A New Flavanone from Cinnamomum Subavenium

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ABSTRACT

One new flavanone, 6,7,4′-trihydroxy-3′-methoxyflavanone (1), was isolated from barks of Cinnamomum subavenium Miq (Lauraceae). The structure of 1 was characterized and identified by spectral analysis.

Keywords
Cinnamomum subavenium, Lauraceae, Flavanone.

Introduction
Cinnamomum subavenium Miq (Lauraceae) is a medium-sized evergreen tree, found in central to southern mainland China, Burma, Cambodia, Taiwan, Malaysia and Indonesia [1]. In the course of screening for biologically and chemically novel agents from Formosan Lauraceous plants [2-13], C. subavenium was chosen for further phytochemical investigation. They have identified a novel cytotoxic monoterpenoid, subamone, a novel sesquiterpenoid, subamol, five new butanolides, subamolide A-E, two new secobutanolides, secosubamolide and secosubamolide A, one new diphenyl ether, 2,2′,7a,7a′,7b,7b′-hexamethyldiphenyl ether, along with 47 known compounds from the stems, roots and leaves of C. subavenium [14-20]. In the course of screening for biologically and chemically novel agents from Formosan plants in the Cinnamomum species, C. subavenium was chosen for further phytochemical investigation. A new flavanone, 6,7,4′-trihydroxy-3′-methoxyflavanone (1) was isolated and identified from these barks. In this paper, we report the isolation and structural elucidation of this new compound.

6,7,4′-Trihydroxy-3′-methoxyflavanone (1) was obtained as a yellow amorphous powder and its molecular formula was deduced as C16H14O6 by HRESIMS (m/z 325.0689 [M + Na]⁺; calc. 325.0688). The UV spectrum showed a λmax at 242 and 284 nm typical for a flavanone skeleton [21]. The IR spectrum exhibited strong absorption bands at 3400, 1680 and 1515 cm⁻¹ due to the hydroxyl, α,β-unsaturated ketone and aromatic C=C functionalities, respectively, in the molecule. 1H and 13C NMR spectra showed the presence of three hydroxyl and one methoxy groups on the flavanone skeleton. The aromatic region of its 1H NMR spectrum showed two singlet protons at δ 7.24 and 6.51, two ortho-coupled protons at δ 7.02 and 6.89 and a meta-coupled proton at δ 7.22. The two singlet signals were assigned to H-5 and H-8 respectively. This suggested that ring A was substituted at C-6 and C-7. In the proton NMR, a pair of double-doubles at δ 2.70 (1H, dd, J = 16.8, 3.0 Hz) and 3.06 (1H, dd, J = 16.8, 13.0 Hz) due to H-3a/H-3b and an oxy-methine proton signal at δ 5.37 (1H, dd, J = 13.0, 3.0 Hz, H-2) further attested the flavanone skeleton [21]. Significant correlations between OMe-3′, H-2′ H-6′, and H-5′, as well as H-2, and H-3, were observed in the NOESY spectrum. Therefore, the methoxy group should be located on the B-ring. The ortho-coupled shielded proton resonating at δ 6.87 (d, J = 8.0 Hz) was assigned at H-5′ while the other proton signal at δ
The specimen of 3 + 16 - 1 was collected to afford 8 fractions. Fraction 7 (2.3 g) was purified by silica gel column and eluted with CH₂Cl₂ to afford a viscous residue (34.1 g). The residue was placed on a silica gel plate (Merck) for TLC, visualized with 10% APEX II 30e spectrometer; Silica gel 60 for CC and precoated (Applied Biosystems); High-resolution ESI-MS, Bruker Daltonics.

Varian (Unity Plus) NMR spectrometer (400 MHz for 1H NMR, 100 MHz for 13C NMR); Low-resolution ESI-MS, API 3000 (Applied Biosystems); High-resolution ESI-MS, Bruker Daltonics APEX II 30e spectrometer; Silica gel 60 for CC and precoated silica gel plates (Merck) were used for TLC, visualized with 10% H₂SO₄.

Plant material: The specimen of C. subavenium was collected from Taipei, Taiwan, February 2013. A voucher specimen was identified by Dr. Fu-Yuan Lu (Department of Forestry and Natural Resources College of Agriculture, National Chiayi University) and was deposited in the School of Medical and Health Sciences, Fooyin University, Kaohsiung, Taiwan.

Extraction and isolation: The barks (2.6 kg) of C. subavenium were extracted with CH₂Cl₂ at room temperature for 24-48 hrs. The CH₂Cl₂ extract was dried and evaporated to afford a viscous residue (34.1 g). The residue was placed on a silica gel column and eluted with CH₂Cl₂ gradually enriched with MeOH to afford 8 fractions. Fraction 7 (2.3 g) was purified by silica gel chromatography (CH₂Cl₂-MeOH, 20:1) to give 6,7,4′-trihydroxy-3′-methoxyflavanone (1) (6 mg).

![Figure 1: Structure of 6,7,4′-trihydroxy-3′-methoxyflavanone (1).](image)

**Experimental**

General: IR, Hitachi 260-30 spectrophotometer; 1D and 2D NMR, Varian (Unity Plus) NMR spectrometer (400 MHz for 1H NMR, 100 MHz for 13C NMR); Low-resolution ESI-MS, API 3000 (Applied Biosystems); High-resolution ESI-MS, Bruker Daltonics APEX II 30e spectrometer; Silica gel 60 for CC and precoated silica gel plates (Merck) were used for TLC, visualized with 10% H₂SO₄.

Plant material: The specimen of C. subavenium was collected from Taipei, Taiwan, February 2013. A voucher specimen was identified by Dr. Fu-Yuan Lu (Department of Forestry and Natural Resources College of Agriculture, National Chiayi University) and was deposited in the School of Medical and Health Sciences, Fooyin University, Kaohsiung, Taiwan.

Extraction and isolation: The barks (2.6 kg) of C. subavenium were extracted repeatedly with CH₂Cl₂ at room temperature for 24-48 hrs. The CH₂Cl₂ extract was dried and evaporated to afford a viscous residue (34.1 g). The residue was placed on a silica gel column and eluted with CH₂Cl₂ gradually enriched with MeOH to afford 8 fractions. Fraction 7 (2.3 g) was purified by silica gel chromatography (CH₂Cl₂-MeOH, 20:1) to give 6,7,4′-trihydroxy-3′-methoxyflavanone (1) (6 mg).

6,7,4′-Trihydroxy-3′-methoxyflavanone (1): Yellow amorphous powder; [α]D24 = 22.8 (c = 0.22; CHCl₃); IR (neat) νmax: 3400 (br, OH), 1680 (C=O, 1515 (C=O); UV/Vis (CH₃CN): λmax (log ε): 242 (3.75), 284 (3.90) nm; MS (ESI): m/z (%): 325 [M + Na]⁺; HRMS-ESI: m/z [M + Na]⁺ calcd for C₁₆H₁₂O₆Na: 325.0689; found: 325.0688; ¹H NMR (400 MHz, CDCl₃): 2.70 (1H, dd, J = 16.8, 3.0 Hz, H-3a), 3.06 (1H, dd, J = 16.8, 13.0 Hz, H-3b), 5.37 (1H, dd, J = 13.0, 3.0 Hz, H-2), 3.90 (3H, s, OMe-3), 6.51 (1H, s, H-8), 6.87 (1H, d, J = 8.0 Hz, H-5'), 7.02 (1H, dd, J = 8.0, 2.0 Hz, H-6), 7.21 (1H, d, J = 2.0 Hz, H-2'), 7.24 (1H, s, H-5). ¹³C NMR (100 MHz, CDCl₃): δ 44.7 (C-1), 144.6 (C-7), 159.1 (C-9), 190.5 (C=O).

**References**


