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Two New Chalcones from the Flowers of *Clerodendrum inerme*

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Two new chalcones, 3-hydroxy-3',4'-dimethoxylchalcone (1) and 3,2'-dihydroxy-3',4'-dimethoxylchalcone (2), were isolated from the flowers of *Clerodendrum inerme* (L.) Gaertn together with two known flavones, 7-O-methylwogonin (3) and eucalyptin (4). The structures of the new compounds 1 and 2 have been established by extensive 2D-NMR and ESI-TOFMS studies.

**Keywords:** *Clerodendrum inerme*, Verbenaceae, Flowers, Chalcones.

The genus *Clerodendrum* Linn. (Syn. *Clerodendron*), family Verbenaceae, consists of 400 species of which 18 occur in India [1]. *C. inerme* (L.) Gaertn is a straggling ornamental shrub chiefly found in coastal regions of India. Various parts of this species have been traditionally used as a febrifuge, antiperiodic, antipyretic, alterative and also in the treatment of tetanus, scrofula, rheumatism and skin diseases [2a-c]. Earlier studies on different parts of this plant have resulted in the isolation of several flavones, di-and triterpenes, iridoids, neolignans and sterols [3a-g]. In our systematic search for polyphenolic constituents from Indian medicinal plants, we have investigated the flowers of *C. inerme* and report herein the isolation and structural elucidation of two new chalcones, 3-hydroxy-3',4'-dimethoxylchalcone (1) and 3,2'-dihydroxy-3',4'-dimethoxylchalcone (2), besides two known flavones, 7-O-methylwogonin (3) and eucalyptin (4).

**Compound 1**, obtained as pale yellow crystals, showed a [M+H]⁺ ion at m/z 285.1120 in its positive ESI-TOFMS corresponding to the molecular formula C\(_{17}\)H\(_{16}\)O\(_4\), which was corroborated by the \(^13\)C NMR spectrum, which displayed 17 carbon signals. The IR absorption bands at 3435 and 1635 cm⁻¹ correspond to phenolic hydroxyl and carbonyl functions, respectively. The UV absorption maxima of 1 in MeOH at 237 (sh) and 333 nm, and a pair of olefinic protons at \(\delta 7.79\) (1H, d, \(J = 15.6\) Hz, H-β) and 7.69 (1H, d, \(J = 15.6\) Hz, H-β) in the ¹H NMR spectrum suggested compound 1 to be a chalcone derivative [4a,b]. The ¹H NMR spectrum also showed a broad signal for a phenolic hydroxyl group at \(\delta 8.50\) and a sharp six-proton singlet for two methoxyl groups at \(\delta 3.90\). The ¹H NMR spectrum further showed ABX-type aromatic proton signals at \(\delta 7.84\) (1H, dd, \(J = 8.4, 2.1\) Hz), 7.66 (1H, d, \(J = 2.1\) Hz) and 7.05 (1H, d, \(J = 8.4\) Hz), and the former two signals were assigned to H-6' and H-2' as these protons showed HMBC correlations (Figure 1) with the carbon at \(\delta 188.2\). This fixes the ortho-coupled aromatic proton signal at \(\delta 7.05\) to H-5', further supported by HMBC correlation of this proton with C-6' and C-1'. The two methoxyl groups at \(\delta 3.90\) were found to be attached to C-3' and C-4' based on the HMBC correlations with these carbons at 150.3 and 154.6 ppm, and two strong NOE correlations with H-2' (\(\delta 7.66\)) and H-5' (\(\delta 7.05\)), respectively in its NOESY spectrum (Figure 1). The four aromatic protons of ring B appearing at \(\delta 7.28\) (1H, m, H-6), 7.27 (1H, m, H-5), 7.25 (1H, m, H-2) and 6.93 (1H, ddd, \(J = 7.8, 2.0, 2.0\) Hz, H-4), respectively are consistent with a 1,3-disubstituted ring B [5]. This fixes the attachment of the non-chelated phenolic hydroxyl at \(\delta 8.50\) to C-3 (\(\delta 158.5\)), which showed cross correlations with H-2 (\(\delta 7.25\)), H-4 (\(\delta 6.93\)) and H-5 (\(\delta 7.27\)). Thus, from the foregoing spectral studies the structure of compound 1 was elucidated as 3-hydroxy-3',4'-dimethoxylchalcone.

**Compound 2**, isolated as yellow amorphous powder, showed a [M+H]⁺ ion at m/z 301.1100 in its positive ESI-TOFMS, consistent with the molecular formula C\(_{17}\)H\(_{16}\)O\(_5\). The ¹C NMR spectrum showed signals for all the 17 carbons of the molecule. The UV absorption maxima of 2 in MeOH at 240 (sh) and 347 nm, and the presence of a pair of AB doublets (\(J = 15.5\) Hz) of transolefinic protons at \(\delta 7.86\) (H-α) and 7.81 (H-β) in the ¹H NMR spectrum suggested compound 2 to be a chalcone derivative [4a,b]. The IR absorption bands at 3435 and 1635 cm⁻¹ correspond to phenolic hydroxyl and carbonyl functions, respectively. The ¹H NMR spectrum of 2 showed two D\(_2\)O exchangeable phenolic hydroxyl signals at \(\delta 13.27\) and 8.60, assigned to a chelated hydroxyl group at C-2' and a non-chelated hydroxyl group, respectively. It also showed two sharp singlets for two methoxyl groups at \(\delta 3.92\) and 3.78. The ¹H NMR spectrum displayed two ortho-coupled aromatic proton signals at \(\delta 8.01\) (1H, d, \(J = 9.1\) Hz) and 6.68 (1H, d, \(J = 9.1\) Hz) assigned to H-6' and H-5' protons as they showed HMBC correlations (Figure 2) with C-2' and carbonyl carbon, and C-1' and C-6', respectively. The methoxyl group at \(\delta 3.92\) was placed at C-4' based on its HMBC correlation with this carbon at 159.9 ppm and a strong NOE correlation (Figure 2) with H-5' (\(\delta 6.68\)). The methoxyl group at \(\delta 3.78\) was placed at C-3' based on the HMBC correlation of the methoxyl protons with this carbon at 137.4 ppm, which showed cross correlation with H-5'.
Experimental

General experimental procedures: Melting points, Kofler hot-stage apparatus; UV, Shimadzu UV-1800 spectrophotometer; IR, JASCO FTIR-5300 spectrophotometer; NMR, Bruker Avance 400; Positive ESI-TOFMS, API Q-Star Pulsar I of Applied Bio-system.

Plant material: The flowers of C. inerme, collected from Tirumala Hills, Andhra Pradesh, South India in February 2011, were identified by Dr K. Madhava Chetty, Plant Taxonomist, Department of Botany, Sri Venkateswara University, Tirupati, India, where a voucher specimen (DG.102) has been deposited.

Extraction and isolation: The shaded-dried and powdered flowers of C. inerme (3.2 kg) were successively extracted with n-hexane (3 x 8 L), Me2CO (3 x 8 L) and MeOH (3 x 8 L) at room temperature. The concentrated n-hexane extract (135 g) on purification over a silica gel column using a n-hexane-EtOAc step gradient (1:9) yielded 3 (48 mg). The Me2CO (42 g) and MeOH (38 g) extracts were found to be similar on paper and thin layer chromatograms and hence combined, defatted with n-hexane and the residue obtained (64 g) was purified over a silica gel column using n-hexane-EtOAc step gradient (9:1, 7:3 and 4:6) to afford 4 (14 mg), 1 (45 mg), and 2 (39 mg) respectively.

References

3-Hydroxy-3',4'-dimethoxychalcone (1)
Pale yellow crystals (MeOH).
MP: 113-115°C.
UV (MeOH) λmax (log ε): 237 (3.11) (sh) and 333 (3.26) nm.
IR (KBr) νmax: 3304 (OH), 2962, 2932, 2843, 2600, 2025, 1753, 1647 (C=O), 1593, 1570, 1516, 1446, 1419, 1373, 1348, 1261, 1199, 1151, 1076, 914, 827, 844, 817, 787, 767, 736 cm⁻¹.
1H NMR (Me4CO-d): δ 8.50 (1H, brs, OH-3), 7.84 (1H, ddd, J= 8.4, 2.1 Hz, H-6'), 7.79 (1H, d, J= 15.6 Hz, H-α), 7.69 (1H, d, J= 15.6 Hz, H-β), 7.66 (1H, d, J= 2.1 Hz, H-2'), 7.28 (1H, m, H-6), 7.25 (1H, m, H-2), 7.05 (1H, d, J= 8.4 Hz, H-5'), 6.93 (1H, ddd, J=7.8, 2.0, 2.0 Hz), 3.90 (6H, s, OMe-3',4').
13C NMR (Me4CO-d): δ 188.2 (C-O), 158.3 (C-5), 154.6 (C-4'), 150.3 (C-3'), 144.0 (C-β), 137.6 (C-1), 132.0 (C-1'), 130.8 (C-5), 123.9 (C-6'), 122.7 (Cα), 120.9 (C-6), 118.2 (C-4), 115.7 (C-2'), 111.8 (C-2'), 111.5 (C-5'), 56.1 (OMe-3',4').
ESI-TOFMS (positive ion mode) m/z: 285.1120 [M+H]+ (calcd for C17H16O6, 285.1127).

3, 2'-Dihydroxy-3', 4'-dimethoxychalcone (2)
Yellow amorphous powder (MeOH).
MP: 138-140°C.
UV (MeOH) λmax (log ε): 240 (3.13) and 347 (3.64) nm.
IR (KBr) νmax: 3435 (OH), 2941, 2841, 1838, 1635 (C=O), 1562, 1504, 1448, 1421,1348, 1278, 1226, 1130, 1074, 999, 978, 912, 848, 825, 779, 742, 698, 673 cm⁻¹.
1H NMR (Me4CO-d): δ 13.27 (1H, s, OH-2'), 8.60 (1H, s, OH-3), 8.01 (1H, d, J= 9.1 Hz, H-6'), 7.86 (1H, d, J= 15.5 Hz, H-α), 7.81 (1H, d, J= 15.5 Hz, H-β), 7.32 (1H, ddd, J= 8.0, 7.8 Hz, H-5'), 7.29 (1H, dd, J= 8.0, 7.8 Hz, H-7), 7.27 (1H, dd, J=2.0, 2.0 Hz, H-2'), 6.95 (1H, ddd, J= 7.8, 2.0, 2.0 Hz, H-4'), 6.68 (1H, dd, J= 9.1 Hz, H-5'), 3.92 (3H, s, OMe-4') 3.78 (3H, s, OMe-3').
13C NMR (Me4CO-d): δ 193.6 (C-O), 159.9 (C-4'), 159.2 (C-2'), 158.7 (C-3), 145.3 (C-β), 137.4 (C-3'), 137.1 (C-1), 130.8 (C-5), 127.6 (C-6'), 121.6 (Cα), 121.2 (C-6), 118.7 (C-4), 116.2 (C-1'), 116.1 (C-2'), 104.2 (C-5'), 60.3 (OMe-3'), 56.5 (OMe-4').
ESI-TOFMS (positive ion mode) m/z: 301.1100 [M+H]+ (calcd for C17H16O6, 301.1080).

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