

瑞香科植物毛瑞香的化学成分研究

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摘要 从瑞香科植物 *Daphne odora* sp. 的根中分得4个化合物, 经化学和光谱方法分析, 鉴定为 β -谷甾醇、双白瑞香素(daphnoretin)、daphneticin和D(-)-lariciresinol。

关键词 毛瑞香 双白瑞香素 daphneticin D(-)-lariciresinol

70年代初, Schildnec^[1]和Stout^[2]等首先从瑞香科植物中分得活性成分欧亚瑞香素(mezerein)和瑞香毒素(daphnotoxin), 结构分析属于二萜原酸酯类化合物。研究表明这一类化合物具有抗肿瘤作用^[3]。我国学者先后从芫花 *Daphne genkwa* Sieb. et Zucc., 中分得4种新的二萜原酸酯类化合物^[4~7], 药理实验证明^[8]它们具有较强的抗生育作用。为了继续寻找新的抗生育、抗肿瘤的活性成分资源, 我们从浙江临安产的毛瑞香 *Daphne odora* sp. 的根中分得8个单体化合物, 其中4个化合物鉴定为 β -谷甾醇、双白瑞香素、daphneticin和D(-)-lariciresinol。

1 仪器和材料

熔点由Koffler显微熔点仪测定(温度计未校正); 紫外光谱用Pye Unicam SP 1800型仪测定; 红外光谱用Perkin-Elmer 599B型仪测定, 质谱由MAT-711及MAT-44型仪测定; 核磁共振用Bruker AM-400和JNM-PS-100型仪测定。

柱层析用硅胶为青岛海洋化工厂生产的硅胶G(200~300目)和硅胶H; 制备性薄层板均为自制, 选用青岛海洋化工厂生产的HF₂₅₄薄层层析用硅胶。中压预制柱为C₁₈反相柱, Emek产。

2 提取和分离

取毛瑞香9kg打粉后, 用乙醇渗漉, 漉液浓缩后加水, 用CHCl₃抽提, 合并CHCl₃液, 用无水Na₂SO₄干燥后, 浓缩得抽提物209g。提取物加CH₂Cl₂回流溶解, 浓缩后用200~300目硅胶G 1200g湿法装柱, 分别以石油醚、乙酸乙酯-石油醚(1:20, 1:10, 1:5, 1:1)和90%乙醇洗脱。各流份以TLC检查后, 合并相同部分。流份第6~19, 浓缩后结晶析出, 过滤, 甲醇中重结晶, 得化合物I。流份第43~84, 有片状结晶析出, 过滤, 乙酸乙酯-石油醚重结晶, 得化合物II。流份第219, 浓缩后有结晶析出, 过滤, 乙酸乙酯-石油醚重结晶, 得化合物III。流份第223~224, 浓缩后, 结晶析出, 乙酸乙酯-石油醚重结晶后得化合物IV。

3 鉴定

化合物I: 白色针状结晶, mp163~164°C。UV $\lambda_{\max}^{\text{MeOH}}$ nm: 228, 280。IR ν_{\max}^{KBr} cm⁻¹: 3510, 3480, 3380, 2940, 2880, 1610, 1460, 1368, 1270, 1240, 1030, 820。¹HNMR (400MHz, CD₃COCD₃) δ : 6.92(1H, s), 6.76(4H, J=8.0Hz), 6.64(1H, q, J=6.2Hz), 4.76(1H, d, J=6.2Hz), 3.89(6H, m, -OCH₃×3), 3.64(3H), 2.94(4H), 2.67(1H, m), 2.51(2H, m), 2.30(1H, t), MS m/z: 360(M⁺), 345, 329, 311,

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299, 283, 236, 219, 206。其理化性质和光谱数据与文献^[9]报道的木脂素类的 D(-)-lariciresinol 一致。

化合物 I: 白色片状结晶, 分子式为 $C_{20}H_{30}O$, mp 135~137°C。IR、UV、MS、TLC R_f 值与标准品对照完全一致, 从而确定化合物 I 为 β -谷甾醇。

化合物 II: 淡黄色丝状或针状结晶, 分子式为 $C_{19}H_{12}O_7$, mp 242~244°C 及 256°C。UV λ_{max}^{EtOH} nm: 228(肩峰), 266, 325, 346。IR ν_{max}^{KBr} cm^{-1} : 3650(OH), 1720, 1613, 1592, 1481, 1282(-C=C-O-), 1242, 1220, 1136, 1087, 1026, 917, 870, 850, 770, 738。¹HNMR(400MHz, DMSO- d_6) δ : 3.82(3H, s, -OMe), 6.30(1H, d, J=9.5Hz, C_{3'}-H), 6.85~7.57(5H, m), 7.80(1H, s, C₄-H), 8.0(1H, d, J=9.5 Hz, C_{4'}-H)。MS m/z: 352(M⁺), 337, 324, 309, 179, 164, 135, 120, 119, 117。上述理化性质和光谱数据与文献^[10]报道的双白瑞香素一致。

化合物 III: 白色柱状结晶, 分子式 $C_{20}H_{18}O_8$, mp 252~253°C。UV λ_{max}^{EtOH} nm: 242, 262, 324。IR ν_{max}^{KBr} cm^{-1} : 3480, 3210, 1730, 1610, 1570, 1450, 1340, 1270, 1115, 1055, 835。¹HNMR(400 MHz, DMSO- d_6) δ : 8.01, 6.36(AB型, J=10.0 Hz, C_{3,4}-H), 7.25, 7.01(AB型, J=9.0Hz C_{5,6}-H), 6.81(2H, s, C_{5''}, 6''-H), 5.10(1H, d, J=7.5Hz, C_{1'}-H), 4.34(1H, m, C₂-H), 3.81(6H, s, 2x-OMe), 3.59(2H, m, C_{5'}-H)。MS m/z: 386(M⁺), 368, 210, 178, 167, 149。根据以上光谱数据和文献^[11]对照鉴定为香豆木脂素类的 daphneticin。化合物 I, II, III 的化学结构式见图。

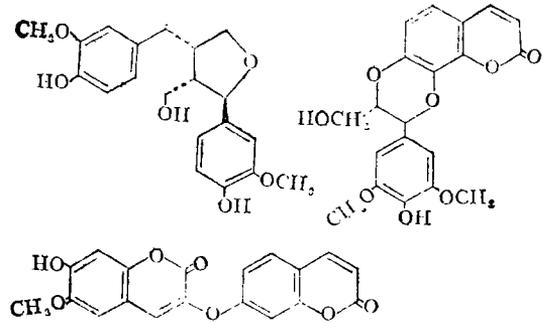


图 化合物 I(上左), II(下)和 III(上右)结构式

参 考 文 献

- Schildknecht H, et al. Chem Zeit, 1970, 94:347
- Stout G H, et al. J Am Chem Soc, 1970, 92(4):1070
- Georgre R P, et al. J Nat Prod, 1983, 46(4):563
- 应白平, 等. 化学学报, 1977, 35:103
- 王成瑞, 等. 化学学报, 1981, 39:421
- 王成瑞, 等. 化学学报, 1982, 40:835
- 胡邦豪, 等. 化学学报, 1985, 43:460
- 王成瑞, 等. 中日天然产物药理学学术讨论会文集.
- Zhuang L G, et al. Phytochem, 1982, 45:172
- Tando S, et al. Phytochem, 1977, 16:1991
- Zhuang L G, et al. Phytochem, 1983, 22:61

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ABSTRACTS OF ORIGINAL ARTICLES

Studies on the Chemical Constituents of Shellfish *Pricklyash*

(*Zanthoxylum dissitum*)

Tang Jun, Zhu Wei, Tu Zhiben

Eight crystalline compounds were isolated from the stem of *Zanthoxylum dissitum* Hemsl. for the first time. Seven of them were identified as dictamnine (I), γ -fagarine (II), skimmianine (III), 4-methoxy-1-methyl-2-quinolone (IV), haplopine (V), β -sitosterol (VI) and daucosterol (VII) on the basis of spectral data. The eighth was a mixed long-chain fatty (VIII) (mainly $C_{26}H_{52}O_2$).

(Original article on page 563)

Studies on the Chemical Constituents of *Maoruixiang* (*Daphne odora*)

Wang Wei wen, Zhou Bingnan, Wang Chengrui

Four compounds were isolated from the root of *Daphne odora* sp.. Their structures were identified by chemical and spectroscopic methods as daphnoretin, daphneticin, D(-)-lariciresinol and β -sitosterol.

(Original article on page 566)

Studies on the Chemical Constituents of Japanese Honeysuckle

(*Lonicera japonica*)

Gao Yumin, Mu Huijun, et al

Four flavonoids were isolated for the first time from *Lonicera japonica* Thunb.. Their structures were identified by spectroscopic (IR, UV, 1H NMR, ^{13}C NMR and MS) and chemical methods as luteolin-7-O- α -D-glucoside (I), luteolin-7-O- β -D-galactoside (II), quercetin-3-O- β -D-glucoside (III) and hyperoside (IV).

(Original article on page 568)

On the Quality Standard of Huichunzhibao Oral Liquid (HZOL)

Guo Tao, Jin Baofeng, et al

Huichunzhibao oral liquid (HZOL) is a traditional Chinese herb preparation composed of *Panax ginseng*, Hairy Antler (*Cervus nippon* Temminck) and *Epimedium brevicornum* Maxim.. The active principle of each component was identified by TLC and icariin, the main active principle of *E. brevicornum* was determined quantitatively by HPLC. The method was found to be accurate, sensitive and reproducible with average recovery 98.97% and RSD=1.53 (n=3).

(Original article on page 572)

Effect of Monoammonium Glycyrrhizinate on

Ascorbic Acid and Lead Complex

Shao Wei, Wang Chunxiang, Mi Guangtai, et al

Stability constant of ascorbic acid and lead complex was measured by pH potentiometry at different temperatures and concentrations of monoammonium glycyrrhizinate (MG). At a concentration of 5.0×10^{-4} mol/L and at biological condition, $\lg k_1 = 8.72$ and $\lg k_2 =$