

CHEMICAL CONSTITUENTS OF *Litsea szemaiois*

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The genus *Litsea* (Lauraceae) comprises nearly 200 species, which are distributed widely throughout tropical and subtropical Asia, North America, and subtropical South America. *Litsea szemaiois* is an endangered species endemic to southern Yunnan, China [1]. To the best of our knowledge, no work has been reported on the chemical constituents of *L. szemaiois*.

As part of the continuous research on plants of the *Litsea* genus, we studied the leaves and twigs of *L. szemaiois* collected from Yunnan. Seven compounds were isolated from this plant for the first time.

The leaves and twigs were collected from a forest near Mengla, Xishuangbanna, Yunnan in August 2005 and were identified by Mr. Yu Chen, senior scientist of Kunming Institute of Botany. The powdered leaves and twigs of *L. szemaiois* (5 kg) were repeatedly extracted with EtOH at room temperature. The extract was then concentrated under reduced pressure to give a brown syrup, which was sequentially partitioned between H₂O and Et₂O and *n*-BuOH.

The Et₂O extract (30 g) was subjected to a series of chromatographic techniques using a silica gel column (mesh 200–300) and Sephadex LH-20.

The *n*-BuOH extracts (70 g) were subjected to silica gel column chromatography, eluting with EtOAc–MeOH (10:1–1:1) and MeOH, and the resulting fractions were subjected to additional separation steps using a silica gel column and Sephadex LH-20 (MeOH).

A total of seven compounds was isolated and identified based on UV, IR, and NMR spectra, including 2D NMR, which allowed complete assignment of the ¹H NMR and ¹³C NMR data, and by direct comparison with authentic samples and the literature.

β-Sitosterol (1): C₂₉H₅₀O, colorless needles. EI-MS *m/z*: 414 [M]⁺. The compound is identical to an authentic sample.

Scopoletin (2): C₁₀H₈O₄, colorless needles. EI-MS *m/z*: 192 [M]⁺, 177, 164, 149, 121, 69. ¹H NMR (300 MHz, CD₃OD, δ, ppm, J/Hz): 3.87 (3H, s, OMe), 6.23 (1H, d, J = 9.4, H-3), 6.79 (1H, s, H-8), 7.88 (1H, d, J = 9.4, H-4), 7.22 (1H, s, H-5). ¹³C NMR (75 MHz, CD₃OD, δ, ppm): 56.1 (q, OMe), 102.8 (d, C-8), 109.6 (d, C-3), 110.1 (s, C-10), 111.7 (d, C-5), 144.2 (d, C-4), 145.3 (s, C-7), 149.5 (s, C-9), 151.1 (s, C-6), 160.8 (s, C-2).

Gallic acid (3): C₇H₆O₅, yellow powder. EI-MS *m/z*: 170 [M]⁺, 153, 135, 126, 79. ¹H NMR (300 MHz, acetone-d₆, δ, ppm, J/Hz): 7.18 (2H, s, H-2, 6), 8.03 (1H, s, C₄-OH), 8.19 (2H, s, 2 × OH). ¹³C NMR (75 MHz, acetone-d₆, δ, ppm): 110.2 (d, C-2, 6), 122.0 (s, C-1), 138.7 (s, C-4), 146.0 (s, C-3, 5), 167.9 (s, -COOH).

***p*-Hydroxybenzaldehyde (4):** C₇H₆O₂, white powder. EI-MS *m/z*: 122 [M]⁺, 121, 93, 65, 55. ¹H NMR (300 MHz, CDCl₃, δ, ppm, J/Hz): 7.19 (2H, d, J = 8.5, H-2, 6), 7.94 (2H, dd, J = 8.6, 1.8, H-3, 5), 9.99 (1H, s). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 116.8 (d, C-3, 5), 129.5 (s, C-1), 132.6 (d, C-2, 6), 165.0 (s, C-4), 190.6 (d, CHO).

Epicatechin (5): C₁₅H₁₄O₆, white needles. EI-MS *m/z*: 290 [M]⁺, 152, 139, 123, 77, 69. ¹H NMR (500 MHz, CDCl₃, δ, ppm, J/Hz): 2.50 (1H, dd, J = 16.4, 3.5, H-4_{eq}), 2.70 (1H, dd, J = 16.4, 4.4, H-4_{ax}), 4.03 (1H, m, H-3), 4.56 (1H, d, J = 4.7, 3-OH), 4.75 (1H, d, J = 7.4, H-2), 5.75 (1H, d, J = 2.3, H-8), 5.91 (1H, d, J = 2.3, H-6), 6.68 (1H, s, H-5'), 6.68 (1H, s, H-6'), 6.91 (1H, s, H-2'), 8.71 (1H, s, 3'-OH), 8.79 (1H, s, 4'-OH), 8.89 (1H, s, 7-OH), 9.10 (1H, s, 5-OH). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 28.2 (C-4), 65.0 (C-3), 78.1 (C-2), 94.2 (C-8), 95.2 (C-6), 98.6 (C-10), 114.8 (C-5'), 114.9 (C-2'), 118.0 (C-6'), 130.7 (C-1'), 144.4 (C-3'), 144.5 (C-4'), 155.8 (C-9), 156.3 (C-7), 156.5 (C-5) [2].

β-Daucosterol (6): C₃₅H₆₀O₆, white powder. FAB⁺-MS *m/z*: 575 [M – 1]⁺, EI-MS *m/z*: 576 [M]⁺, 414, 396. The compound was directly compared with authentic samples.

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Staphylionoside D (7): C₁₉H₃₀O₈, amorphous powder. FAB⁻MS *m/z* 385 [M – H]⁻. ¹H NMR (500 MHz, CD₃OD, δ, ppm, J/Hz): 1.06 (3H, s, Me-12), 1.29 (3H, s, Me-11), 1.30 (3H, s, Me-13), 1.37 (2H, ddd, J = 4.3, 12, 4.4, H-4), 2.28 (1H, dd, J = 3.6, 13.2, H-2_{eq}), 2.00 (1H, dd, J = 4.0, 12.9, H-2_{ax}), 2.10 (3H, s, Me-10), 3.05 (1H, t, J = 8.0, H-2'), 3.60 (1H, dd, J = 12.1, 4.5, H-6'a), 3.77 (1H, d, J = 11.6, H-6'b), 4.25 (1H, m, H-3), 4.34 (1H, d, J = 7.9, H-1'), 5.74 (1H, s, H-8). ¹³C NMR (125 MHz, CD₃OD, δ, ppm): 37.5 (C-1), 47.1 (C-2), 73.0 (C-3), 48.9 (C-4), 72.8 (C-5), 120.5 (C-6), 201.3 (C-7), 101.6 (C-8), 211.9 (C-9), 27.0 (C-10), 29.9 (C-11), 32.7 (C-12), 31.3 (C-13), 103.1 (C-1'), 75.5 (C-2'), 78.6 (C-3'), 72.1 (C-4'), 78.3 (C-5'), 63.2 (C-6') [3].

All compounds were isolated from *L. szemaiois* for the first time. The occurrence of a megastigmane-type sesquiterpenoid glucoside with an allenic side chain, staphylionoside D (7), was the first report in the genus *Litsea*, which was isolated first from the leaves of *Staphylea bumalda* DC. in 2005 [3].

Phytochemical studies of the plant are continuing.

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