

羊角天麻中的两个新倍半萜

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TWO NEW SESQUITERPENES FROM DOBINEA DELAVAYI

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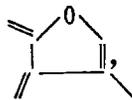
关键词 羊角天麻; 倍半萜; 羊角天麻素 I; 羊角天麻素 II

Key words *Dobinea delavayi*; sesquiterpenes; dobinin I; dobinin II

羊角天麻 (*Dobinea delavayi* Baill.) 分布于我国云南省和西喜马拉雅山区^[1], 在云南民间是用作消痈肿、抗肿瘤的有效药^[2], 其化学成分未见报道, 本文将报道从羊角天麻根部中分得的两个新倍半萜 (Dobinin I 和 Dobinin II^[3-7])。作者通过 IR、UV、EIMS、¹H NMR、¹³C NMR、DEPT 以及 X-衍射对其结构进行了解释。

取羊角天麻根 8 kg 用 95% 乙醇在室温下浸泡 15 天, 回收乙醇后, 用石油醚萃取, 萃取部分进行硅胶柱层析, 用石油醚-乙酸乙酯系统梯度洗脱, 合并相同部分, 一部分经石油醚重结晶, 得方块状结晶 Dobinin I, 另一部分再上氧化铝柱纯化, 得无色油状化合物 Dobinin II。

Dobinin I, mp 79-81 °C (petrol), UV λ_{max}^{EtOAc} nm (long ϵ) 218(0.45), IR ν_{max}^{KBr} cm⁻¹ 3120, 2910, 1720, 1710, 1650, 1635, 1555, 1450, 1410, 1360, 1350, 1315, 1245, 1230, 1200, 1160, 1135, 1080, 1070, 1040, 1010. EIMS m/z (%) 374 (M⁺, 5), 315 (M-CH₃COO, 20), 314 (M-CH₃COOH, 60), 214 [M-CH₃COOH, CH₃CH=C(CH₃)COOH, 80], 103 (



¹H NMR (400 MHz, CDCl₃) δ ppm: 1.70-1.80 (m, H-1, H-2), 4.82 [dd, J(2 α , 3) = 11, J(2 β , 3) = 5 Hz, H-3], 1.74 [dd, J(5, 6 α) = J(5, 6 β) = 5.6 Hz, H-5], 2.14 [d(br), J(6 α , 6 β) = 16 Hz, H-6 α], 2.27 [d(br), J(6 α , 6 β) = 16 Hz, H-6 β], 2.49 [d, J(9 α , 9 β) = 16 Hz, H-9 α], 2.36 [d, J(9 α , 9 β) = 16 Hz, H-9 β], 7.04 (s, H-11), 1.95 (s, H-13), 0.94 (s, H-14), 1.47 (s, H-15), 1.93 [d, J(18, 19) = 1.7 Hz, H-18], 6.06 [dq, J(19, 20) = 7.2, J(18, 19) = 1.7 Hz, H-19], 1.89 [d, J(19, 20) = 7.2 Hz, H-20], 1.96 (s, H-22), ¹³C NMR (400 MHz, CDCl₃) δ ppm: 18.2 (C-1), 25.8 (C-2), 81.5 (C-3), 87.8 (C-4), 44.6 (C-5), 38.1 (C-6), 119.4 (C-7), 149.0 (C-8), 42.5 (C-9), 35.6 (C-10), 137.2 (C-11), 115.7 (C-12), 19.7 (C-13), 8.1 (C-14), 15.7 (C-15), 167.0 (C-16), 137.4 (C-

17), 20.6 (C-18), 128.3 (C-19), 17.4 (C-20), 170.0 (C-21), 22.8 (C-21)。

Dobinin I, oil, IR $\nu_{\text{max}}^{\text{film}}$

cm^{-1} 3470, 2920, 2850, 1760,
1700, 1640, 1560, 1450, 1410,
1380, 1350, 1340, 1260, 1230,
1150, 1090, 1040, UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm
(log ϵ) 217(0.69)。EIMS m/z (%)
332(M^+ , 28), 231[M-CH₃CH=C
(CH₃)COOH, 4], 214[M-CH₃CH=C(CH₃)COOH, H₂O,

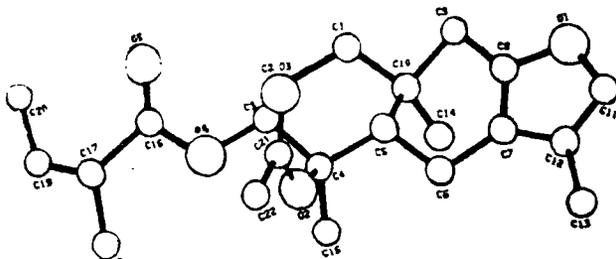
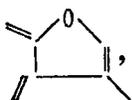
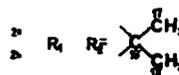
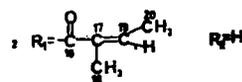
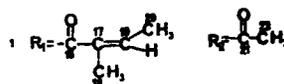
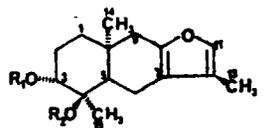


Fig. 1 Perspective view of compound 1

18], 108[, 60], ¹H NMR (400MHz, CDCl₃)

δ ppm: 1.70—1.80(m, H-1, H-2), 4.80 [dd, J(2 α , 3)=11, J(2 β , 3)=5 Hz, H-3], 1.72[dd, J(5, 6 α)=J(5, 6 β)=5.6 Hz, H-5], 2.41[d (br), J(6 α 6 β)=16 Hz, H-6 α], 2.27 [d (br), J(6 α , 6 β)=16 Hz, H-6 β], 2.49 [d, J(9 α , 9 β)=16 Hz, H-9 α], 2.36 [d, J(9 α , 9 β)=16 Hz, H-9 β]. 7.04(s, H-11), 1.94 (s, H-13), 0.94 (s, H-14), 1.30(s, H-15), 1.92 [d, J(18, 19)=1.7 Hz, H-18], 6.10[dq, J(19, 20)=7.2, J(18, 19)=1.7 Hz, H-19], 1.88 [d, J(19, 20)=7.2 Hz, H-20], 1.60 (m, OH-4)。¹³C NMR (400 MHz,



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CDCl₃) δ ppm: 18.6 (C-1), 25.6 (C-2), 81.4 (C-3), 74.6 (C-4), 40.5 (C-5), 38.6 (C-6), 119.6 (C-7), 148.6 (C-8), 42.2 (C-9), 35.0 (C-10), 137.1 (C-11), 116.2 (C-12), 19.2 (C-13), 8.0 (C-14), 15.8 (C-15), 166.2 (C-16), 138.2 (C-17), 20.6 (C-18), 128.0 (C-19), 17.9 (C-20)。

比较 Dobinin I 和 Dobinin II 的 ¹H NMR, ¹³C NMR, MS 发现 Dobinin II 比 Dobinin I 在 C-4 位少一个乙酰基, 而且由 ¹H NMR 谱比较可见, 3 位质子和 4 位上甲基质子有位移, 从 Dobinin I 4.82, 1.47 ppm 移到 Dobinin II 的 4.80, 1.30 ppm; ¹³C NMR 谱 Dobinin I 的 4 位碳从 87.8 ppm 移到 Dobinin II 的 74.6 ppm. 其余碳的位移基本未变。

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