LIGNANS FROM *Gnetum montanum* Markgr. f. *megalocarpua*

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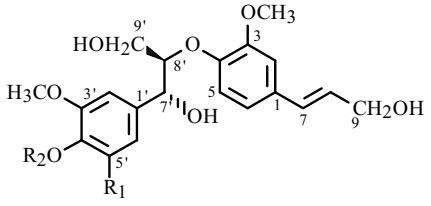
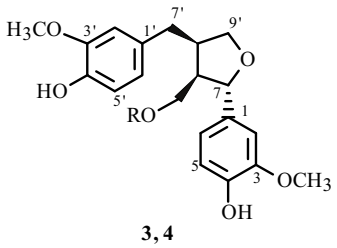
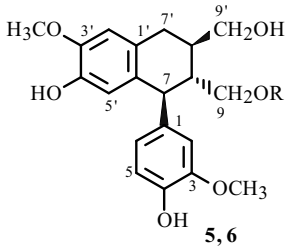
The plants of *Gnetum* (Gnetatae, member of Gnetales) are a special group of gymnospermous plants that share several angiospermous morphological features [1, 2]. Worldwide, there are more than 30 species, among which nine species are distributed in China. The Gentales and angiosperms are regarded as closely related. Whether this view is justified from the secondary metabolites of the plants, we decided to investigate the chemical components of the plants of *Gnetum* genus. In this paper, we present the isolation and structure elucidation of nine lignans (**1**–**9**) from the ethanol extracts of lignans from *Gnetum montanum* Markgr. f. *megalocarpua* Markgr. They are *threo*-3,3′-dimethoxy-4,8′-oxyneolignan-9,4′,7′,9′-tetraol-7(8)-ene (**1**) [3], longifloroside B (**2**) [4], (+)-lariciresinol (**3**) [5], (+)-lariciresinol-9-*O*-β-D-glucopyranoside (**4**) [5], (–)isolariciresinol-9-*O*-β-D-glucopyranoside (**5**) [6], (–)isolariciresinol (**6**) [6], medioresinol (**7**) [7], syringaresinol (**8**) [7], and pinoresinol (**9**) [7]. All the compounds were isolated from this plant for the first time.



1, 2



3, 4



5, 6

1: $R_1 = R_2 = H$; **2:** $R_1 = OCH_3$, R_2 = Glc; **3, 6:** R = H, **4, 5:** R = Glc

The NMR spectra were recorded on Bruker AV-400 and Bruker DRX-500 spectrometers in pyridine-d_5 solution with TMS as an internal standard. The multiplicity of ^{13}C NMR was determined as DEPT. MS data were obtained on a VG Autospec-3000 spectrometer.

The materials were collected in 2003 from Xishuangbanna in Yunnan province in China and identified by *Cui Jingyun* in Xishuangbanna botanical garden.

Extraction and Isolation. The air-dried and powdered lignans of *Gnetum montanum* Markgr. f. *megalocarpua* Markgr. (11 kg) were extracted with EtOH (3 ×) under reflux to give a crude extract. After concentration of the combined extracts, the resulting gummy material was suspended in water and then partitioned with $CHCl_3$ to afford $CHCl_3$ and aqueous residues (160 and 370 g, respectively); 130 g $CHCl_3$ residues was subjected to CC over silicon gel and eluted with $CHCl_3$–CH_3OH (9:1) to give three fractions. The third fraction was repeatedly subjected to CC over silicon gel, Sephadex LH-20, and RP-18 to afford compounds **3** (443 mg), **6** (11 mg), **7** (38 mg), **8** (83 mg), and **9** (194 mg); 170 g aqueous residue was subjected to CC over silicon gel and eluted with $CHCl_3$–CH_3OH–H_2O (7:3:0.5) to give four fractions. Each fraction was repeatedly subjected to CC over silicon gel, Sephadex LH-20, and RP-18 to afford compounds **1** (81 mg) from the first fraction, **4** (97 mg) and **5** (17 mg) from the second fraction, and **2** (72 mg) from the third fraction.

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***threo*-3,3′-Dimethoxy-4,8′-oxyneoligna-9,4′,7′,9′-tetraol-7(8)-ene (1),** yellow solid, $C_{20}H_{24}O_7$, ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 7.02 (1H, br.s, H-2), 6.98 (1H, br.s, H-2′), 6.75 (1H, d, J = 8.0, H-5), 6.85 (1H, d, J = 8.0, H-6), 6.83 (1H, d, J = 8.0, H-6′), 6.75 (1H, d, J = 8.0, H-5′), 6.50 (1H, d, J = 15.8, H-7), 6.24 (1H, dt, J = 15.8, 5.7, H-8), 4.37 (1H, d, J = 5.4, H-7′), 4.18 (1H, m, H-8′), 3.85 (4H, m, H-9, 9′), 3.77, 3.73 (3H each, s, 2ArOCH$_3$);^{13}C NMR (100 MHz, CD_3OD, δ): 151.7 (s, C-3), 148.7 (s, C-3′), 148.6 (s, C-4), 146.9 (s, C-4′), 133.9 (s, C-1′), 132.9 (s, C-1), 131.4 (d, C-8), 128.4 (d, C-7), 120.9 (d, C-6), 120.6 (d, C-6′), 118.7 (d, C-5), 115.6 (d, C-5′), 111.8 (d, C-2), 111.3 (d, C-2′), 86.0 (d, C-8′), 73.9 (d, C-7′), 63.7 (t, C-9), 61.9 (t, C-9′), 56.4 (q, 3-OCH$_3$), 56.3 (q, 3′-OCH$_3$); negative FAB-MS *m*/*z* (%): 375 [M-1]$^-$ (71), 264 (59), 187 (74).

Longifloroside B (2), yellow solid, $C_{27}H_{36}O_{13}$, ^{1}H NMR (400 MHz, CD_3COCD_3, δ, ppm, J/Hz): 7.06 (1H, br.s, H-2), 6.88 (1H, br.d, J = 8.3, H-6), 7.10 (1H, d, J = 8.3, H-5), 6.71 (2H, s, H-2′, -6′), 6.54 (d, J = 15.8, H-7), 6.32 (dt, J = 15.8, 5.5, H-8), 3.51 (6H, s, 3′, 5′-OCH$_3$), 3.53 (3H, s, 3-OCH$_3$), 4.72 (1H, d, J = 7.1, H-7′); ^{13}C NMR (100 MHz, CD_3COCD_3, δ): 134.7 (s, C-1′), 104.8 (d, C-2′, 6′), 154.5 (s, C-3′, C-5′), 137.4 (s, C-4′), 73.7 (d, C-7′), 87.3 (d, C-8′), 61.5 (t, C-9′), 147.2 (s, C-4), 150.4 (s, C-3), 117.5 (d, C-5), 120.7 (d, C-6), 136.3 (s, C-1), 112.4 (d, C-2), 131.4 (d, C-8), 129.9 (d, C-7), 63.6 (t, C-9), 56.6 (q, 3', 5'- OCH$_3$), 56.4 (q, 3-OCH$_3$), 102.9 (d, *β*-D-Glc C-1″), 74.8, 77.8, 71.3, 78.1 (d, *β*-D-Glc C-2″, 3″, 4″, 5″), 62.5 (t, *β*-D-Glc C-6″); negative FAB-MS *m*/*z*: 567 [M-1]$^-$ (20), 405 [M-Glc-1]$^-$ (42).

(+)-Lariciresinol (3), yellow solid, $C_{20}H_{24}O_6$, ^{1}H NMR (500 MHz, CD_3COCD_3, δ, ppm, J/Hz): 6.65–6.95 (6H, m, H-2, 2′, 5, 5′, 6, 6′), 4.87 (1H, d, J = 6.1, H-7), 4.03, 3.99 (4H, m, H-9, 9′), 2.98, 2.76 (2H, m, H-8, 8′), 2.56, 2.44 (2H, m, H-7′), 3.77, 3.73 (3H each, s, 2ArOCH$_3$); ^{13}C NMR (125 MHz, CD_3COCD_3, δ): 148.0 (s, C-3), 148.0 (s, C-3′), 146.2 (s, C-4′), 145.2 (s, C-4), 135.8 (s, C-1), 133.0 (s, C-1′), 121.7 (d, C-6), 119.2 (d, C-6′), 112.8 (d, C-2′), 110.0 (d, C-2), 115.7 (d, C-5), 115.4 (d, C-5′), 83.0 (d, C-7), 72.8 (d, C-9′), 60.1 (t, C-9), 53.4 (d, C-8), 43.0 (d, C-8′), 33.1 (t, C-7′), 55.9 (q, 3-OCH$_3$, 3′-OCH$_3$); positive FAB-MS *m*/*z* (%): 360 [M]$^+$ (100), 237 (38), 219(74), 69 (44).

(+)-Lariciresinol-9-*O*-*β*-D-glucopyranoside (4), yellow solid, $C_{26}H_{34}O_{11}$, ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 6.65–6.95 (6H, m, H-2, 2′, 5, 5′, 6, 6′), 4.87 (1H, d, J = 6.8, H-7), 4.33, 4.22 (2H, m, H-6″), 3.98–3.26 (6H, m, H-9, 9′, 2″, 3″, 4″, 5″), 3.01, 2.75 (2H, m, H-8, 8′), 2.56, 2.44 (2H, m, H-7′), 3.86, 3.85 (each, s, 2ArOCH$_3$); ^{13}C NMR (100 MHz, CD_3OD, δ): 148.9 (s, C-3′), 148.9 (s, C-3′), 146.9 (s, C-4′), 145.7 (s, C-4), 135.6 (s, C-1), 133.8 (s, C-1′), 122.2 (d, C-6), 119.9 (d, C-6′), 113.5 (d, C-2′), 110.8 (d, C-2), 116.2 (d, C-5), 115.9 (d, C-5′), 84.1 (d, C-7), 73.7 (d, C-9′), 68.4 (t, C-9), 51.7 (d, C-8), 43.9 (d, C-8′), 33.7 (t, C-7′), 56.4 (q, 3-OCH$_3$, 3′-OCH$_3$), 104.5 (d, C-1″), 78.2 (d, C-3″), 77.9 (d, C-5″), 75.1 (d, C-2″), 71.6 (d, C-4″), 62.8 (t, C-6″); negative FAB-MS *m*/*z* (%): 521 [M-1]$^-$ (40).

(–)-Isolariciresinol-9-*O*-glucopyranoside (5), yellow solid, $C_{26}H_{34}O_{11}$, ^{1}H NMR (500 MHz, CD_3OD, δ, ppm, J/Hz): 6.68 (1H, d, J = 1.7, H-2), 6.65 (1H, d, J = 8.3, H-5), 6.74 (1H, d, J = 8.3, H-6), 6.18 (1H, s, H-2′), 6.64 (1H, s, H-5′), 2.75 (1H, m, H-7), 1.95 (1H, m, H-8, 8′), 3.16, 2.88 (2H, m, H-7′), 4.04 (1H, d, J = 7.7, H-1″), 3.84–3.63 (9H, m, H-9, 9′, 2″, 3″, 4″, 5″), 3.79, 3.77 (3H each, s, 2ArOCH$_3$); ^{13}C NMR (125 MHz, CD_3OD, δ): 149.0 (s, C-3), 147.3 (s, C-3′), 145.3 (s, C-4), 146.0 (s, C-4′), 138.7 (s, C-1), 129.3 (s, C-1′), 123.5 (d, C-6), 133.7 (s, C-6′), 112.4 (d, C-2′), 114.1 (d, C-2), 116.0 (d, C-5), 117.4 (d, C-5′), 48.5 (d, C-7), 65.5 (t, C-9′), 70.8 (t, C-9), 45.3 (d, C-8), 41.2 (d, C-8′), 33.7 (t, C-7′), 56.4, 56.4 (q, 3-OCH$_3$, 3′-OCH$_3$), 103.8 (d, C-1″), 78.2 (d, C-3″), 77.9 (d, C-5″), 75.0 (d, C-2″), 71.5 (d, C-4″), 62.5 (t, C-6″); negative FAB-MS *m*/*z* (%): 521 [M-1]$^-$ (53).

(–)-Isolariciresinol (6), yellow solid, $C_{20}H_{24}O_6$, ^{1}H NMR (500 MHz, CD_3COCD_3, δ, ppm, J/Hz): 6.75 (1H, s, H-2), 6.63 (1H, d, J = 7.7, H-5), 6.77 (1H, d, J = 7.7, H-6), 6.18 (1H, s, H-2′), 6.65 (1H, s, H-5′), 3.41 (1H, d, J = 7.2, H-7), 1.98 (1H, m, H-8), 2.75 (2H, m, H-7′), 1.81 (1H, m, H-8′), 3.82 (4H, m, H-9, 9′), 3.77, 3.78 (3H each, s, 3,3′-OCH$_3$); ^{13}C NMR (125 MHz, CD_3COCD_3, δ): 148.2 (s, C-3′), 146.4 (s, C-3), 145.8 (s, C-4′), 145.2 (s, C-4), 138.4 (s, C-6′), 133.9 (s, C-1), 128.5 (s, C-1′), 122.8 (d, C-6), 116.9 (d, C-5′), 115.5 (d, C-5), 113.6 (d, C-2), 111.9 (d, C-2′), 65.9 (t, C-9′), 62.2 (t, C-9), 48.3 (d, C-7), 48.1 (d, C-8), 40.4 (d, C-8′), 33.7 (t, C-7′), 56.3, 56.2 (q, 3, 3′-OCH$_3$); negative FAB-MS *m*/*z* (%): 359 [M-1]$^-$ (10), 281 (100), 255 (97).

Medioresinol (7), pale yellow needles (petrol ehter–CH_3COCH_3), $C_{21}H_{24}O_7$, ^{1}H NMR (500 MHz, CD_3COCD_3, δ, ppm, J/Hz): 6.69 (2H, s, H-2, 6), 6.98 (1H, d, J = 1.6, H-2′), 6.79 (1H, d, J = 8.3, H-5′), 6.84 (1H, dd, J = 1.6, 8.3, H-6′), 4.67 (2H, m, H-7, 7′), 4.24, 3.87 (each 2H, m, H-9, 9′), 3.12 (2H, m, H-8, 8′), 3.82 (6H, s, 3-, 5-OCH$_3$), 3.83 (3H, s, 3′-OCH$_3$); ^{13}C NMR (125 MHz, CD_3COCD_3, δ): 148.6 (s, C-3), 148.3 (s, C-3′), 136.1 (s, C-4), 146.8 (s, C-4′), 133.1 (s, C-1), 134.1 (s, C-1′), 104.4 (d, C-2, 6), 119.5 (d, C-6′), 110.5 (d, C-2′), 148.6 (s, C-5), 115.5 (d, C-5′), 86.7 (d, C-7), 72.2 (d, C-9, 9′), 55.3 (d, C-8), 55.1 (d, C-8′), 86.6 (t, C-7′), 56.6, 56.6, 56.2 (q, 3, 5-OCH$_3$, 3′-OCH$_3$); negative FAB-MS *m*/*z* (%): 387 [M-1]$^-$ (100).

(+)-Syringaresinol (8), yellow solid, $C_{22}H_{26}O_8$, ^{1}H NMR (500 MHz, CD_3COCD_3, δ, ppm, J/Hz): 6.68 (4H, s, H-2, 6, 2′ and 6′), 4.67 (2H, d, J = 4.3, H-7, 7′), 4.24, 3.85 (each 2H, m, H-9, 9′), 3.10 (2H, m, H-8, 8′), 3.80 (12H, s, 4×OCH_3); ^{13}C NMR (125 MHz, CD_3COCD_3, δ): 55.2 (d, C-8 and 8′), 56.6 (q, 4×OCH_3), 72.3 (t, C-9 and 9′), 86.7 (d, C-7 and 7′), 104.3 (d, C-2′, 6′, 2 and 6), 133.1 (s, C-1′ and 1), 136.0 (s, C-4′ and 4), 148.6 (s, C-3′, 5′, 3 and 5); positive FABMS *m/z* (%): 418 $[M]^+$ (34), 342 (32), 125 (100).

Pinoresinol (9), yellow solid, $C_{20}H_{22}O_6$, ^{13}C NMR (125 MHz, CD_3COCD_3, δ): 54.9 (d, C-8 and 8′), 56.1 (q, 2×OCH_3), 72.0 (t, C-9 and 9′), 86.5 (d, C-7, 7′), 110.5 (d, C-2 and 2′), 115.6 (d, C-5 and 5′), 119.6 (d, C-6 and 6′), 133.8 (s, C-1 and 1′), 146.6 (s, C-4 and 4'), 148.2 (s, C-3 and 3′); positive FABMS *m/z* (%): 358 $[M]^+$ (100), 235 (36), 205 (22).

REFERENCES

1. *Flora Yunnannica*, Tomus **4**, Institutum Botanicum Kunmingense Academiae Sinicae Edita, Science Press, 1986, pp. 128.
2. *Flora Reipublicae Popularis Sinicae*, Tomus **7**, Delectis Flora Reipublicae Popularis Sinicae Edita, Science Press, 1978, pp. 498.
3. Y. X. Zhao, X. D. Luo, and J. Zhou, *Acta Botanica Yunnanica*, **26**, 229 (2004).
4. C. Z. Wang and Z. J. Jia, *Planta Med.*, **63**, 241 (1997).
5. M. Sugiyama and M. Kikuchi, *Heterocycles*, **36**, 117 (1993).
6. A. Hans, L. Matthias, and W. Reiner, *Planta Med.*, **58**, 270 (1992).
7. F. Abe and T. Yamauchi, *Phytochemistry*, **27**, 575 (1988).