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墨西哥落羽杉的化学成分

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摘　要:从墨西哥落羽杉(*Taxodium mucronatum*)枝叶中首次分离得到10个化合物,通过MS与NMR等方法将它们分别鉴定为quercetin 3′-methoxy-3-*O*-β-*D*-galactopyranoside (**1**),quercetin 3′-methoxy-3-*O*-β-*D*-arabinopyranoside (**2**),quercetin 3′-methoxy-3-*O*-α-*L*-arabinofuranoside (**3**),quercetin (**4**),avicularin (**5**),quercetin 3-*O*-β-*D*-galactopyranoside (**6**),(7′*S*,8′*R*)-4,7′-epoxy-3,3′-dimethoxy-4,9,3′,4′,9′-lignanepentol-4′-*O*-β-*D*-glucopyranoside (**7**),(7′*S*,8′*S*)-3,3′-dimethoxy-9,4′,9′-trihydroxy-4,8′-oxyneolignan-7′-*O*-β-*D*-glucopyranside (**8**),methyl shikimate (**9**)和β-sitosterol (**10**)。

关键词:墨西哥落羽杉;化学成分;黄酮;新木脂素苷

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Chemical Constituents of *Taxodium mucronatum*

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Abstract: Ten known compounds were isolated from the leaves and branches of *Taxodium mucronatum* for the first time. On the basis of MS and NMR data, they were identified as quercetin 3′-methoxy-3-*O*-β-*D*-galactopyranoside (**1**), quercetin 3′-methoxy-3-*O*-β-*D*-arabinopyranoside (**2**), quercetin 3′-methoxy-3-*O*-α-*L*-arabinofuranoside (**3**), quercetin (**4**), avicularin (**5**), quercetin 3-*O*-β-*D*-galactopyranoside (**6**), (7′*S*,8′*R*)-4,7′-epoxy-3,3′-dimethoxy-4,9,3′,4′,9′-lignanepentol-4′-*O*-β-*D*-glucopyranoside (**7**), (7′*S*,8′*S*)-3,3′-dimethoxy-9,4′,9′-trihydroxy-4,8′-oxyneolignan-7′-*O*-β-*D*-glucopyranside (**8**), methyl shikimate (**9**) and β-sitosterol (**10**).

Key words: *Taxodium mucronatum*; chemical constituents; flavonoid; neolignan glycoside

墨西哥落羽杉(*Taxodium mucronatum* Tenore)为杉科(Taxodiaceae)落羽杉属落叶大型乔木,原产北美[1],是墨西哥的典型树种,其叶和果实在当地民间入药[2]。人们对该种的化学研究工作鲜见报道,到目前为止,前人从该种中分离得到了6个双黄酮和1个新的二萜类化合物[2,3]。作为系统的杉科植物的化学和活性成分研究计划,我们对墨西哥落羽杉的枝叶进行了较深入的化学和生物活性研究,发现双黄酮amentoflavone, podocarpusflavone A和4′,7-dimethylamentoflavone为新的组织蛋白酶B的天然抑制剂,且具有细胞毒活性[4,5]。本文介绍该植物中另外10个已知化合物的分离与结构鉴定。

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1　仪器和材料

质谱用VG Autospec-3000型质谱仪测定。核磁共振谱用Bruker AM-400和DRX-500超导核磁共振仪测定,TMS为内标。旋光经JASCO DIP-370型数字旋光仪测定。薄层色谱硅胶和柱色谱硅胶由青岛美晶化工厂生产。Sephadex LH-20为Pharmacia公司生产。

植物样品于2002年8月采于云南省昆明市昆明植物园内,标本由中国科学院昆明植物所岳中书副研究员鉴定为*Taxodium mucronatum* Tenore,标本保存于中国科学院昆明植物研究所标本馆,标本号为0040515。

2　提取和分离

12.8 kg干燥墨西哥落羽杉枝,粉碎后分步以工业石油醚、丙酮及甲醇各加热回流提取3次(3×50

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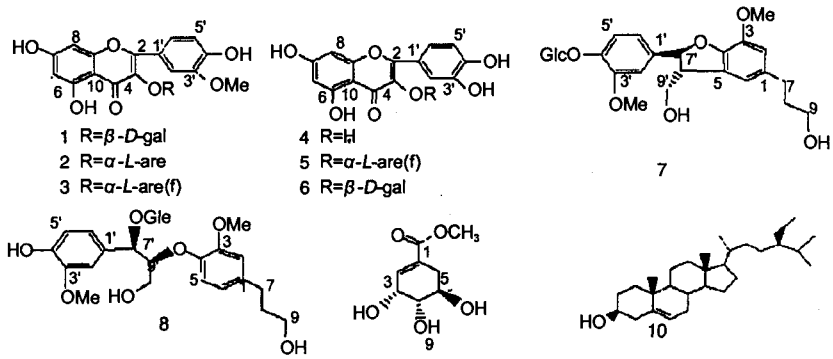

图 1 墨西哥落羽杉中分离得到的化合物 1 ~ 10

Fig. 1 Compounds **1-10** isolated from *Taxodium mucronatum*

L),将各部分提取液分别过滤减压浓缩,得石油醚部分浸膏 137 g,丙酮部分浸膏 188 g,甲醇部分浸膏 420 g。丙酮部分经硅胶柱以氯仿-丙酮、石油醚-乙酸乙酯和氯仿-甲醇多次反复梯度洗脱,再经 Sephadex LH-20 凝胶柱以氯仿-甲醇纯化,得到化合物 **1** (168 mg)、**2** (49 mg)、**3** (134 mg)、**4**(25 mg)、**5**(63 mg)和 **6**(23 mg)。甲醇部分经硅胶柱以氯仿-甲醇-水系统多次反复层析,最后经 Sephadex LH-20 凝胶柱以甲醇-水纯化,得到化合物 **7**(14 mg)、**8**(51 mg)和 **9**(12 mg)。石油醚部分经硅胶柱以石油醚-丙酮反复层析得到化合物 **10**(138 mg)。

3 结构鉴定

Quercetin 3′-methoxy-3-*O*-β-*D*-galactopyranoside (1) $C_{22}H_{22}O_{12}$,黄色粉末。^{1}H NMR (CD_3OD + DMSO,400 MHz)δ:6.23 (1H,d,*J* = 1.97 Hz,H-6),6.44 (1H,d,*J* = 1.97 Hz,H-8),8.05 (1H,d,*J* = 1.85 Hz,H-2′),6.92 (1H,d,*J* = 8.45 Hz,H-5′),7.59 (1H,dd,*J* = 1.97,8.43 Hz,H-6′),5.41 (1H,d,*J* = 7.77 Hz,H-1″),3.85 ~ 2.15 (6H,m,H-2″ ~ H-6″),3.97 (3H,s,H-OMe)。FAB-MS *m/z*:477[M-1]$^-$。其波谱数据(碳谱数据见表 1)与文献报道的一致[6]。

Quercetin 3″-methoxy-3-*O*-β-*D*-arabinopyranoside (2) $C_{21}H_{20}O_{11}$,黄色粉末。^{1}H NMR (C_5D_5N,400 MHz)δ:6.72 (1H,d,*J* = 2.00 Hz,H-6),6.77 (1H,d,*J* = 1.76 Hz,H-8),7.57 (1H,s,H-2′),7.25 (1H,d,*J* = 8.40 Hz,H-5′),7.86 (1H,dd,*J* = 2.20,8.40 Hz,H-6′)。FAB-MS *m/z*:447[M-1]$^-$。其波谱数据(碳谱数据见表 1)与文献报道的一致[6,7]。

Quercetin 3′-methoxy-3-*O*-α-*L*-arabinofuranoside (3) $C_{21}H_{20}O_{11}$,黄色粉末。^{1}H NMR (DMSO,500 MHz)δ:6.20 (1H,s,H-6),6.46 (1H,s,H-8),7.66 (1H,s,H-2′),6.91 (1H,d,*J* = 8.45 Hz,H-5′),7.59 (1H,d,*J* = 8.20 Hz,H-6′),5.62 (1H,s,H-1″),4.16 ~ 3.28 (5H,m,H-2″ ~ H-5″),3.86 (3H,s,H-OMe)。FAB-MS *m/z*:447[M-1]$^-$。其波谱数据(碳谱数据见表 1)与文献报道的一致[6,8]。

Quercetin (4) $C_{15}H_{10}O_7$,黄色粉末。^{1}H NMR (CD_3OD,400 MHz)δ:6.17 (1H,d,*J* = 1.88 Hz,H-6),6.38 (1H,d,*J* = 1.84 Hz,H-8),7.72 (1H,d,*J* = 1.82 Hz,H-2′),6.87 (1H,d,*J* = 8.47 Hz,H-5′),7.62 (1H,dd,*J* = 1.84,8.47 Hz,H-6′)。FAB-MS *m/z*:301[M-1]$^-$。其波谱数据(碳谱数据见表 1)与文献报道的一致[6]。

Avicularin (5) $C_{20}H_{18}O_{11}$,黄色粉末。^{1}H NMR (CD_3OD,400 MHz)δ:6.21 (1H,d,*J* = 2.04 Hz,H-6),6.40 (1H,d,*J* = 2.07 Hz,H-8),7.50 (1H,d,*J* = 2.16 Hz,H-2′),6.91 (1H,d,*J* = 8.34 Hz,H-5′),7.53 (1H,dd,*J* = 2.14,8.04 Hz,H-6′),5.52 (1H,s,H-1″),4.34 ~ 3.30 (5H,m,H-2″ ~ H-5″)。FAB-MS *m/z*:433[M-1]$^-$。其波谱数据(碳谱数据见表 1)与文献报道的一致[8]。

Quercetin 3 - *O* - β - *D* - galactopyranoside (6) $C_{21}H_{20}O_{12}$,黄色粉末。^{1}H NMR (CD_3OD,400 MHz)δ:6.20 (1H,s,H-6),6.40 (1H,s,H-8),7.53 (1H,s,H-2′),6.81 (1H,d,*J* = 8.48 Hz,H-5′),7.63 (1H,d,*J* = 8.44 Hz,H-6′),5.34 (1H,d,*J* = 7.64 Hz,H-1″),3.65 ~ 2.49 (6H,m,H-2″ ~ H-6″)。FAB-MS *m/z*:463[M-1]$^-$。其波谱数据(碳谱数据见表 1)与文献报道的一致[6]。

(7′*S*,8′*R*)-4,7′-Epoxy-3,3′-dimethoxy-4,9,

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3′, 4′, 9′-lignanepentol-4′-*O*-β-*D*-glucopyranoside (7) $C_{26}H_{34}O_{11}$,无色粘稠状物质。$[\alpha]_D^{22}$-38.8°(*c* 0.56, CH_3OH)。^1H NMR (CD_3OD, 400 MHz) δ: 6.74 (2H, s, H-2, H-6), 2.64 (2H, t, *J* = 7.56 Hz, H-7), 1.83 (2H, m, H-8), 3.88 (3H, m, H-9, H-9′a), 7.05 (1H, s, H-2′), 7.15 (1H, d, *J* = 8.33 Hz, H-5′), 6.95 (1H, d, *J* = 8.30 Hz, H-6′), 5.57 (1H, d, *J* = 5.74 Hz, H-7′), 3.47 (1H, m, H-8′), 3.78 (1H, d, *J* = 7.48 Hz, H-9′b), 4.89 (1H, m, H-1″), 3.47 (1H, m, H-2″), 3.41 (1H, m, H-3″), 3.33 (1H, m, H-4″), 3.37 (1H, s, H-5″), 3.84 (1H, m, H-6″a), 3.70 (1H, d, *J* = 11.75 Hz, H-6″b)。FAB-MS *m/z*: 521[M-1]⁻。其波谱数据(碳谱数据见表1)与文献报道的一致[9]。

(7′*S*,8′*S*)-3,3′-Dimethoxy-9,4′,9′-trihydroxy-4,8′-oxyneolignan-7′-*O*-β-*D*-glucopyranside (8) $C_{26}H_{36}O_{12}$,无色粘稠状物质。$[\alpha]_D^{21}$-34.1°(*c* 0.47, CH_3OH)。^1H NMR (CD_3OD, 500 MHz) δ: 6.77 (1H, s, H-2), 6.65 (1H, d, *J* = 8.14 Hz, H-5), 6.82 (1H, d, *J* = 8.08 Hz, H-6), 2.59 (2H, dd, *J* = 6.87, 17.20 Hz, H-7), 1.78 (2H, m, H-8), 3.54 (2H, m, H-9a, 9′a), 3.85 (2H, m, H-9b, 9′b), 7.11 (1H, s, H-2′), 6.97 (1H, d, *J* = 8.40 Hz, H-5′), 6.69 (1H, d, *J* = 8.26 Hz, H-6′), 4.30 (1H, d, *J* = 5.00 Hz, H-7′), 4.24 (1H, m, H-8′), 4.93 (1H, d, *J* = 5.38 Hz, H-1″), 3.49 ~ 3.39 (4H, m, H-2″ ~ 5″), 3.68 (2H, m, H-6″), 3.79 (3H, s, H-OMe), 3.81 (3H, s, H-OMe)。FAB-MS *m/z*: 539[M-1]⁻。其波谱数据(碳谱数据见表1)与文献报道的一致[10]。

Methyl Shikimate (9) $C_8H_{12}O_5$,白色针状结晶。$[\alpha]_D^{21}$-134.7° (*c* 0.45, MeOH)。^{13}C NMR (CD_3OD, 100 MHz) δ: 139.0 (C-1), 130.2 (C-2), 67.3 (C-3), 72.6 (C-4), 68.4 (C-5), 31.5 (C-6), 168.7 (C-7), 52.3 (C-9)。^1H NMR (CD_3OD, 500 MHz) δ: 6.78 (1H, m, H-2), 4.36 (1H, m, H-3), 3.69 (1H, q, *J* = 4.18, 7.21 Hz, H-4), 3.98 (1H, m, H-5), 2.68 (1H, m, H-6a), 2.20 (1H, m, H-6b), 3.73 (3H, s, H-8)。EI-MS *m/z*: 188 [M]⁺。其波谱数据与文献报道的一致[11]。

β-Sitosterol (10) 白色针状结晶,该化合物TLC与对照品 R_f 值一致。

表1 化合物1~8的^{13}C NMR数据(^{13}C: 100 MHz; δ: ppm)

Table 1 ^{13}C NMR data of compounds 1-8 (^{13}C: 100 MHz; δ: ppm)

C	1[a]	2[d]	3[c]	4[b]	5[d]	6[b]	7[b]	8[b]
1	-	-	-	-	-	-	137.1	137.4
2	158.4	157.4	156.5	158.8	158.4	156.2	117.9	117.6
3	135.4	135.0	133.5	137.3	134.9	133.5	145.2	147.9
4	179.4	178.9	177.8	177.4	179.8	177.4	147.5	147.3
5	163.0	162.9	161.3	162.5	162.9	161.2	129.6	121.8
6	99.9	99.9	98.8	99.3	99.9	98.6	114.1	119.5
7	165.9	166.0	164.3	165.6	165.9	164.1	32.9	32.6
8	94.8	94.7	93.9	94.4	94.8	93.4	35.8	35.4
9	158.5	157.7	156.9	158.2	159.1	156.3	62.2	62.5
10	105.8	105.4	104.1	104.5	105.6	103.9	-	-
1′	123.1	122.1	121.1	124.2	123.0	121.1	138.3	138.1
2′	114.8	114.4	112.8	116.2	116.5	115.1	111.2	114.1
3′	150.9	151.4	149.6	148.0	149.8	148.4	150.9	151.8
4′	148.5	148.2	147.3	146.2	146.3	144.7	147.6	147.1
5′	116.1	116.4	115.6	116.0	116.9	116.0	118.0	121.0
6′	123.6	123.4	122.8	121.7	123.0	121.9	119.3	122.0
7′	-	-	-	-	-	-	88.5	86.3
8′	-	-	-	-	-	-	55.6	87.1
9′	-	-	-	-	-	-	65.0	61.5
1″	104.3	104.0	108.1	-	109.4	101.9	102.7	103.0
2″	73.2	74.2	82.5	-	83.3	71.2	74.9	74.9
3″	75.0	73.1	77.2	-	78.6	73.2	78.2	78.1
4″	69.9	68.8	86.2	-	87.9	67.9	71.3	71.3
5″	77.3	67.2	60.8	-	62.5	75.8	77.8	77.8
6″	62.2	-	-	-	-	60.1	62.5	62.2
OMe	57.1	56.4	55.8	-	-		56.7	56.7
OMe	-	-	-	-	-	-	56.5	56.5

注: [a]在氘代甲醇+氘代二甲亚砜中测定; [b]在氘代甲醇中测定; [c]在氘代吡啶中测定; [d]在氘代二甲亚砜中测定

Note: [a]in CD_3OD + DMSO; [b]in CD_3OD; [c]in C_5D_5N; [d]in DMSO

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