

RARE NATURAL PRODUCTS FROM THE WOOD OF *Magnolia grandiflora*

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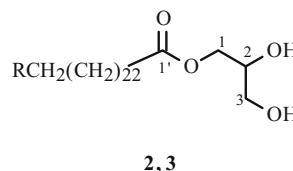
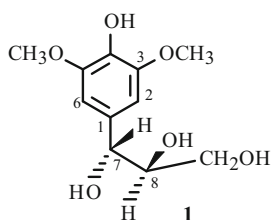
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Magnolia grandiflora L. (Magnoliaceae) is used in traditional Chinese medicine for the treatment of colds, headaches, and stomachache [1]. The plant has also been used for the treatment of fever, diarrhea, rheumatism and arthritis [2]. Various class of compounds such as sesquiterpenoids [3–5], coumarins [4], phenylpropanoids [6], lignans [7], glycosides [7, 8], alkaloids [9], and other compounds [10] have been reported from this plant. The present study describes the isolation and structure determination of seven compounds **1–7** from the wood of *M. grandiflora*.

Shade air-dried and powdered wood of *M. grandiflora* (22.0 kg) was extracted with 95% ethanol. The EtOH extract was concentrated under vacuum until EtOH was completely removed. The dried EtOH extract (170.17 g) was dissolved in distilled water and successively partitioned with *n*-hexane, dichloromethane, ethyl acetate, and *n*-butanol saturated with water. The dichloromethane-soluble fraction (27.40 g) was chromatographed on a silica gel column with increasing polarity of *n*-hexane–EtOAc (80:20→70:30→60:40→50:50→40:60→30:70→20:80, v/v). Elution by 70:30 gave compound **2** (227 mg), 60:40 gave compounds **6** (7.3 mg) and **7** (2.1 mg), 50:50 gave compound **3** (200 mg), and 20:80 gave compound **5** (89 mg). The *n*-butanol soluble fraction (47.74 g) was chromatographed on a silica column with increasing polarity of *n*-hexane–ethyl acetate (70:30→10:90→0:100, v/v). Elution by 0:100 yielded compound **4** (19.0 mg). On the other hand, fractions eluted by *n*-hexane:ethyl acetate (10:90, v/v) were further chromatographed twice on silica gel columns using CHCl₃–MeOH (90:10, 94:6, v/v) as an eluent to give compound **1** (24.5 mg).

Erythro-1-C-syringylglycerol (1). White powder, mp 105–107°C. C₁₁H₁₆O₆, EI-MS *m/z* 244 [M]⁺, PMR (500 MHz, MeOD, δ, ppm, J/Hz): 3.37 (1H, dd, J = 6.2, 11.3, H-9b), 3.49 (1H, dd, J = 4.0, 11.3, H-9a), 3.66 (1H, ddd, J = 2.1, 4.0, 6.2, H-8), 3.83 (6H, s, 3-OCH₃, 5-OCH₃), 4.51 (1H, d, J = 6.1, H-7), 6.67 (2H, s, H-2, H-6). ¹³C NMR (125 MHz, MeOD, δ, ppm): 56.75 (3-OCH₃, 5-OCH₃), 64.25 (C-9), 75.60 (C-7), 77.55 (C-8), 105.21 (C-2, C-6), 134.05 (C-1), 136.01 (C-4), 149.11 (C-3, C-5) [11].

2,3-Dihydroxypropyltetracosanoate (2). White amorphous powder, mp 86–88°C. C₂₇H₅₄O₄, EI-MS *m/z* 442 [M]⁺, PMR (500 MHz, C₅D₅N, δ, ppm, J/Hz): 0.87 (3H, t, J = 6.2, H-24'), 1.22–1.32 (40H, brs, H-4'–H-23'), 1.64 (2H, m, H-3'), 2.36 (2H, t, J = 7.4, H-2'), 4.11 (2H, d, J = 5.4, H-3), 4.43 (1H, m, H-2), 4.62 (1H, dd, J = 4.6, 6.5, H-1b), 4.69 (1H, dd, J = 4.5, 6.5, H-1a). ¹³C NMR (125 MHz, C₅D₅N, δ, ppm): 14.3 (C-24'), 23.0 (C-23'), 25.4 (C-3'), 29.4–30.1 (C-4'–C-21'), 32.2 (C-22'), 34.5 (C-2'), 64.3 (C-3), 66.8 (C-1), 71.0 (C-2), 173.8 (C-1') [12].



2: R = H; **3:** R = OH

2,3-Dihydroxypropyl-24'-hydroxytetracosanoate (3). White amorphous powder, mp 101–103°C. C₂₇H₅₄O₅, FAB-MS *m/z* 458 [M]⁺, PMR (500 MHz, C₅D₅N, δ, ppm, J/Hz): 1.22–1.31 (36H, br.s, H-4'–H-21'), 1.51 (2H, m, H-22'), 1.64 (2H, m, H-3'), 1.75 (2H, m, H-23'), 2.35 (2H, t, J = 7.3 Hz, H-2'), 3.87 (2H, t, J = 6.4, H-24'), 4.10 (2H, d, J = 5.3, H-3), 4.37 (1H, m, H-2), 4.63 (1H, dd, J = 4.6, 6.5, H-1b), 4.71 (1H, dd, J = 4.4, 6.5, H-1a). ¹³C NMR (125 MHz, C₅D₅N, δ, ppm): 25.4 (C-3'), 26.6 (C-22'), 29.6–30.1 (C-4'–C-21'), 33.8 (C-23'), 34.5 (C-2'), 62.2 (C-24'), 64.3 (C-3), 66.8 (C-1), 71.0 (C-2), 173.8 (C-1') [13].

3-Hydroxy-4,5-dimethoxyphenyl-β-D-glucopyranoside (4). White crystals, mp 184–186°C. C₁₄H₂₀O₉, EI-MS *m/z* 332 [M]⁺, PMR (500 MHz, C₅D₅N, δ, ppm, J/Hz): 3.71 (3H, s, 5-OCH₃), 3.84 (3H, s, 4-OCH₃), 4.05 (1H, m, H-5'), 4.31–4.35 (3H, m, H-2', H-3', H-4'), 4.36 (1H, m, H-6'b), 4.50 (1H, dd, J = 2.2, 12.0, H-6'a), 5.57 (1H, d, J = 6.7, H-1'), 6.66 (1H, d, J = 2.7, H-6), 6.96 (1H, d, J = 2.7, H-2). ¹³C NMR (125 MHz, C₅D₅N, δ, ppm): 55.87 (5-OCH₃), 60.60 (4-OCH₃), 62.44 (C-6'), 71.43 (C-4'), 75.06 (C-2'), 78.62 (C-3'), 78.94 (C-5'), 94.05 (C-6), 98.76 (C-2), 102.90 (C-1'), 133.08 (C-4), 152.65 (C-3), 154.5 (C-5), 155.5 (C-1) [14].

Daucosterol (5). White amorphous powder; all spectral values are in agreement with literature [15].

Syringic Acid (6). Brown crystal, mp 201–203°C. C₉H₁₀O₅, EI-MS *m/z* 198 [M]⁺, PMR (500 MHz, CDCl₃+MeOD, δ, ppm, J/Hz): 3.85 (6H, s, 3-OCH₃, 5-OCH₃), 7.34 (2H, s, H-2, H-6). ¹³C NMR (125 MHz, CDCl₃+MeOD, δ, ppm): 56.42 (3-OCH₃, 5-OCH₃), 107.22 (C-2, C-6), 120.98 (C-1), 139.81 (C-4), 147.03 (C-3, C-5), 168.96 (C-7) [16].

Syringaldehyde (7). Brown solid, mp 110–112°C. C₉H₁₀O₄, EI-MS *m/z* 182 [M]⁺, PMR (500 MHz, CDCl₃, δ, ppm, J/Hz): 4.08 (6H, s, 3-OCH₃, 5-OCH₃), 7.37 (2H, s, H-2, H-6), 9.92 (1H, s, H-7). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 56.50 (3-OCH₃, 5-OCH₃), 106.72 (C-2, C-6), 128.46 (C-1), 140.83 (C-4), 147.37 (C-3, C-5), 190.67 (C-7) [17].

All the compounds **1–7** were isolated for the first time from the genus *Magnolia*. Compounds **1–4** are very rare in the plant kingdom and to the best of our knowledge this is only the second time when compounds **1–3** were isolated from any natural sources.

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