),3.90 (3H,s,OMe); ^{13}C NMR (100 MHz,CD_3COCD_3) δ_C: 160.5 (s,C-2),113.4 (d,C-3),144.6 (d,C-4),110.2 (d,C-5),146.0 (s,C-6),150.5 (s,C-7),103.8 (d,C-8),151.9 (s,C-9),112.0 (s,C-10),56.8 (q,OMe); EIMS m/z 192 [M]$^+$(100),177 (70),164 (41),149 (60),135 (17),121 (32),105 (9),92 (12),79 (35),69 (54),62 (25). ^{1}H NMR 和^{13}C NMR 数据与文献报道[9]一致。

硬脂酸(9) 无色针晶(丙酮);与硬脂酸标准品进行 TLC 对照,多种展开系统下 R_f 值一致。

二十八碳醇(10) 白色无定形粉末; $C_{28}H_{57}OH$; ^{1}H NMR (400 MHz,C_5D_5N) δ_H: 3.86 (2H,t,J = 5.23 Hz,H-1),1.75-1.50 (52H,26 × CH_2),0.88 (3H,t,J = 3.04 Hz,H-28); ^{13}C NMR (100 MHz,C_5D_5N) δ_C: 62.4 (t,C-1),14.4 (q,C-28),23.1-34.1 (t,26 × CH_2); EIMS m/z 410[M]$^+$ (3),392 (35),364 (13),308 (3),264 (3),222 (3),167 (5),125 (23),111 (52),97 (92),83 (100),69 (73),57 (99)。

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