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大蒜果树的化学成分

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摘要：从大蒜果树（*Dysoxylum hainanense* Merr.）树皮的乙醇提取物中分离得到 10 个化合物，通过波谱方法鉴定它们分别是（+）evofolin B（1），20S、24－epoxy－24、25－dihydroxy－3，4－secodammar－4（28）－en－3－oic acid（2），4（14）－eudesmene－6?，11－diol（3），stigmast－5－ene－3β，7α－diol（4），stigmast－5－en－3β－ol linoleate（5），sitoindoside I（6），methyl 3，4－dihydroxy－benzoate（7），scopoletin（8），β－谷甾醇和胡萝卜甙。其中 1 为新化合物。

关键词：大蒜果树；楝科；（+）evofolin B
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Chemical Constituents from *Dysoxylum hainanense*

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Abstract：A new compound，（+）evofolin B（1），together with nine other known compounds，20S，24－epoxy－24，25－dihydroxy－3，4－secodammar－4（28）－en－3－oic acid（2），4（14）－eudesmene－6α，11－diol（3），stigmast－5－ene－3β，7α－diol（4），stigmast－5－en－3β－ol linoleate（5），sitoindoside I（6），methyl 3，4－dihydroxy－benzoate（7），scopoletin（8），β－sitosterol and daucosterol were obtained from the EtOH extract from the bark of *Dysoxylum hainanense* Merr.

Key words：*Dysoxylum hainanense*；Meliaceae；（+）evofolin B

The genus *Dysoxylum* Bl. is distributad in India，Southeast Asia，Australia and New Zealand，and comprises about 200 species. Fourteen of them are distributed in China. About 10 species of this genus have been found in Yunnan Province. *D. hainanense* Merr. is distributed in the Guangxi Zhuang Autonomous Region，Hainan Province，and Xishuangbanna of Yunnan Province（Wu *et al*，1977）. In the previous reports（Aalbersberg *et al*，1991；Singh *et al*，1992；Govindachari *et al*，1994），many dammarane triterpenoids were isolated from this genus. However，no chemical work has been done on *D. hainanense*. As part of a program of seeking bioactive compounds from Meliaceae plants（Luo *et al*.，1999），we examined the extracts from the bark of *D. hainanense*. In this paper，we describe the isolation and structural elucidation of a new compound，（+）evofolin B（1），as well as known compounds，20S，24－epoxy－24，25－dihydroxy－3，4－secodammar－4（28）－en

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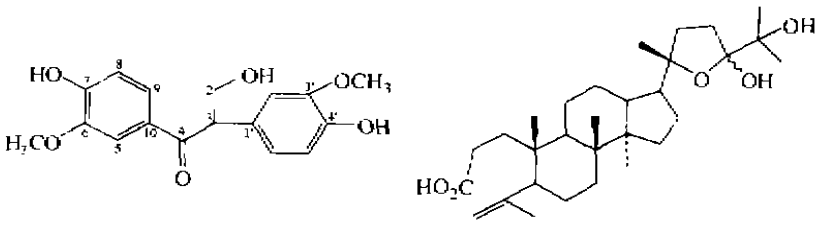
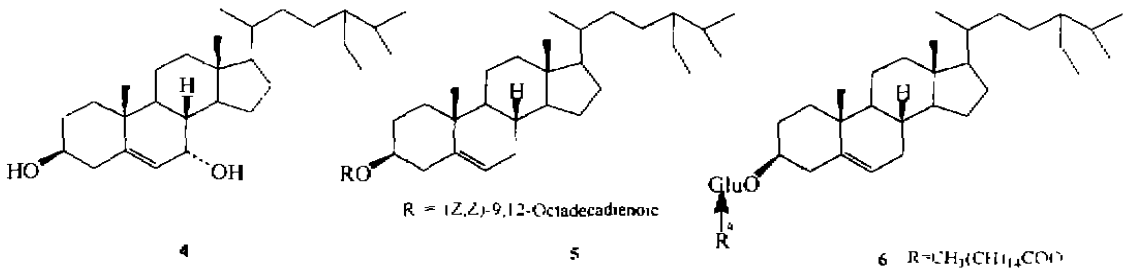
- 3 - oic acid (2), 4 (14) - eudesmene - 6α, 11 - diol (3) (De Pascual - T *et al*, 1980), stigmast - 5 - ene - 3β, 7α - diol (4) (Fukuyama *et al*, 1988), stigmast - 5 - en - 3β - ol linoleate (5) (Paasonen, 1967), sitoindoside I (6) (Kiribuchi *et al*, 1967), methyl 3, 4 - dihydroxy benzoate (7), scopoletin (8) (Cheng *et al*, 1989).

Results and Discussion

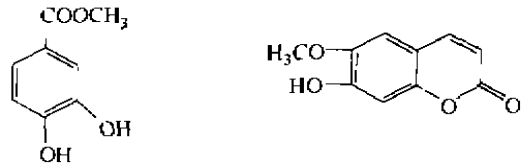
Compound 1 was assigned the molecular formula of $C_{17}H_{18}O_6$ by HRFAB - MS, which possessed nine degrees of unsaturation. The ^{13}C and ^1H NMR spectra showed signals due to two substituted phenyls [δ_C 150.6 (s), 147.1 (s), 146.6 (s), 145.3 (s), 121.4 (s), 128.6 (s), 124.4 (d), 121.7 (d), 115.1 (d), 114.0 (d), 110.8 (d), 110.4 (d)], two methoxyls (δ_C 55.6, 55.6), a oxymethylene (δ_C 65.4), a methine (δ_C 56.0), and a ketone carbonyl (δ_C 198.6). These data were almost identical to those of evofolin B (Wu *et al*, 1995).



1　　2　　3



4　　5　　6 R=CH$_3$(CH$_{14}$COO



7　　8

Two methoxyls were placed C - 6 and C - 3′ respectively, by the presence of cross peaks between δ_H 3.94 (3H, s, OCH_3) to 147.1 (s, C - 3′), and 3.87 (3H, s, OCH_3) to 146.6 (s, C - 6) in the HMBC spectrum. Based on the detailed analysis of HMBC, HMQC and $^1H - ^1H$ COSY spectra of 1, we proposed the structure for compound 1. The optical rotation of 1 was almost the same as magnitude, but opposite sign with that of evofolin B (Wu *et al*, 1995). Because only one chiral carbon ex-

isted in their structure, compound 1 was determined as an epimer of evofolin B, named as (+) evofolin B.

Experimental

Mps: uncorr.; UV: MeOH; IR: KBr; ^{1}H NMR, ^{13}C NMR and 2D-NMR spectra were recorded on a Bruker AM-400 MHz and a DRX-500 spectrometer with TMS as internal standard and $CDCl_3$ as solvent, chemical shift values were reported in δ (ppm) and coupling constants in Hz units; FAB-MS data were recorded on a VG Autospec-3000 spectrometer; EIMS: 70eV.

The bark of *D. hainanense* Merr. was collected from Xishuangbanna, Yunnan Province, P. R. China, in December 1996. The plant was identified by Prof. G. D. Tao, Xishuangbanna Tropical Botanical Garden, Chinese Academy Sciences. A voucher specimen was deposited in the herbarium of the Department of Plant Taxonomy, Kunming Institute of Botany, Chinese Academy of Sciences.

The dried and powdered bark (4.2 kg) of *D. hainanense* was extracted with EtOH under reflux, the solvent was evaporated *in vacuo*. The residue was partitioned in H_2O and extracted with EtOAc. The EtOAc extracts were concentrated *in vacuo* to afford 72g of residue, which was subjected to silica gel column chromatography, using $CHCl_3$-Me_2CO (from $CHCl_3$ to $CHCl_3$-Me_2CO 1: 1) as eluent. The fractions were combined with TLC monitoring. Then, the fractions 1-12 were further purified on silica gel CC with various eluent system and finally on reversed-phase C_{18} silica gel CC, eluted with CH_3OH-H_2O (3: 1-1: 1) to yield 1 (8 mg), 2 (284 mg), 3 (4 mg), 4 (10 mg), 5 (432 mg), 6 (122 mg), 7 (16 mg) and 8 (8 mg).

(+) **Evofolin B** (1) was obtained as yellow oil: $[\alpha]_D^{26}$+ 16.7° (c 0.30, CH_3OH); UV (MeOH) λ_{max} 203.5, 231, 279 nm; IR ν_{max}^{KBr} cm^{-1} 2927, 2854, 2360, 1717, 1700, 1651, 1594, 1558, 1519, 1458, 1427, 1275, 1033; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (1H, dd, J = 6.8 Hz, H-9), 7.56 (1H, d, J = 1.8 Hz, H-5), 6.90 (1H, d, J = 8.0 Hz, H-8), 6.87 (1H, d, J = 8.2 Hz, H-5'), 6.84 (1H, dd, J = 8.0, 2.1 Hz, H-6'), 6.75 (1H, d, J = 1.9 Hz, H-2'), 4.70 (1H, dd, J = 8.4, 4.8 Hz, H-3), 4.27 (1H, dd, J = 11.2, 8.4 Hz, H-2a), 3.92 (1H, dd, J = 11.2, 4.7 Hz, H-2b), 3.94 (3H, s, OCH_3), 3.87 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.6 (s, C-4), 150.6 (s, C-7), 147.1 (s, C-4'), 146.6 (s, C-6), 145.3 (s, C-3'), 129.4 (s, C-10), 128.6 (s, C-1'), 124.4 (d, C-9), 121.7 (d, C-5'), 115.1 (d, C-6'), 114.0 (d, C-8), 110.8 (d, C-2'), 110.4 (d, C-5), 65.4 (t, C-2), 56.0 (d, C-3), 55.6 (q, OCH_3); EIMS m/z 318 $[M]^+$ (15), 300 (3), 288 (10), 259 (6), 167 (12), 151 (100), 137 (10), 123 (15), 107 (17), 95 (5), 79 (16), 65 (13); HRFAB-MS 317.1047 $[M-1]^-$ (calcd. for $C_{17}H_{17}O_6$, 317.1025).

20S, 24-Epoxy-24, 25-dihydroxy-3, 4-secodammar-4 (28)-en-3-oic acid (2): Crystalline solids (Me_2CO); mp 148-150℃; EIMS m/z (70eV): 472 $[M-H2O]^+$ (46), 454 (5), 431 (12), 414 (18), 397 (15), 329 (40), 315 (15), 235 (22), 189 (15), 175 (26), 161 (37), 141 (81), 123 (60), 107 (11), 95 (78), 81 (88), 69 (71), 59 (100); IR ν_{max}^{KBr} cm^{-1}:

3387, 3079, 2971, 2873, 1711, 1638, 1458, 1421, 1384, 1311, 1284, 1227, 1209, 1181, 1162, 1053, 959, 930, 778; ^1H, ^{13}C NMR and TLC were identical to authentic sample.

4 (14) - Eudesmene - 6α, 11 - diol (3): Viscous oil; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8 (s, C-4), 110.5 (t, C-14), 75.1 (s, C-11), 73.4 (d, C-6), 57.0 (d, C-7), 42.4 (d, C-5), 40.8 (t, C-1), 36.2 (t, C-3), 34.7 (t, C-9), 34.1 (s, C-10), 32.7 (t, C-8), 30.1 (q, C-13), 23.2 (t, C-2), 22.1 (q, C-15), 21.5 (q, C-12); IR, EIMS and ^1H NMR were identical to the published data (De Pascual *et al*, 1980).

Stigmast - 5 - ene - 3β, 7α - diol (4): Colorless needles (Me_2CO); mp 220-221 ℃; IR $\nu_{max}^{KBr}cm^{-1}$ 3605, 3403, 2960, 2935, 2870, 1665, 1464, 1380, 1228, 1192, 1111, 1057, 1010, 952, 928, 892, 866; ^1H and ^{13}C NMR were identical to the published data (Fukuyama *et al*, 1988).

Stigmast - 5 - en - 3β - ol linoleate (5): Viscous oil; IR $\nu_{max}^{KBr}cm^{-1}$: 3453, 3009, 2931, 2857, 1734, 1669, 1467, 1379, 1246, 1174, 1138, 1029, 1010, 959, 923, 886, 840, 724; ^1H NMR ($CDCl_3$, 400 MHz) δ5.32 (1H, d, J = 4.2 Hz, H-6), 5.28 (4H, m, H-9', 10', 12', 13'), 4.55 (1H, m, H-3), 0.96 (3H, s, Me), 0.82 (3H, d, J = 6.5 Hz, Me), 0.82 (3H, t, J = 6.4 Hz, Me), 0.81 (3H, d, J = 6.7 Hz, Me), 0.78 (3H, d, J = 6.8 Hz, Me), 0.61 (3H, s, Me); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 37.1 (t, C-1), 28.3 (t, C-2), 73.7 (c, C-3), 39.8 (t, C-4), 139.8 (s, C-5), 122.6 (d, C-6), 32.0 (t, C-7), 31.5 (t, C-8), 50.2 (d, C-9), 36.7 (s, C-10), 21.1 (t, C-11), 29.7 (t, C-12), 42.4 (s, C-13), 56.7 (d, C-14), 24.3 (t, C-15), 38.2 (t, C-16), 56.2 (d, C-17), 11.9 (q, C-18), 19.1 (q, C-19), 36.2 (d, C-20), 18.8 (q, C-21), 34.0 (t, C-22), 28.3 (t, C-23), 46.0 (d, C-24), 29.3 (d, C-25), 19.3 (q, C-26), 19.8 (q, C-27), 23.2 (t, C-28), 12.0 (q, C-29), 173.2 (s, C-1'), 34.0 (t, C-2'), 31.5 (t, C-3'), 29.1 (t, C-4'), 27.2 (t, C-5'), 29.1 (t, C-6'), 28.3 (t, C-7'), 29.6 (t, C-8'), 130.2 (d, C-9'), 128.0 (d, C-10'), 31.5 (t, C-11'), 130.1 (d, C-12'), 128.1 (d, C-13'), 29.3 (t, C-14'), 29.3 (t, C-15'), 24.3 (t, C-16'), 22.6 (t, C-17'), 14.0 (q, C-18'); EIMS m/z 676 [M] + (3), 414 [M - R + 1] + (12), 396 (91), 382 (39), 329 (6), 303 (8), 282 (12), 268 (20), 255 (25), 215 (23), 199 (12), 173 (14), 159 (32), 145 (47), 109 (50), 95 (59), 69 (78), 55 (100).

Sitoindoside I (6): Viscous oil; IR $\upsilon_{max}^{KBr}cm^{-1}$: 3417, 2927, 2854, 1740, 1466, 1379, 1174, 1083, 1021, 723; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.33 (1H, d, J = 4.6 Hz, H-6), 4.35 (1H, d, J = 7.6 Hz, H-1'), 4.30 (2H, m, H-6'), 3.52 (2H, m, H-3', H-4'), 3.45 (1H, m, H-3), 3.40 (2H, m, H-2', H-5'), 0.98 (3H, s, H-19), 0.88 (3H, d, J = 6.4 Hz, H-21), 0.84 (3H, d, J = 7.0 Hz, H-27), 0.82 (3H, t, J = 7.8 Hz, H-29), 0.81 (3H, d, J = 7.0 Hz, H-26), 0.65 (3H, s, H-18); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.4 (s, RCOO), 140.4 (s, C-5), 122.1 (d, C-6) 101.3 (d, C-1'), 79.6 (d, C-3), 76.2 (d, C-3'), 73.9 (d, C-5'), 73.6 (d, C-4'), 70.3 (d, C-2'), 63.4 (t, C-6'), 56.8 (d, C-14), 56.2 (d, C-17), 50.3 (d, C-9), 45.9 (d, C-24), 42.4 (s, C-13), 39.8 (t, C-12), 39.0 (t, C-4), 37.3 (t, C-1), 36.8 (s, C-10), 36.1 (d, C-20), 34.3 (t, C-22,) 31.9

(d, C-8), 19.8 (q, C-27), 19.4 (q, C-19), 19.1 (q, C-21), 18.8 (q, C-18), 14.1 (q, CH_3 $(CH_2)_{16}COO$), 12.0 (q, C-29), 11.9 (q, C-18); FAB-MS m/z 813 $[M-H]^-$; EIMS m/z 414 $[M-Glu-R+H_2O]^+$ (18), 396 (100), 322 (81), 329 (7), 275 (5), 255 (10), 213 (10), 161 (10), 147 (12), 109 (7), 95 (11), 85 (13), 69 (20), 57 (100).

Methyl 3, 4-dihydroxy-benzoate (7): Colorless needles (Me_2CO); mp 182-185 ℃; UV (MeOH) λ_{max} (logε) 206.5 (4.39), 212 (4.28), 257 (4.15), 289.5 (3.84) nm; IRν_{max}^{KBr} cm^{-1}: 3486, 3100, 2854, 2652, 1682, 1598, 1523, 1473, 1456, 1380, 1300, 1282, 1239, 1206, 1186, 1113, 1029, 820, 805, 763, 722; ^1H NMR (pyridine-d_5, 400 MHz) δ 8.17 (1H, dd, J = 8.4, 1.6 Hz, H-6), 8.07 (1H, d, J = 1.4 Hz, H-2), 7.30 (1H, d, J = 8.3 Hz, H-5), 3.73 (3H, s, OCH_3); ^{13}C NMR (pyridine-d_5, 100 MHz) δ 169.1 (s, COO-), 152.8 (s, C-1), 148.4 (s, C-3), 125.0 (d, C-6), 116.2 (d, C-2), 114.0 (d, C-5), 55.9 (q, OCH_3); FAB-MS m/z 167 $[M-H]^-$ (100), 117 (73).

Scopoletin (8): Colorless needles (Me_2CO); UV, IR, ^1H, ^{13}C NMR and EIMS were identical to authentic sample.

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