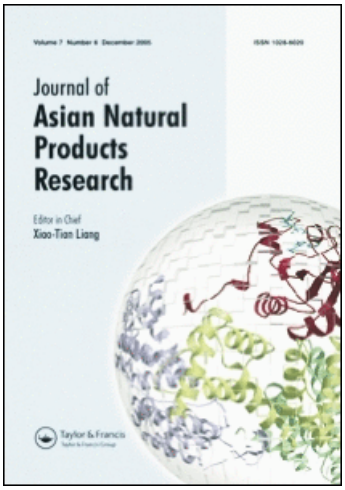

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CONSTITUENTS FROM *LIMONIA CRENULATA*

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A new indole alkaloid, crenulatine (**1**), along with twenty known compounds, was isolated from the stems of *Limonia Crenulata*. Their structures were identified by spectral means. Those compounds include four alkaloids, four coumarins, two flavanones, three tetranortriterpenoids, one triterpenoid, three steroids, two lignans and two aromatic compounds.

Keywords: *Limonia crenulata*; *Rutaceae*; Alkaloid; Crenulatine; Coumarin; Flavanone; Lignan; Tetranortriterpenoid; Triterpenoid; Steroid

INTRODUCTION

Many studies have been carried out during the past decades on *Limonia crenulata* Roxb. (*Rutaceae*) [1–4], a small tree widely distributed in dry warm regions of southeastern Asia. It has been reported to have antiepileptic, purgative and sudorific effects and used for colic trouble and cardialgia [1–3]. Various parts of the plant were employed in indigenous medicine. It has also been used as a cosmetic by the women of Myanma and immediately adjoining countries to this day. They paint their faces yellow with the mash ground from the waterlogged stems of *L. crenulata* for

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preventing ultraviolet radiation and being anti-inflammatory. Coumarins were reported to be rich in this plant [2]. Our investigation on the stems of *L. crenulata* led to the isolation of various types of compounds, which include four alkaloids, four coumarins, two flavanones, three tetranortriterpenoids, one triterpenoid, three steroids, two lignans and two aromatic compounds. Among them crenulatine (**1**) was a new simple indole alkaloid, tembamid (**3**) [6], 2′,4′,5,7-tetrahydroxyflavanone (**5**) [7], 3,4′,5,7-hydroxyflavanone (**6**) [8], syringaldehyde (**7**) [9], 1,3,5-trimethoxybenzene (**8**) [9], angustifolin (**10**) [10], moellendorffilin (**12**) [11], limonexin (**14**) [13], deacetylnomilinate (**16**) [14], schleicheol 2 (**18**) [16] and lyoniresinol (**21**) [18] were obtained from the plant for the first time. N-Benzoyltyramine methyl ether (**2**) [4], 4-methoxy-6-hydroxy-1-methyl-2-quinolone (**4**) [5], 7-hydroxycoumarin (**9**) [1], pimpinellin (**11**) [11], lupeol (**13**) [12], limonin (**15**) [5], stigmast-4-en-6β-ol-3-one (**17**) [15], 3β-Hydroxy-5α,8α-epidioxyergosta-6,22-diene (**19**) [17] and syringaresinol (**20**) [1] were also isolated.

RESULTS AND DISCUSSION

Crenulatine (**1**), obtained as white amorphous powder, showing a molecular ion peak at *m/z* 259, has a molecular formula of $C_{16}H_{21}NO_2$ based on HREIMS (found 259.1543, calcd. 259.1572) and ^1H and ^{13}C NMR spectra. The presence of four aromatic protons at δ 7.62 (1H, d, $J = 8.0$ Hz), 7.00 (1H, m) 7.02 (1H, m) and 7.28 (1H, d, $J = 8.0$ Hz) and one NH proton at δ 10.18 (1H, brs) in ^1H NMR spectrum, in association with the exhibition of four methines at δ 121.6, 121.1, 119.6 and 111.7, and four quaternary carbons at δ 141.5, 137.6, 129.0 and 107.7 in the ^{13}C NMR spectrum, suggested that this compound possessed a 2,3-disubstituted indole alkaloid skeleton. This was confirmed by its UV [λ_{max} (logε) 223.5 (4.54), 281 (3.87), 289 (3.79) nm] spectrum [1]. The relationships of H-4/H-5/H-6/H-7 were established by a ^1H-^1H COSY experiment. In addition, four methyls in the highfield of ^{13}C NMR spectrum were divided into two groups of *gem*-methyls, which were connected with two oxy-quaternary carbons respectively, as supported by HMBC correlations (Fig. 1). Further, the cross-peaks between the oxy-methylene protons at δ 4.30 (1H, d, $J = 12.1$ Hz) and 3.82 (1H, dd, $J = 12.1, 3.6$ Hz) and the methine proton at δ 2.76 (1H, d, $J = 3.6$ Hz) in ^1H-^1H COSY spectrum, combined with the long-range correlations of the *gem*-methyls at δ 1.29 (3H, s) and 1.34 (3H, s) with the methine carbon at δ 45.6, and of the oxy-methylene protons δ 4.30 (1H, d, $J = 12.1$ Hz) and 3.82 (1H, dd, $J = 12.1, 3.6$ Hz) with the two

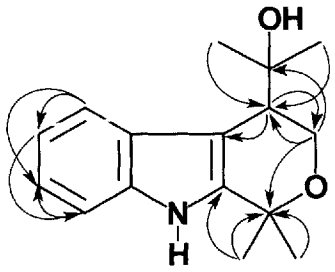


FIGURE 1 HMBC correlations of 1.

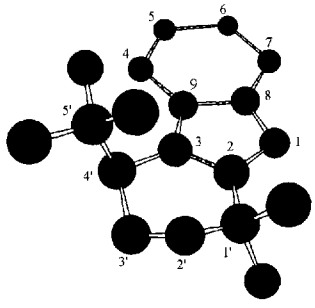


FIGURE 2 Molecular model of 1.

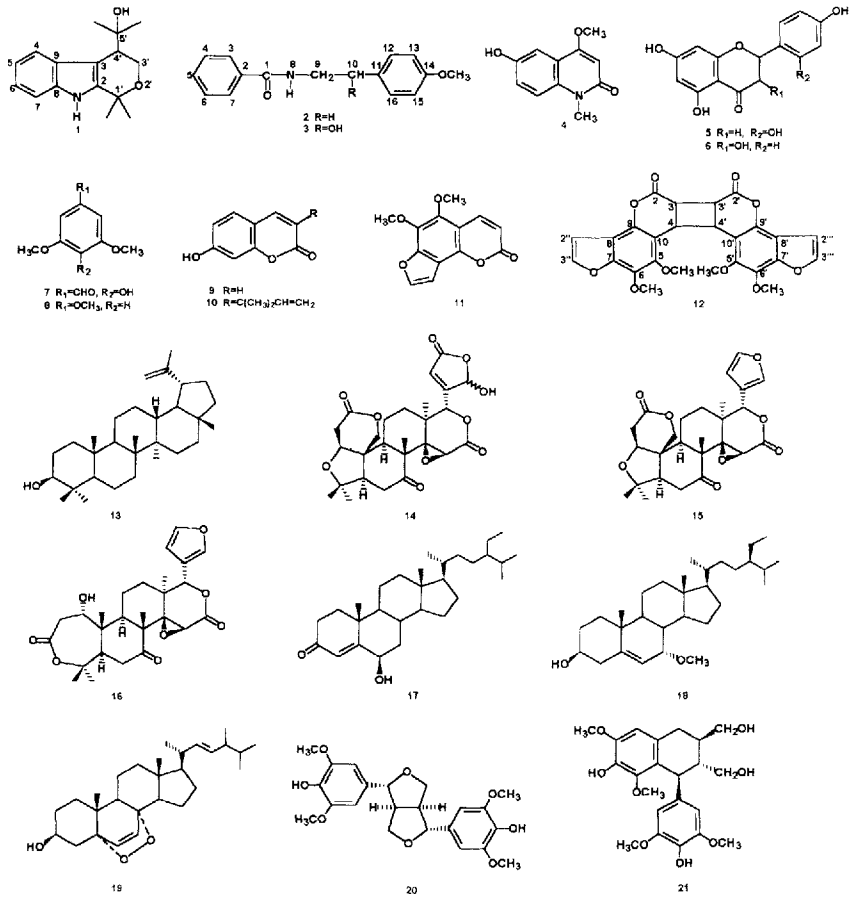
oxy-quaternary carbons at δ 74.1 and 72.7 in HMBC spectrum, suggested the structure of crenulatine as **1**. The formation of the third ring was supported by the 7 degrees of unsaturation of its molecular formula. The stereochemistry of C-4′ still remains unknown.

Because **1** did not crystallize, the X-ray diffraction could not be realized. Figure 2 was obtained on the basis of minimizing energy calculated on computer by using Chemdraw MM2 program.

EXPERIMENTAL SECTION

General Experimental Procedures

Optical rotation was taken on a Horiba SEPA-300 spectropolarimeter. IR spectra were measured on a Bio-Rad FTS-135 infrared spectrometer with KBr pellets. UV spectra were obtained on a Shimadzu double-beam 210A spectrophotometer. MS were recorded with a VG Auto Spec-3000 spectrometer. NMR spectra were run on Bruker AM-400 and DRX-500



instruments with TMS as internal standard. Column chromatography was performed on silica gel 200–300 or 300–400 mesh and reverse-phase materials (including RP-18 and MCI-gel CHP-20P).

Plant Material

The stems of *L. crenulata* were collected in Dehong prefecture of Yunnan province in October, 1997, and air-dried. The plant material was identified by Prof. Zhong-Wen Lin, and a voucher specimen (KIB 97-10-10-014 Lin) is deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, Academia Sinica, People's Republic of China.

Extraction and Isolation

The powdered stems of *L. crenulata* (6.78 kg) were extracted with 70% acetone (3 × 20L). After evaporation of the acetone *in vacuo*, the crude extract 300 g was suspended in water and extracted with EtOAc to afford 150.0 g of residue, which was subjected to column chromatography over silica gel eluting with chloroform, chloroform/acetone (9 : 1, 4:1) and acetone. The fractions were collected and combined by monitoring with TLC. Fraction I (obtained from chloroform) was chromatographed on silica gel column using petroleum-ether/EtOAc as eluent to yield compounds **10** (15 mg), **11** (8 mg), **12** (14 mg), **13** (200 mg), **17** (30 mg) and **19** (20 mg) respectively. Fraction II (obtained from $CHCl_3/Me_2CO$ 9 : 1) was repeatedly subjected to CC on silica gel eluted with petroleum-ether/EtOAc, $CHCl_3/Me_2CO$, $CHCl_3/CH_3OH$ in stepwise mode to afford compounds **2** (9 mg), **3** (12 mg), **5** (4 mg), **6** (5 mg), **7** (16 mg), **8** (7 mg), **9** (5 mg), **15** (300 mg), **16** (23 mg), **18** (6 mg), **20** (45 mg). Fraction III (obtained from $CHCl_3/Me_2CO$ 4 : 1) was purified by CC over MCI-gel CHP-20P with aqueous MeOH and the eluate was rechromatographed over silica gel eluting with $CHCl_3/Me_2CO$, $CHCl_3/CH_3OH$ repeatedly to give compounds **1** (8 mg), **4** (15 mg), **14** (20 mg), **21** (11 mg).

Crenulatine (1)

$C_{16}H_{21}NO_2$, white amorphous powder; $[\alpha]_D^{24}$ − 12.50 (*c* 0.4, MeOH), UV (MeOH) λ_{max} (logε): 223.5 (4.54), 281 (3.87), 289 (3.79); IR (KBr) ν_{max} 3400, 3274, 2973, 2877, 1496, 1406, 1381, 1363, 1313, 1268, 1224, 1182, 1146, 1052, 1027, 1009, 991, 966, 947, 887, 867, 783, 764, 746, 724, 666, 618, 593, 575 cm^{-1}; ^1H NMR (acetone-d_6, 500 MHz), see Table I; ^{13}C NMR (acetone-d_6, 125 MHz), see Table I; EIMS *m/z* 259 $[M]^+$ (51), 201 (100), 186 (75), 172 (75), 158 (31), 143 (25), 130 (17), 115 (15), 101 (10), 89 (4), 77 (6), 59 (27); HREIMS *m/z* 259.1543 (calcd. for $C_{16}H_{21}NO_2$, 259.1572).

N-Benzoyltyramine Methyl Ether (2)

$C_{16}H_{17}NO_2$, colorless needles; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.69 (2H, d, J = 8.5 Hz, H-3, 7), 7.48 (1H, d, J = 8.5 Hz, H-5), 7.41 (2H, m, H-4, 6), 7.16 (2H, d, J = 7.5 Hz, H-13, 15), 6.87 (2H, d, J = 7.5 Hz, H-12, 16), 6.14 (1H, brs, NH), 3.80 (3H, s, OCH_3), 3.69 (2H, m, H-9), 2.88 (2H, t, J = 6.9 Hz, H-10); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.4 (s, C-1), 158.3 (s, C-14), 134.7 (s, C-2), 131.4 (d, C-5), 130.8 (s, C-11), 129.7 (d, C-3, 7),

TABLE 1 The ^1H (500 MHz) and ^{13}C NMR (125 MHz) data of 1 in CD_3COCD_3 (δ in ppm; J in Hz)

Position	*Carbon*	*Proton*
1		10.18 (brs)
2	141.5 (s)	
3	107.7 (s)	
4	121.1 (d)	7.62(1H, d, $J = 8.0$ Hz)
5	119.6 (d)	7.00 (1H, m)
6	121.6 (d)	7.02 (1H, m)
7	111.7 (d)	7.28(1H, d, $J = 8.0$ Hz)
8	137.6 (s)	
9	129.0 (s)	
1′	72.7 (s)	
3′	62.9 (t)	4.30(1H, d, $J = 12.1$ Hz), 3.82(1H, dd, $J = 12.1, 3.6$ Hz)
4′	45.6 (d)	2.76(1H, d, $J = 3.6$ Hz)
5′	74.1 (s)	
1′ – 2 × CH_3	29.2 (q), 26.5 (q)	1.57 (s), 1.47 (s)
5′ – 2 × CH_3	30.7 (q), 28.6 (q)	1.34 (s), 1.29 (s)

128.5 (d, C-4, 6), 126.8 (d, C-12, 16), 114.1 (d, C-13, 15), 55.3 (q, OCH_3), 41.3 (t, C-9), 34.8 (t, C-10); EIMS *m/z* 255 $[M]^+$ (14), 233 (3), 217 (5), 203 (18), 181 (21), 165 (11), 151 (11), 135 (26), 134 (100), 121 (43), 105 (55), 91 (17), 83 (30), 77 (39), 69 (21), 57 (24).

Tembamid (3)

$C_{10}H_{17}NO_3$, colorless needles; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.76 (2H, d, $J = 7.2$ Hz, H-3, 7), 7.51 (1H, d, $J = 7.2$ Hz, H-5), 7.44 (2H, m, H-4, 6), 7.34 (2H, d, $J = 6.8$ Hz, H-13, 15), 6.90 (2H, d, $J = 6.8$ Hz, H-12, 16), 6.59 (1H, brs, NH), 4.92 (1H, brd, $J = 7.2$ Hz, H-10), 3.90 (1H, m H-9a), 3.81 (3, —OCH_3), 3.50 (1H, m, H-9b); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.5 (s, C-1), 160.0 (s, C-14), 134.3 (s, C-2), 134.0 (s, C-11), 131.6 (d, C-5), 128.6 (d, C-3, 7), 127.1 (d, C-4, 6), 127.0 (d, C-12, 16), 114.1 (d, C-13, 15), 73.3 (d, C-10), 55.3 (q, —OCH_3), 47.8 (t, C-9); EIMS *m/z* 271 $[M]^-$ (7), 254 (5), 150 (71), 135 (100), 122 (21), 109 (45), 105 (87), 94 (44), 77 (88), 66 (32), 51 (45), 39 (23).

4-Methoxy-6-hydroxy-1-methyl-2-quinolone (4)

$C_{11}H_{11}O_3$, off-white amorphous powder; ^1H NMR (C_5D_5N, 400 MHz) δ 7.77 (1H, d, $J = 2.4$ Hz, H-5), 7.44 (1H, dd, $J = 9.0, 2.4$ Hz, H-7), 7.21 (1H, d, $J = 9.0$ Hz, H-8), 6.12 (1H, s, H-3), 3.69 (3H, s, —OCH_3), 3.63 3H, s, *N*—CH_3; ^{13}C NMR (C_5D_5N, 100 MHz) δ 163.1 (s, C-2), 162.3 (s, C-4),

153.7 (s, C-6), 133.9 (s, C-9), 120.9 (d, C-7), 117.8 (s, C-10), 116.1 (d, C-8), 108.5 (d, C-5), 97.4 (d, C-3), 55.8 (q, —OCH_3), 29.0 (q, N—CH_3); EIMS *m/z* 205 $[M]^+$ (100), 190 (48), 162 (40), 148 (20), 133 (7), 116 (5), 105 (6), 92 (7), 77 (8), 65 (10).

2′,4′,5,7-Tetrahydroxyflavanone (5)

$C_{15}H_{12}O_6$, pale-yellow needles; ^{1}H NMR (acetone-d_6, 400 MHz) δ 12.21 (1H, s, 5-OH), 9.77 (1H, s, 7-OH), 8.77 (1H, s, 2′-OH), 8.50 (1H, s, 4′-OH), 7.30 (1H, d, J = 8.4 Hz, H-6′), 6.45 (1H, d, J = 2.4 Hz, H-3′*), 6.42 (1H, dd, J = 8.4, 2.4 Hz, H-5′), 5.94 (1H, d, J = 2.4 Hz, H-6*), 5.93 (1H, d, J = 2.4 Hz, H-8*), 5.69 (1H, dd, J = 2.8, 13.6 Hz, H-2), 3.17 (1H, dd, J = 17.6, 13.6 Hz, H-3a), 2.69 (2H, dd, J = 17.6, 2.8 Hz, H-3b); ^{13}C NMR (acetone-d_6, 100 MHz) δ 198.3 (s, C-4), 167.4 (s, C-7), 165.4 (s, C-4′), 165.0 (s, C-9), 160.0 (s, C-5), 156.5 (s, C-2′), 129.0 (d, C-6′), 118.0 (s, C-1′), 108.0 (d, C-5′), 103.7 (d, C-3′), 101.7 (s, C-10), 98.8 (d, C-8), 95.9 (d, C-6), 75.5 (d, C-2), 42.7 (t, C-3); EIMS *m/z* 288 $[M]^+$ (45), 270 (100), 245 (5), 179 (11), 163 (10), 153 (96), 136 (54), 124 (31), 107 (27), 96 (17), 79 (22), 77 (21), 69 (46). (*The assignments may be interchanged.)

3,4′,5,7-Tetrahydroxyflavanone (6)

$C_{15}H_{12}O_6$, pale-yellow needles; ^{1}H NMR (CD_3OD, 400 MHz) δ 7.34 (2H, brd, J = 6.7 Hz, H-3′, 5′), 6.82 (2H, brd, J = 6.7 Hz, H-2′, 6′), 5.91 (1H, brs, H-6), 5.87 (1H, brs, H-8), 4.97 (1H, brd, J = 9.2 Hz, H-3), 4.53 (1H, brd, J = 9.2 Hz, H-2); EIMS *m/z* 288 $[M]^+$ (36), 259 (38), 165 (15), 153 (100), 136 (40), 134 (40), 124 (16), 107 (68), 96 (10), 77 (27), 69 (29).

Syringlaldehyde (7)

$C_9H_{10}O_4$, off-white needles; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.78 (1H, s, —CHO), 7.12 (2H, s, H-2, 6), 3.92 (6H, s, —OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.6 (d, —CHO), 147.4 (s, C-3, 5), 141.0 (s, C-4), 128.5 (s, C-1), 106.5 (d, C-2, 6), 56.5 (q, 2-OCH_3); EIMS *m/z* 182 $[M]^+$ (100), 167 (13), 149 (22), 134 (71), 121 (20), 105 (24), 83 (82), 72 (24), 55 (24).

1,3,5-Trimethoxybenzene (8)

$C_9H_{12}O_3$, needles; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.94 (3H, s, H-2, 4, 6), 3.91 (9H, s, 3 × OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.4 (s, C-1, 3, 5), 107.5

(d, C-2, 4, 6), 56.4 (q, 3 × OCH_3); EIMS *m/z* 168 $[M]^+$ (59), 155 (7), 138 (25), 125 (16), 112 (6), 97 (18), 80 (39), 69 (100), 59 (24), 53 (39).

7-Hydroxycoumarin (9)

$C_9H_6O_3$, colorless crystal; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.62 (1H, brs, —OH), 7.85 (1H, d, $J = 9.6$ Hz, H-4), 7.50 (1H, d, $J = 8.5$ Hz, H-5), 6.82 (1H, dd, $J = 8.5, 2.4$ Hz, H-6), 6.73 (1H, d, $J = 2.4$ Hz, H-8), 6.15 (1H, d, $J = 9.6$ Hz, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.2 (s, C-7), 161.1 (s, C-2), 157.2 (s, C-9), 144.7(d, C-4), 130.4 (d, C-5), 113.8 (d, C-3, 10), 112.9 (d, C-6), 103.4 (d, C-8); EIMS *m/z* 162 $[M]^+$ (90), 134 (100), 105 (36), 78 (55), 69 (19), 63 (31).

Angustifolin (10)

$C_{14}H_{14}O_3$, colorless crystal; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.59 (1H, s, H-4), 7.34 (1H, d, $J = 8.6$ Hz, H-5), 7.07 (1H, d, $J = 2.0$ Hz, H-8), 6.86 (1H, dd, $J = 2.0, 8.6$ Hz, H-6), 6.16 (1H, dd, $J = 10.9, 17.2$ Hz, H-2′), 5.11 (1H, d, $J = 10.9$ Hz, H-3′a)., 5.08 (1H, d, $J = 17.2$ Hz, H-3′b), 1.48 (6H, s, *gem*-dimethyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.2 (s, C-7), 159.4 (s, C-2), 154.8 (s, C-9), 145.5 (d, C-4), 138.6 (d, C-2′), 131.3 (s, C-3), 129.0 (d, C-5), 113.5 (d, C-6), 112.9 (s, C-10), 112.3 (t, C-3′), 102.6 (d, C-8), 40.4 (s, C-1′), 26.2 (q, $2CH_3$); EIMS *m/z* 230 $[M]^-$ (96), 215 (100), 203 (20), 201 (19), 187 (81), 175 (79), 160 (13), 147 (27), 131 (22), 115 (30), 105 (14), 100 (16), 91 (21), 77 (27), 59 (42), 43 (91).

Pimpinellin (11)

$C_{13}H_{10}O_5$, pale-yellow crystal; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.07 (1H, d, $J = 9.6$ Hz, H-4), 7.63 (1H, d, $J = 2.4$ Hz, H-2′), 7.06 (1H, d, $J = 2.4$ Hz, H-3′), 6.35 (1H, d $J = 9.6$ Hz, H-3), 4.12 (3H, s, 5-OCH_3), 4.01 (3H, s, 6-OCH_3); EIMS *m/z* 246 $[M]^+$ (100), 231 (92), 217 (7), 203 (45), 188 (45), 175 (54), 160 (60), 147 (67), 132 (28), 119 (28), 104 (42), 91 (32), 76 (41), 66 (47).

Moellendorffiline (12)

$C_{26}H_{20}O_{10}$, colorless crystal; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.44 (2H, d, $J = 2.2$ Hz, H-2″, 2‴), 6.73 (2H, d, $J = 2.2$ Hz, H-3″, 3‴), 4.38 (2H, m, H-4, 4′), 4.02 (2H, m, H-3, 3′), 3.82 (6H, s, 5-OCH_3, 5′-OCH_3), 3.66 (6H, s, 6-OCH_3, 6′-OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.5 (s, C-2, 2′), 148.3 (s, C-7, 7′),

147.6 (s, C-9, 9′), 144.5 (d, C-2″, 2‴), 139.6 (s, C-5, 5′), 134.6 (s, C-6, 6′), 113.9 (s, C-8, 8′), 106.5 (s, C-10, 10′), 104.0 (d, C-3″, 3‴), 60.7 (q, 5-OCH_3, (5′-OCH_3), 6-OCH_3, 6′-OCH_3), 39.9 (d, C-3, 3′), 38.3 (d, C-4, 4′); EIMS *m/z* 492 $[M]^+$ (0.5), 246 (100), 231 (80), 147 (20).

Lupeol (13)

$C_{30}H_{50}O$, colorless needles; ^1H NMR ($CDCl_3$, 400 MHz) δ 4.66 (1H, brs, H-30a), 4.54 (1H, brs, H-30b), 3.16 (1H, m, H-3), 2.35 (1H, m, H-19), 1.88 (1H, m, H-13), 1.65 (3H, s, 29-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.9 (s, C-20), 109.3 (t, C-30), 79.0 (d, C-3), 55.4 (d, C-5), 50.5 (d, C-9), 48.4 (d, C-19), 48.0 (d, C-18), 43.0 (s, C-17), 42.9 (s, C-14), 41.0 (s, C-8), 40.0 (t, C-22), 38.9 (s, C-4), 38.8 (t, C-1), 38.2 (d, C-13), 37.2 (s, C-10), 35.6 (t, C-16), 34.4 (t, C-7), 29.9 (t, C-21), 28.0 (q, C-23), 27.5 (t, C-2), 27.5 (t, C-15), 25.3 (t, C-12), 21.0 (t, C-11), 19.3 (q, C-29), 18.4 (t, C-6), 18.0 (q, C-28), 16.1 (q, C-25), 16.0 (q, C-26), 15.4 (q, C-24), 14.6 (q, C-27); EIMS *m/z* 426 $[M]^+$ (100), 411 (17), 316 (15), 315 (15), 299 (5), 272 (5), 234 (12), 218 (46), 207 (55), 189 (51), 175 (20), 161 (23), 149 (32), 135 (53), 121 (57), 109 (61), 95 (67), 83 (65), 68 (65), 55 (67).

Limonexin (14)

$C_{26}H_{30}O_{10}$, colorless crystal; ^1H NMR (C_5D_5N, 400 MHz) δ 6.63 (1H, s, H-21), 6.61 (1H, s, H-22), 5.83 (1H, s, H-17), 5.26 (1H, d, $J = 13.1$ Hz, H-19a), 4.70 (1H, d, $J = 13.1$ Hz, H-19b), 4.50 (1H, s, H-15), 4.34 (1H, d, $J = 3.8$ Hz, H-1), 3.30 (1H, t, $J = 14.4$ Hz, H-6a), 3.18 (1H, dd, $J = 3.8, 16.4$ Hz, H-2a), 3.07 (1H, d, $J = 16.4$ Hz, H-2b), 2.84 (1H, dd, $J = 3.0, 11.8$ Hz, H-9), 2.65 (1H, d, $J = 3.0$ Hz, H-5), 2.55 (1H, dd, $J = 14.4, 3.0$ Hz, H-6a), 2.28 (1H, m, H-12a), 2.03 (2H, m, H-11), 2.00 (1H, m, H-12b), 1.37 (3H, s, 18-CH_3), 1.26 (3H, s, 28-CH_3), 1.25 (3H, s, 30-CH_3), 1.16 (3H, s, 29-CH_3); ^1C NMR (C_5D_5N, 100 MHz) δ 209.2 (s, C-7), 170.0 (s C-3), 167.7 (s, C-16), 164.0 (s, C-20), 162.0 (s, C-23), 123.5 (d, C-22), 99.5 (d, C-21), 80.4 (s, C-4), 79.6 (d, C-1), 78.9 (d, C-17), 66.5 (s, C-14), 65.9 (t, C-19), 60.6 (d, C-5), 54.2 (d, C-15), 52.1 (s, C-8), 48.3 (d, C-9), 46.5 (s, C-10), 38.8 (s, C-13), 36.9 (t, C-6), 36.5 (t, C-2), 30.4 (t, C-12), 29.9 (q, C-29), 21.7 (q, C-28), 20.8 (q, C-18), 19.0 (t, C-11), 17.1 (q, C-30); EIMS *m/z* 502 $[M]^+$ (0.5), 487 (23), 458 (5), 445 (7), 429 (4), 415 (5), 385 (5), 373 (6), 358 (4), 347 (20), 332 (9), 318 (6), 281 (4), 248 (8), 235 (13), 207 (11), 187 (13), 168 (21), 149 (22), 135 (28), 121 (31), 109 (45), 91 (70), 69 (56), 56 (100).

Limonin (15)

$C_{26}H_{30}O_8$, colorless crystal; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.42 (1H, s, H-21), 7.40 (1H, d, $J = 1.6$ Hz, H-23), 6.34 (1H, d, $J = 1.6$ Hz, H-22), 5.47 (1H, s, H-17), 4.77 (1H, d, $J = 13.1$ Hz, H-19a), 4.47 (1H, d, $J = 13.1$ Hz, H-19b), 4.04 (1H, m, H-1), 4.04 (1H, s, H-15), 2.97 (1H, dd, $J = 3.8$, 16.7 Hz, H-2a), 2.85 (1H, d, $J = 15.8$ Hz, H-6a), 2.69 (1H, dd, $J = 1.7$, 16.7 Hz, H-2b), 2.56 (1H, dd, $J = 2.5$, 11.7 Hz, H-9), 2.47 (1H, d, $J = 3.4$ Hz, H-5), 2.21 (1H, dd, $J = 3.4$, 15.8 Hz, H-6b), 1.87 (1H, m, H-11a), 1.80 (1H, m, H-11b), 1.80 (1H, m, H-12a), 1.48 (1H, m, H-12b), 1.27(3H, s, 29-CH_3), 1.14 (6H, s, 28-CH_3, 18-CH_3), 1.04 (3H, s, 30-CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 206.1 (s, C-7), 169.0 (s, C-3), 166.6 (s, C-16), 143.2 (d, C-23), 141.1 (d, C-21), 120.1 (s, C-20), 109.7 (d, C-22), 80.3 (s, C-4), 79.2 (d, C-1), 77.8 (d, C-17), 65.8 (s, C-14), 65.4 (t, C-19), 60.6 (d, C-5), 53.9 (d, C-15), 51.4 (s, C-8), 48.1 (d, C-9), 46.0 (s, C-10), 38.0 (s, C-13), 36.4 (t, C-6), 35.6 (t, C-2), 30.3 (t, C-12), 30.1 (q, C-29), 21.4 (q, C-28), 20.7 (q, C-18), 18.9 (t, C-11), 17.6 (q, C-30); EIMS *m/z* 471 $[M+H]^+$ (1), 455 (3), 427 (1), 413 (7), 347 (100), 331 (7), 329 (7), 287 (3), 159 (5), 148 (12), 135 (16), 121 (10), 104 (38), 95 (31), 76 (30), 67 (14), 55 (15).

Deacetylnomilinate (16)

$C_{26}H_{32}O_8$, colorless crystal; ^1H NMR (C_5D_5N, 400 MHz) δ 7.68 (1H, brs, H-21), 7.60 (1H, d, $J = 1.5$ Hz, H-23), 6.48 (1H, brs, H-22), 5.72 (1H, s, H-17), 4.27 (1H, s, H-15), 4.05 (1H, brd, $J = 7.2$ Hz, H-1), 3.56 (1H, d, $J = 15$ Hz, H-2a), 3.21 (1H, m, H-2b), 3.19 (1H, m, H-9), 3.01 (1H, m, H-6a), 3.00 (1H, m, H-5), 2.60 (1H, m, H-6b), 2.00 (1H, m, H-11a), 1.86 (1H, m, H-12a), 1.62 (1H, m, H-11b), 1.56 (1H, m, H-12b), 1.53 (3H, s, 28-CH_3), 1.32 (3H, s, 30-CH_3), 1.31 (6H, s, 29-CH_3, 19-CH_3), 1.29 (3H, s, 18-CH_3); ^{13}C NMR (C_5D_5N, 100 MHz) δ 209.1 (s, C-7), 171.7 (s, C-3), 168.1 (s, C-16), 143.8 (d, C-23), 141.9 (d, C-21), 121.4 (s, C-20), 110.8 (d, C-22), 84.4 (s, C-4), 78.8 (d, C-17), 69.5 (d, C-1), 66.8 (s. C-14), 54.3 (d, C-15), 53.2 (s, C-8), 50.4 (d, C-5), 45.4 (s, C-10), 44.7 (d, C-9), 40.3 (t, C-2), 39.8 (t, C-6), 38.2 (s, C-13), 33.4 (q, C-30), 32.2 (t, C-12), 23.8 (q, C-28), 20.8 (q, C-18), 18.0 (t, C-11), 17.2 (q, C-19), 17.0 (q, C-29); EIMS *m/z* 472 $[M]^+$ (5), 457 (1), 415 (2), 384 (2), 349 (95), 331 (7), 305 (4), 291 (11), 261 (21), 243 (15), 229 (8), 215 (10), 201 (18), 187 (12), 173 (18), 154 (19), 147 (20), 133 (29), 121 (31), 105 (45), 95 (100), 93 (73), 69 (57), 59 (53).

Stigmast-4-en-6β-ol-3-one (17)

$C_{29}H_{48}O_2$, colorless needles; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.80 (1H, s, H-4), 4.33 (1H, brs, H-7); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.1 (s, C-3), 168.3 (s, C-5), 126.4 (d, C-4), 73.4 (d, C-6), 56.2 (d, C-17), 56.1 (d, C-14), 53.8 (d, C-9), 46.0 (d, C-24), 42.6 (s, C-13), 39.7 (t, C-12), 38.7 (t, C-7), 38.0 (s, C-10), 37.2 (t, C-1), 36.2 (d, C-20), 34.3 (t, C-2). 34.0 (t, C-22), 29.8 (d, C-8), 29.4 (d, C-25), 28.2 (t, C-16), 26.4 (t, C-23), 24.2 (t, C-15), 23.2 (t, C-28), 21.1 (t, C-11), 19.8 (q, C-26), 19.6 (q, C-19), 19.1 (q, C-21), 18.8 (q, C-27), 12.2 (q, C-29), 12.0 (q, C-18); EIMS *m/z* 428 $[M]^+$ (100), 414 (46), 399 (10), 365 (15), 328 (4), 314 (10), 297 (6), 287 (15), 269 (24), 246 (100), 231 (56), 152 (50), 135 (16), 123 (18), 109 (22), 95 (34), 81 (42), 69 (43).

Schleicheol 2 (18)

$C_{30}H_{52}O_2$, white amorphous powder: ^{1}H NMR (acetone-d_6, 400 MHz) δ 5.74 (1H, m, H-6), 3.43 (1H, m, H-3), 3.27 (3H, s, —OCH_3), 3.28 (1H, m, H-7); ^{13}C NMR (acetone-d_6, 100 MHz) δ 147.5 (s, C-5), 121.3 (d, C-6), 74.1 (d, C-7), 71.7 (d, C-3), 57.0 (d, C-17), 56.3 (q, —OCH_3), 50.0 (d, C-14), 46.9 (d, C-24), 43.8 (d, C-9), 43.4 (t, C-4), 43.0 (s, C-13), 40.3 (t, C-12), 40.0 (s, C-10), 38.3 (d, C-8). 38.0 (t, C-1), 37.0 (d, C-20), 34.8 (t, C-22), 32.4 (t, C-2), 29.2 (t, C-25), 27.0 (t, C-23), 24.9 (t, C-15), 23.9 (t, C-28), 21.6 (t, C-11), 20.1 (q, C-27), 19.4 (q, C-26), 19.3 (q, C-21), 18.7 (q, C-19), 12.3 (q, C-29), 11.9 (q, C-18); EIMS *m/z* 444 $[M]^+$ (36), 426 (37), 412 (100), 398 (24), 379 (7), 271 (11), 253 (8), 229 (5), 211 (10), 189 (9), 175 (15), 159 (19), 145 (27), 133 (21), 121 (38), 107 (22), 95 (29), 81 (45), 69 (53), 55 (83).

3β-Hydroxy-5α,8α-epidioxyergosta-6,22-diene (19)

$C_{28}H_{44}O_3$, colorless needles; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.48 (1H, d, J = 8.3 Hz, H-7), 6.22 (1H, d, J = 8.3 Hz, H-6), 5.20 (1H, dd, J = 7.5, 15.2 Hz, H-23), 5.10 (1H, dd, J = 7.5, 15.2 Hz, H-22), 3.95 (1H, m, H-3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.4 (d, C-6), 135.2 (d, C-7), 132.4 (d, C-23), 130.8 (d, C-22), 82.2 (s, C-5), 79.4 (s, C-8), 66.5 (d, C-3), 56.3 (d, C-17), 51.7 (d, C-14), 51.2 (d, C-9), 44.6 (s, C-13), 42.8 (d, C-24), 39.7 (d, C-20), 39.4 (t, C-12), 37.0 (t, C-4), 34.7 (t, C-1), 33.1 (d, C-25), 30.2 (t, C-2), 28.6 (t, C-16), 23.4 (t, C-11), 20.9 (q, C-21), 20.7 (t, C-15), 19.9 (q, C-26), 19.6 (q, C-27), 18.2 (q, C-19), 17.6 (q, C-28), 12.9 (q, C-18); EIMS *m/z* 410 (27), 396 (100), 377 (13), 363 (50), 337 (24), 251 (28), 211 (18), 152 (39), 107 (33), 95 (40), 81 (58), 69 (82), 55 (84), 43 (72).

Syringaresinol (20)

$C_{22}H_{26}O_8$, colorless needles; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.55 (4H, d, $J = 2.0$ Hz, H-2, 6, 2′, 6′), 5.55 (2H, s, —OH), 4.70 (2H, d, $J = 4.3$ Hz, H-7, 7′), 4.26 (2H, dd, $J = 6.8, 9.0$ Hz, H-9b, 9′b), 3.90 (14H, m, 4-OCH_3, H-9a, 9′a), 3.07 (2H, m, H-8, 8′); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.2 (s, C-3, 5, 3′, 5′), 134.5 (s, C-4, 4′), 132.2 (s, C-1, 1′), 102.6 (d, C-7, 7′), 86.1 (d, C-7, 7′), 71.8 (t, C-9, 9′), 56.4 (q, —OCH_3), 54.3 (d, C-8, 8′); EIMS *m/z* 418 $[M]^+$ (100), 403 (4), 387 (10), 319 (4), 251 (9), 235 (20), 221 (17), 210 (27), 193 (35), 181 (67), 167 (60), 161 (29), 154 (30), 151 (18), 139 (15), 123 (19), 111 (14), 93 (15), 79 (17), 65 (18), 55 (21).

Lyoniresinol (21)

$C_{22}H_{28}O_8$, white amorphous powder; ^{1}H NMR (CD_3OD, 400 MHz) δ 6.58 (1H, s, H-8), 6.37 (2H, s H-2′, 6′), 4.29 (1H, d, $J = 4.5$ Hz, H-4), 3.85 (3H, s, 5-OCH_3), 3.73 (6H, s, 3′, 5′-OCH_3), 3.36 (3H, s, 7-OCH_3), 3.58 (1H, dd, $J = 3.9, 8.6$ Hz, H-2), 3.48 (2H, m, 3-CH_2), 3.30 (2H, m, 2-CH_2), 2.69 (1H, dd, $J = 3.9, 12.1$ Hz, H-1a), 2.56 (1H, m, H-1b), 1.95 (1H, m, H-3), 1.60 (1H, m, H-2); ^{13}C NMR (CD_3OD, 100 MHz) δ 149.0 (s, C-3′, 5′), 148.7 (s, C-5), 147.7 (s, C-7), 139.3 (s, C-1′), 138.9 (s, C-6), 134.5 (s, C-4′), 130.2 (s, C-9), 126.2 (s, C-10), 107.7 (d, C-8), 106.8 (d, C-2′, 6′), 66.8 (t, 2-CH_2), 64.1 (t, 3-CH_2), 60.1 (q, 5-OCH_3), 56.7 (q, 3′, 5′-OCH_3), 56.6 (q, 7-OCH_3), 49.2 (d, C-3), 42.3 (d, C-4), 40.9 (d, C-2), 33.6 (t, C-1); EIMS *m/z* 420 $[M]^+$ (100), 403 (5), 389 (6), 371 (20), 357 (5), 339 (9), 301 (10), 285 (5), 269 (7), 249 (16), 235 (12), 217 (48), 205 (53), 183 (59), 167 (65), 153 (18), 145 (19), 131 (11), 115 (18), 91 (16), 79 (13), 69 (18), 55 (26), 41 (28).

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