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云南油杉的化学成分研究

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摘 要: 从云南油杉(*Keteleeria evelyniana*)枝条中首次分离得到 19个化合物, 通过 MS与 NMR等方法将它们分别鉴定为(-)-epinortrachelogenin (**1**), (-)-α-conidendrin (**2**), cedrusin (**3**), (+)-dihydrodehydrodiconiferyl alcohol (**4**), oxomatairesinol (**5**), (-)-7′(*S*)-5-hydroxymatairesinol (**6**), vladinol D (**7**), (*E*)-3-hydroxy-5-methoxy-stilbene (**8**), resveratrol-3-O-β-*D*-glucopyranoside (**9**), pinocembrin (**10**), (2*S*, 3*R*)-3, 5, 7, 3′, 4′-pentahydroxyflavan (**11**), kaempferol (**12**), kaempferol-3-O-β-*D*-glucopyranoside (**13**), (*E*)-ferulic acid tetracosyl ester (**14**), ω-hydroxypropioquaiacone (**15**), vanillin (**16**), hemisceramide (**17**), β-sitosterol (**18**)和 β-daucosterol (**19**)。

关键词: 云南油杉; 松科; 化学成分; 木脂素; 黄酮

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Chemical Constituents of *Keteleeria evelyniana*

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Abstract Nineteen known compounds were isolated from the branches of *Keteleeria evelyniana* for the first time. On the basis of MS and NMR data, they were identified as (-)-epinortrachelogenin (**1**), (-)-α-conidendrin (**2**), cedrusin (**3**), (+)-dihydrodehydrodiconiferyl alcohol (**4**), oxomatairesinol (**5**), (-)-7′(*S*)-5-hydroxymatairesinol (**6**), vladinol D (**7**), (*E*)-3-hydroxy-5-methoxy-stilbene (**8**), resveratrol-3-O-β-*D*-glucopyranoside (**9**), pinocembrin (**10**), (2*S*, 3*R*)-3, 5, 7, 3′, 4′-pentahydroxyflavan (**11**), kaempferol (**12**), kaempferol-3-O-β-*D*-glucopyranoside (**13**), (*E*)-ferulic acid tetracosyl ester (**14**), ω-hydroxypropioquaiacone (**15**), vanillin (**16**), hemisceramide (**17**), β-sitosterol (**18**) and β-daucosterol (**19**).

Key words *Keteleeria evelyniana*; Pinaceae; chemical constituents; lignans; flavonoids

云南油杉(*Keteleeria evelyniana* Mast)为松科(Pinaceae)油杉属常绿乔木, 为我国特有种, 产于云南、贵州西部及西南部、四川西南部安宁河流域至西部大渡河流域海拔 700~2600米的地带, 常混生于云南松林中或组成小片纯林, 亦有人工林[1]。其根皮涩、平, 消肿止痛、活血祛瘀、解毒生肌, 用于跌打损伤、骨折、疮痈、漆疮[2]。人们对该种植物的化学及活性成分研究工作尚未见报导, 作为系统的裸子植物的化学与活性成分研究计划的一部分, 我们对云南油杉的枝条进行了较深入的化学研究。本文介绍该植物中 19个已知化合物的分离与结构鉴定。

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 2005年 9月采于云南省昆明市昆明植物园内。植物样品由中国科学院昆明植物研究所岳中书副研究员鉴定, 标本保存于中国科学院昆明植物研究所标本馆, 标本号为 0010482。

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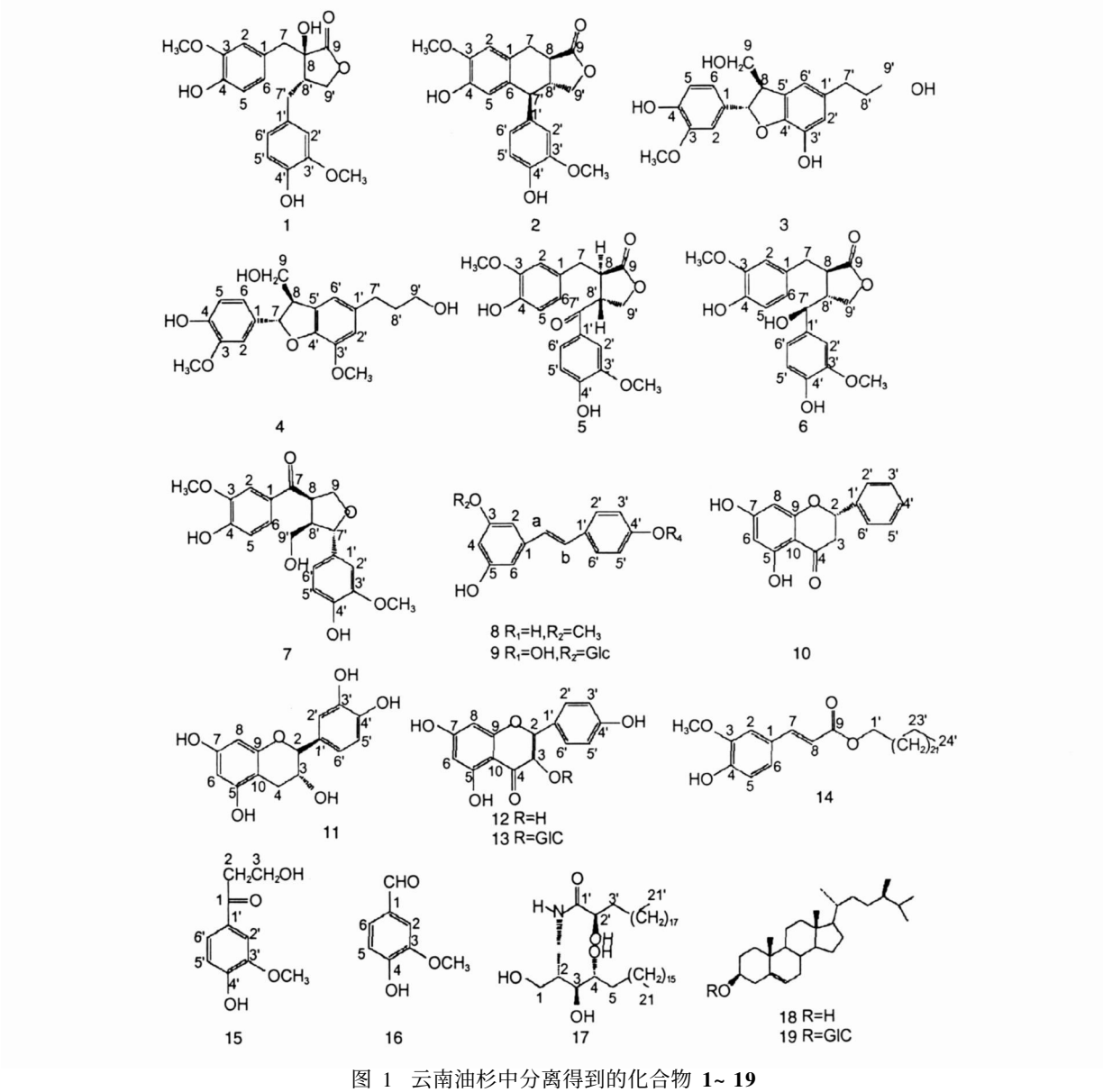

图 1 云南油杉中分离得到的化合物 **1~19**

Fig 1 Compounds **1-19** isolated from *Keteleeria evelyniana*

2 提取和分离

20 kg干燥云南油杉枝条, 粉碎后用 95% 工业乙醇加热提取 3次, 提取液合并浓缩, 得总浸膏 1. 2 kg。将浸膏溶于热水, 滤去水不溶物, 滤液分别用石油醚、乙酸乙酯、正丁醇萃取, 减压浓缩各萃取物, 得石油醚浸膏 100 g 乙酸乙酯浸膏 225 g 正丁醇浸膏 630 g 水浸膏 120 g。石油醚部分经硅胶柱以石油醚-乙酸乙酯、石油醚-丙酮反复层析得到化合物 8 (20 mg)。乙酸乙酯部分经硅胶柱以石油醚-乙酸乙酯、石油醚-丙酮和氯仿-甲醇多次反复梯度洗脱, 再经 Sephadex LH-20凝胶柱以氯仿-甲醇、丙酮、甲醇纯化, 得到化合物 **1** (4 mg)、**2** (40 mg)、**3** (40 mg)、**4** (13 mg)、**5** (50 mg)、**6** (10 mg)、**7** (200 mg)、**9** (5 mg)、**10** (13 mg)、**11** (4 g)、**12** (60 mg)、**13** (21 mg)、**14** (6 mg)、**15** (16 mg)、**16** (38 mg)、**17** (1 g)、**18** (20 mg)、**19** (26 mg)。

3 结构鉴定

(-)-Epinortrachelogenin (1) 白色粉末。$[\alpha]_D^{27}$ -15. 3° (*c* 0. 23, MeOH)。^{1}H NMR (CD_3OD, 500 MHz) δ 6. 78~6. 69 (4H, m, H-2, 5′, 6, 6′), 6. 58 (1H, dd, *J* = 8. 0, 1. 6 Hz, H-5), 3. 06 (1H, d, *J* = 14. 4 Hz, H-7a), 2. 95 (1H, d, *J* = 14. 4 Hz, H-7b),

6.91 (1H, d, J = 1.4 Hz, H-2′), 2.73-2.65 (3H, m, H-7′, 8′), 4.05 (1H, dd, J = 8.7, 7.2 Hz, H-9′a), 3.73 (1H, t, J = 9.0 Hz, H-9′b), 3.84, 3.81 (6H, s, 2×OMe)。FAB⁻-MS m/z: 373[M-1]⁻。其波谱数据(碳谱数据见表 1)与文献报道的一致[3]。

(-)-α-Conilendrin (2) 白色粉末。$[\alpha]_D^{27}$ -81.6° (c 0.34, MeOH)。^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.58 (1H, s, H-2), 6.26 (1H, s, H-5), 3.27 (1H, s, H-7a), 3.09 (1H, dd, J = 15.6, 4.1 Hz, H-7b), 2.51~2.46 (2H, m, H-8, 8′), 6.47 (1H, s, H-2′), 6.73 (1H, d, J = 8.0 Hz, H-5′), 6.55 (1H, d, J = 8.0 Hz, H-6′), 2.88 (1H, m, H-7′), 4.14 (1H, dd, J = 8.7, 6.1 Hz, H-9′a), 3.95 (1H, t, J = 10.2 Hz, H-9′b), 3.71, 3.78 (6H, s, 2×OMe)。FAB⁺-MS m/z: 357[M+1]⁺。其波谱数据(碳谱数据见表 1)与文献报道的一致[4,8]。

Cedrusin (3) 无色粘稠状物质。$[\alpha]_D^{27}$ +13.2° (c 0.57, Me$_2$CO)。^{1}H NMR ((CD$_3$)$_2$CO, 400 MHz) δ 7.05 (1H, d, J = 1.8 Hz, H-2), 6.80 (1H, d, J = 8.1 Hz, H-5), 6.89 (1H, dd, J = 8.1, 1.8 Hz, H-6), 5.50 (1H, d, J = 6.5 Hz, H-7), 3.51 (1H, t, J = 6.5 Hz, H-8), 3.87 (1H, dd, J = 10.8, 5.4 Hz, H-9a), 3.78 (1H, t, J = 3.5 Hz, H-9b), 6.61 (1H, br. s, H-2′), 6.63 (1H, br. s, H-6′), 2.56 (2H, t, J = 7.5 Hz, H-7′), 1.77 (2H, m, H-8′), 3.56 (2H, t, J = 6.5 Hz, H-9′), 3.81 (3H, s, OMe)。FAB⁻-MS m/z: 345[M-1]⁻。其波谱数据(碳谱数据见表 1)与文献报道的一致[5,6]。

(+)-Dihydrodehydrodiconiferyl alcohol (4) 无色粘稠状物质。$[\alpha]_D^{27}$ +8.5° (c 0.80, CHCl$_3$)。^{1}H NMR (CDCl$_3$, 500 MHz) δ 6.92 (1H, s, H-2), 6.26 (1H, d, J = 8.1 Hz, H-5), 6.81 (1H, d, J = 8.2 Hz, H-6), 5.49 (1H, d, J = 7.1 Hz, H-7), 3.54 (1H, q, J = 6.1 Hz, H-8), 3.84 (2H, overlapped, H-9), 6.66 (1H, s, H-2′), 6.64 (1H, s, H-6′), 2.62 (2H, t, J = 7.3 Hz, H-7′), 1.83 (2H, dt, J = 6.6 Hz, H-8′), 3.61 (2H, m, H-9′), 3.83 (3H, s, OMe), 3.81 (3H, s, OMe)。FAB⁻-MS m/z: 359[M-1]⁻。其波谱数据(碳谱数据见表 1)与文献报道的一致[5,6]。

Oxomatairesinol (5) 白色粉末。$[\alpha]_D^{23.5}$ +21.8° (c 0.22, Me$_2$CO)。^{1}H NMR ((CD$_3$)$_2$CO, 400 MHz) δ 6.77 (1H, s, H-2), 6.65 (2H, d, J = 7.9 Hz, H-5, 6), 2.84 (1H, dd, J = 13.9, 8.6 Hz, H-7a), 3.04 (1H, dd, J = 13.9, 5.0 Hz, H-7b), 3.37 (1H, m, H-8), 7.37 (1H, d, J = 2.0 Hz, H-2′), 6.82 (1H, d, J = 8.3 Hz, H-5′), 7.33 (1H, dd, J = 8.3, 2.0 Hz, H-6′), 4.07 (1H, m, H-8′), 4.34 (1H, d, J = 7.8 Hz, H-9′a), 4.53 (1H, t, J = 8.5 Hz, H-9′b), 3.86 (3H, s, OMe), 3.66 (3H, s, OMe)。FAB⁺-MS m/z: 373[M+1]⁺。其波谱数据(碳谱数据见表 1)与文献报道的一致[7]。

(-)-7′(S)-5-Hydroxymatairesinol (6) 白色粘稠状物质。$[\alpha]_D^{27}$ -5.5° (c 1.56, Me$_2$CO)。^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.60 (1H, s, H-2), 6.85 (1H, d, J = 8.1 Hz, H-5), 6.59 (1H, d, J = 7.2 Hz, H-6), 2.98 (1H, t, J = 7.6 Hz, H-7′a), 2.91 (2H, m, H-7′b, 8′), 2.59 (1H, t, J = 7.4 Hz, H-8), 6.65 (1H, d, J = 1.4 Hz, H-2′), 6.77 (1H, d, J = 8.2 Hz, H-5′), 6.70 (1H, d, J = 8.1 Hz, H-6′), 4.63 (1H, d, J = 6.5 Hz, H-7′), 3.95 (2H, m, H-9′), 3.83 (3H, s, OMe), 3.80 (3H, s, OMe)。FAB⁻-MS m/z: 373[M-1]⁻。其波谱数据(碳谱数据见表 1)与文献报道的一致[8]。

Vladinol D (7) 淡黄色粘稠状物质。$[\alpha]_D^{26}$ +0.6° (c 0.40, Me$_2$CO)。^{1}H NMR ((CD$_3$)$_2$CO, 400 MHz) δ 7.06 (1H, d, J = 1.7 Hz, H-2), 6.78 (1H, d, J = 8.0 Hz, H-5), 6.86 (1H, dd, J = 8.1, 1.8 Hz, H-6), 2.68 (1H, m, H-8), 3.66 (1H, dd, J = 10.3, 5.3 Hz, H-9a), 3.78 (1H, m, H-9b), 7.65 (1H, d, J = 1.9 Hz, H-2′), 6.93 (1H, d, J = 8.4 Hz, H-5′), 7.64 (1H, d, J = 7.4 Hz, H-6′), 4.67 (1H, d, J = 8.5 Hz, H-7′), 4.27 (1H, m, H-8′), 4.11 (1H, dd, J = 8.3, 5.5 Hz, H-9′a), 4.19 (1H, t, J = 8.4 Hz, H-9′b), 3.91 (3H, s, OMe), 3.84 (3H, s, OMe)。FAB⁻-MS m/z: 373[M-1]⁻。其波谱数据(碳谱数据见表 1)与文献报道的一致[9]。

(E)-3-Hydroxy-5-methoxy-stilbene (8) 黄色粘稠状物质。^{1}H NMR (CDCl$_3$, 500MHz) δ 6.62 (1H, s, H-2), 6.36 (1H, d, J = 1.7 Hz, H-4), 6.67 (1H, s, H-6), 7.50 (2H, d, J = 7.6 Hz, H-2′, 6′), 7.36 (2H, d, J = 7.6 Hz, H-3′, 5′), 7.28 (1H, t, J = 6.8 Hz, H-4′), 7.07 (1H, d, J = 16.3 Hz, H-a), 7.00 (1H, d, J = 16.3 Hz, H-b), 3.83 (3H, s, OMe)。^{13}C NMR (CDCl$_3$, 125MHz) δ 139.7 (C-1), 105.0 (C-2), 156.8 (C-3), 101.0 (C-4), 161.1 (C-5), 106.0 (C-6), 137.0 (C-1′), 128.7 (C-2′), 126.6 (C-3′), 128.3 (C-4′), 126.6 (C-5′), 128.7 (C-6′), 129.4

(C-a), 127.8 (C-b), 55.4 (OMe)。EI-MS *m/z* 226 $[M]^+$。其波谱数据与文献报道的一致[10,11]。

Resveratrol-3-O-β-*D*-glucopyranoside (9) 白色粉末。^{1}H NMR ((CD$_3$)$_2$CO, 500 MHz) δ 6.80 (1H, s, H-2), 6.48 (1H, d, *J* = 2.0 Hz, H-4), 6.67 (1H, s, H-6), 7.41 (1H, d, *J* = 8.5 Hz, H-2′), 6.83 (1H, d, *J* = 8.6 Hz, H-3′), 6.83 (1H, d, *J* = 8.6 Hz, H-5′), 7.41 (1H, d, *J* = 8.5 Hz, H-6′), 6.90 (1H, d, *J* = 16.3 Hz, H-a), 7.07 (1H, d, *J* = 16.3 Hz, H-b), 4.94 (1H, d, *J* = 7.7 Hz, H-1″), 3.55~3.44 (4H, m, H-2″, 3″, 4″, 5″), 3.92 (1H, dd, *J* = 11.8, 2.5 Hz, H-6″a), 3.72 (1H, dd, *J* = 11.8, 5.7 Hz, H-6″b)。^{13}C NMR ((CD$_3$)$_2$CO, 100 MHz) δ 140.5 (C-1), 106.0 (C-2), 160.1 (C-3), 103.8 (C-4), 159.6 (C-5), 108.0 (C-6), 129.4 (C-1′), 128.6 (C-2′), 116.3 (C-3′), 158.5 (C-4′), 116.3 (C-5′), 128.6 (C-6′), 126.1 (C-a), 129.2 (C-b), 101.9 (C-1″), 74.5 (C-2″), 77.9 (C-3″), 71.1 (C-4″), 77.8 (C-5″), 62.3 (C-6″)。FAB$^-$-MS *m/z* 389 $[M-1]^-$。其波谱数据与文献报道的一致[11]。

Pinocembrin (10) 黄色粉末。$[\alpha]_D^{23.7}$ -11.6° (*c* 0.22, CHCl$_3$)。^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.43 (1H, dd, *J* = 13.0, 2.9 Hz, H-2), 3.09 (1H, dd, *J* = 17.2, 13.1 Hz, H-3a), 2.82 (1H, dd, *J* = 17.2, 3.0 Hz, H-3b), 6.00 (2H, s, H-6, 8), 7.45~7.26 (5H, m, H-2′, 3′, 4′, 5′, 6′), 12.05 (1H, s, 5-OH)。^{13}C NMR (CDCl$_3$, 100 MHz) δ 79.2 (C-2), 43.3 (C-3), 195.8 (C-4), 164.3 (C-5), 95.5 (C-6), 164.6 (C-7), 96.7 (C-8), 163.1 (C-9), 103.2 (C-10), 138.2 (C-1′), 126.1 (C-2′), 128.9 (C-3′), 128.9 (C-4′), 128.9 (C-5′), 126.1 (C-6′)。FAB$^-$-MS *m/z* 255 $[M-1]^-$。其波谱数据与文献报道的一致[12]。

(2*S*, 3*R*)-3, 5, 7, 3′, 4′-Pentahydroxyflavan (11) 白色粉末。$[\alpha]_D^{27}$ -0.5° (*c* 0.32, MeOH)。^{1}H NMR ((CD$_3$)$_2$CO, 400 MHz) δ 4.54 (1H, d, *J* = 7.8 Hz, H-2), 4.00 (1H, dd, *J* = 13.6, 8.0 Hz, H-3), 2.85 (1H, dd, *J* = 16.1, 5.4 Hz, H-4a), 2.49 (1H, dd, *J* = 16.0, 8.5 Hz, H-4b), 5.85 (1H, d, *J* = 1.9 Hz, H-6), 6.00 (1H, s, H-8), 6.86 (1H, s, H-2′), 6.77 (1H, d, *J* = 8.1 Hz, H-5′), 6.70 (1H, dd, *J* = 8.1, 1.5 Hz, H-6′)。^{13}C NMR ((CD$_3$)$_2$CO, 100 MHz) δ 81.9 (C-2), 67.8 (C-3), 28.2 (C-4), 156.7 (C-5), 95.0 (C-6), 156.1 (C-7), 96.0 (C-8), 157.0 (C-9), 100.2 (C-10), 131.3 (C-1′), 115.1 (C-2′), 145.3 (C-3′), 145.2 (C-4′), 115.7 (C-5′), 119.7 (C-6′)。FAB$^-$-MS *m/z*: 289 $[M-1]^-$。其波谱数据与文献报道的一致[13]。

Kaempferol (12) 黄色粉末。^{1}H NMR ((CD$_3$)$_2$CO, 500 MHz) δ 6.17 (1H, s, H-6), 6.42 (1H, s, H-8), 8.02 (2H, d, *J* = 8.6 Hz, H-2′, 6′), 6.91 (2H, d, *J* = 8.6 Hz, H-3′, 5′)。^{13}C NMR ((CD$_3$)$_2$CO, 125 MHz) δ 147.0 (C-2), 135.8 (C-3), 176.0 (C-4), 160.8 (C-5), 98.4 (C-6), 164.0 (C-7), 93.6 (C-8), 156.3 (C-9), 103.2 (C-10), 121.8 (C-1′), 129.7 (C-2′), 115.6 (C-3′), 159.3 (C-4′), 115.6 (C-5′), 129.7 (C-6′)。FAB$^-$-MS *m/z* 285 $[M-1]^-$。其波谱数据与文献对照基本一致[14]。

Kaempferol 3-O-β-*D*-glucopyranoside (13) 黄色粘稠状物质。^{1}H NMR (CD$_3$OD, 400 MHz) δ 6.18 (1H, s, H-6), 6.37 (1H, s, H-8), 8.04 (2H, d, *J* = 8.4 Hz, H-2′, 6′), 6.87 (2H, d, *J* = 8.1 Hz, H-3′, 5′), 5.23 (1H, d, *J* = 7.0 Hz, H-1″), 3.93~3.22 (6H, m, H-2″, 3″, 4″, 5″, 6″)。^{13}C NMR (CD$_3$OD, 400 MHz) δ 158.5 (C-2), 135.4 (C-3), 179.4 (C-4), 163.0 (C-5), 100.0 (C-6), 166.2 (C-7), 94.8 (C-8), 159.0 (C-9), 105.6 (C-10), 122.7 (C-1′), 132.3 (C-2′), 116.1 (C-3′), 161.5 (C-4′), 116.1 (C-5′), 132.3 (C-6′), 104.1 (C-1″), 75.7 (C-2″), 78.4 (C-3″), 71.3 (C-4″), 78.0 (C-5″), 62.6 (C-6″)。FAB$^-$-MS *m/z* 447 $[M-1]^-$。其波谱数据与文献报道的一致[15]。

(*E*)-Ferulic acid tetracosyl ester (14) 白色粉末。^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.04 (1H, d, *J* = 1.7 Hz, H-2), 6.92 (1H, d, *J* = 8.2 Hz, H-5), 7.08 (1H, dd, *J* = 8.2, 1.8 Hz, H-6), 7.62 (1H, d, *J* = 15.9 Hz, H-7), 6.30 (1H, d, *J* = 15.8 Hz, H-8), 4.19 (2H, t, *J* = 6.8 Hz, H-1′), 1.73-1.64 (4H, m, H-2′, 3′), 1.26 (40H, br. s, H-4′~23′), 0.89 (3H, t, *J* = 6.9 Hz, H-24′), 3.94 (3H, s, OMe), 5.91 (1H, s, OH)。^{13}C NMR (CDCl$_3$, 125 MHz) δ 127.1 (C-1), 109.4 (C-2), 147.9 (C-3), 146.8 (C-4), 114.7 (C-5), 123.0 (C-6), 144.6 (C-7), 115.7 (C-8), 167.3 (C-9), 64.6 (C-1′), 31.9 (C-2′), 26.0 (C-3′), 29.7-28.7 (C-4′-22′), 22.7 (C-23′), 14.1 (C-24′), 55.9 (OMe)。FAB$^+$-MS *m/z*: 531 $[M+1]^+$。其波谱数据与文献报道的一致[16]。

ω-Hydroxypropioquaiacone (15) 淡黄色粘

稠状物质。^{1}H NMR (CDCl$_3$, 400 MHz) δ 3.10 (2H, t, J = 5.6 Hz, H-2), 3.94 (2H, t, J = 5.6 Hz, H-3), 7.41 (1H, s, H-2′), 6.82 (1H, d, J = 8.1 Hz, H-5′), 7.43 (1H, dd, J = 9.4, 1.8 Hz, H-6′), 3.82 (3H, s, OMe)。^{13}C NMR (CDCl$_3$, 100 MHz) δ 198.9 (C-1), 39.7 (C-2), 57.9 (C-3), 129.0 (C-1′), 109.9 (C-2′), 151.2 (C-3′), 147.0 (C-4′), 114.2 (C-5′), 123.5 (C-6′), 55.7 (OMe)。FAB$^+$-MS m/z: 197[M + 1]$^+$。其波谱数据与文献报道的一致[17]。

Vanillin (16) 淡黄色粉末。^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.02 (1H, d, J = 8.5 Hz, H-5), 7.40 (2H, overlapped, H-2, 6), 9.79 (1H, d, J = 1.6 Hz, CHO), 3.92 (3H, s, OMe)。^{13}C NMR (CDCl$_3$, 100 MHz) δ 129.7 (C-1), 108.7 (C-2), 147.2 (C-3), 151.8 (C-4), 114.4 (C-5), 127.5 (C-6), 191.0 (CHO), 56.0 (OMe)。EI-MS m/z: 152[M]$^+$。其波谱数据与文献报道的一致[18]。

Hemisceramide (17) 白色粉末。^{1}H NMR (C$_5$D$_5$N, 400 MHz) δ 4.44 (1H, overlapped, H-1a), 4.37 (1H, dd, J = 10.9, 5.2 Hz, H-1b), 5.00 (1H, dd, J = 8.3, 4.1 Hz, H-2), 4.29 (1H, t, J = 5.9 Hz, H-3), 4.24 (1H, overlapped, H-4), 2.05 ~ 2.23 (4H, m, H-5, 3′), 1.91 (2H, m, H-6), 1.44 ~ 1.32 (60H, m, H-7 ~ 20, 5′ ~ 20′), 0.91 (6H, t, J = 5.5 Hz, H-21, 21′), 4.58 (1H, dd, J = 7.4, 3.9 Hz, H-2′), 1.75 (2H, m, H-4′), 8.42 (1H, d, J = 8.6 Hz, NH)。^{13}C NMR (C$_5$D$_5$N, 100 MHz) δ 62.2 (C-1), 53.1 (C-2), 76.9 (C-3), 73.1 (C-4), 35.8 (C-5), 32.1 (C-6), 30.3-29.6 (C-7-18, 5′-18′), 26.6 (C-19), 22.9 (C-20), 14.2 (C-21), 175.3 (C-1′), 72.6 (C-2′), 34.2 (C-3′), 32.1 (C-4′), 25.8 (C-19′), 22.9 (C-20′), 14.2 (C-21′)。FAB$^-$-MS m/z: 682 [M-1]$^-$。其波谱数据与文献报道的一致[19]。

β-Sitosterol (18) 白色针状结晶, 该化合物 TLC 与对照品 R_f 值一致。

β-Daucosterol (19) 白色粉末, 该化合物 TLC 与对照品 R_f 值一致。

表 1 化合物 **1**~**7** 的 ^{13}C NMR 数据 (^{13}C: 100/125 MHz, δ in ppm)

Table 1 ^{13}C NMR data of compounds **1**-**7** (^{13}C: 100/125 MHz, δ in ppm)

C	1[a]	2[b]	3[c]	4[b]	5[c]	6[b]	7[c]
1	127.5	125.8	134.7	135.2	129.9	129.5	130
2	113	111.5	110.6	109	113.5	111.9	111.9
3	148.6	145.9	148.4	146.2	148.2	146.6	148.2
4	146.2	144.8	147.2	145.6	146.2	144.5	152.2
5	115.9	114.7	116.3	114.3	115.7	114.4	115.3
6	121.9	131.3	119.6	119.1	122.7	122.5	124.1
7	39.3	28.9	88.1	87.7	35.5	35.1	198.1
8	78.2	41.7	55.3	53.7	45.7	43.7	49.7
9	180.5	177.8	64.8	63.7	177.9	179.5	60.7
1′	131.5	133.8	129.8	133.1	129.1	133.4	134
2′	115	110.5	115.7	112.4	111.7	108.2	110.8
3′	149.2	147.3	141.6	143.9	148.5	146.8	146.7
4′	146.7	144.1	146.1	146.8	153	145.7	148
5′	116.3	115.3	136.3	128.1	115.4	114	115.1
6′	124.2	121.1	116.8	116.2	124.4	118.8	120.2
7′	32.6	49.5	35.9	31.8	196	75.3	84.1
8′	50.6	47.2	32.5	34.3	47.3	45.1	54
9′	70.6	72.1	61.9	61.6	69	68.5	71
OMe	56.3	55.7	56.3	55.9	56.2	55.9	56.1
OMe	56.3	55.6		55.8	55.9	55.8	56

a 在氘代甲醇中测定; b 在氘代氯仿中测定; c 在氘代丙酮中测定

a in CD_3OD; b in $CDCl_3$; c in $(CD_3)_2CO$

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man-Burchard反应阳性。EI-MS m/z 412 (M^+), 395, 364, 351, 345, 271, 255。与豆甾醇标准品混合熔点不下降, TCL上的斑点位置及显色行为相同, 鉴定该化合物为豆甾醇。

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