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### **Androechin, A New Chalcone Glucoside from *Andrographis Echioides***

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## ANDROECHIN, A NEW CHALCONE GLUCOSIDE FROM *ANDROGRAPHIS ECHIOIDES*

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A new chalcone glucoside, androechin, and a known flavone glucoside, echiodinin 5-*O*-glucoside, were isolated from the whole plant of *Andrographis echioides*. Androechin was characterized as 2,2',6'-trihydroxy-4'-methoxychalcone 2'-*O*-β-D-glucopyranoside by spectral and chemical studies.

**Keywords:** *Andrographis echioides*; Acanthaceae; Chalcone glucoside; Androechin

### INTRODUCTION

*Andrographis echioides* Nees (Acanthaceae) is an erect herb found widely in the dry districts of tropical India and Sri Lanka [1] and is used in indigenous medicine as a remedy for fevers [2]. In a previous study on the hexane and Me<sub>2</sub>CO extracts of the whole plant of *A. echioides*, we have reported a new flavanone, dihydroechiodinin (**3**) besides four known flavones [3]. Continuing our investigations on the whole plant of this species, we now report the isolation and structure elucidation of a new chalcone glucoside, designated as androechin (**1**) together with a known flavone glucoside, echiodinin 5-*O*-β-D-glucopyranoside (**2**) [4].

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## RESULTS AND DISCUSSION

Androechin (**1**) was obtained as yellow crystals, m.p. 128–130°C. Its molecular formula  $C_{22}H_{24}O_{10}$  was deduced from HRFABMS ( $m/z$  471.1266  $[M + Na]^+$ ) in conjunction with  $^{13}C$  NMR spectral data. The UV absorption maxima at 252, 310 and 365 nm [5], colour reactions [6] and positive Molisch test suggested that androechin was a chalcone glycoside. Its UV spectral maxima were unaffected by the addition of NaOAc indicating the absence of a free hydroxyl at C-4'. A downfield signal at  $\delta$  13.55 in its  $^1H$  NMR spectrum and a bathochromic shift of 43 nm in band I of the UV spectrum with  $AlCl_3/HCl$  revealed the presence of a chelated hydroxyl in **1**.

The  $^1H$  NMR spectrum of **1** showed another phenolic hydroxyl signal at  $\delta$  10.17. A pair of AB doublets ( $J = 16.0$  Hz) at  $\delta$  8.07 and 8.0 were consistent with *trans* olefinic protons of a chalcone moiety [7]. The methoxyl singlet at  $\delta$  3.82 was assigned to C-4' as it showed  $^3J$  correlation with this carbon at 165.2 ppm in its HMBC spectrum (Fig. 1). A set of *meta* coupled doublets ( $J = 2.3$  Hz) at  $\delta$  6.33 and 6.17, each integrating for one proton, were attributed to H-3' and H-5', as both these protons showed NOE cross peaks with methoxyl protons at C-4' in its NOESY spectrum and HMBC correlation with C-4' (Fig. 1). The  $\beta$ -carbon in C-2 unsubstituted chalcones usually resonates around 144 ( $\pm 2$ ) ppm. However, in androechin (**1**) it appeared at 137.8 ppm, which is unusually upfield, indicating the presence of C-2 oxygenation [8]. The chemical shift values of the B-ring carbons of **1** were very similar to the literature values of 2-hydroxychalcones [9] and

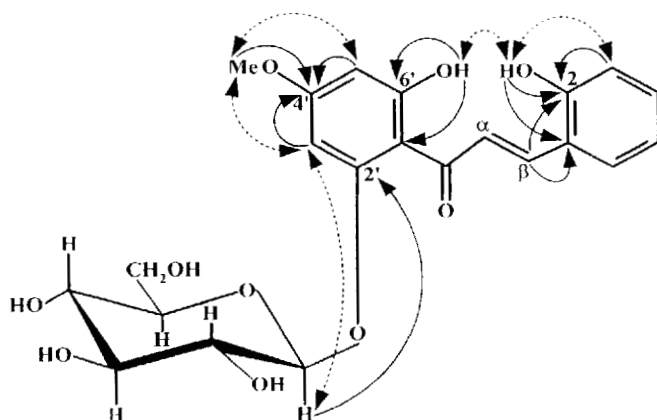
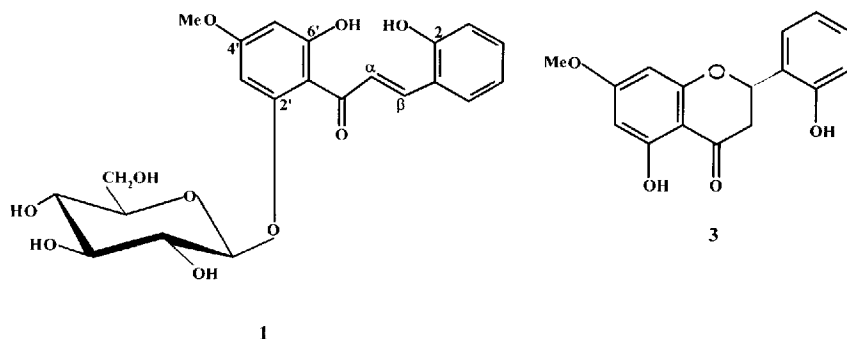


FIGURE 1 Selected HMBC ( $\rightarrow$ ) and NOESY ( $\leftrightarrow$ ) correlations observed in androechin (**1**).

hence the non-chelated hydroxyl ( $\delta$  10.17) in **1** was placed at C-2. The position of C-2 hydroxyl in **1** was further evidenced by the presence of a strong NOE cross peak between the hydroxyl ( $\delta$  10.17) and C-3 proton ( $\delta$  6.91) in its NOESY spectrum, and  $^2J$  and  $^3J$  correlation with C-2 (157.0 ppm) and C-1 (121.7 ppm), respectively in its HMBC spectrum (Fig. 1). The presence of four aromatic proton signals at  $\delta$  6.91, 7.25, 6.84 and 7.79 in the  $^1H$  NMR spectrum of **1** were assigned to protons at 3, 4, 5 and 6 positions of ring B.

An anomeric proton doublet ( $J = 7.0$  Hz) at  $\delta$  5.13 in **1** indicated the presence of a sugar residue with  $\beta$ -configuration. Acid hydrolysis of **1** afforded D-glucose and an isomerized aglycone [10,11], identified as dihydroechioidinin (**3**) [3]. The presence of two phenolic hydroxyls and a glucose residue in **1** was also evidenced by the formation of an hexaacetate. The glucose residue in **1** was found to be linked to C-2' as a strong NOE was observed between H-1'' and H-3' in its NOESY spectrum, and a cross peak between H-1'' and C-2' (159.7 ppm) in its HMBC spectrum (Fig. 1).

Thus from the foregoing spectral and acid hydrolytic studies, androechin was characterized as 2,2',6'-trihydroxy-4'-methoxychalcone 2'-*O*- $\beta$ -D-glucopyranoside (**1**).



To the best of our knowledge, isolation of androechin (**1**) constitutes the first report of a chalcone glycoside with 2-oxygenation in nature.

## EXPERIMENTAL SECTION

### General Experimental Procedures

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. UV spectra were determined in MeOH on a Shimadzu UV-240

spectrophotometer. IR spectra were obtained in KBr discs on a Perkin-Elmer 283 double beam spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian FT 200 and Bruker Avance 400 spectrometers using  $\text{DMSO-}d_6$  and  $\text{CDCl}_3$  with TMS as internal standard. HMBC and NOESY spectra were obtained using standard pulse sequences. FAB and HRFAB mass spectra were acquired on a 700 JEOL mass spectrometer in NBA matrix. CC was performed on Acme silica gel finer than 200 mesh (0.08 mm).

### Plant Material

The whole plant of *A. echioides* Nees was collected in May, 1998 at Tirupati, Andhra Pradesh, India. A voucher specimen (DG-199) has been deposited in the herbarium of the Department of Botany, Sri Venkateswara University, Tirupati.

### Extraction and Isolation

The shade dried and ground whole plant of *A. echioides* (3 kg) was successively extracted with *n*-hexane,  $\text{Me}_2\text{CO}$  and MeOH. The EtOAc soluble part of MeOH extract on purification over a silica gel column using hexane EtOAc (2 : 8) yielded **1** (25 mg) and **2** (20 mg).

### *Androechin (1)*

Yellow needles from MeOH, m.p. 128–130°C,  $[\alpha]_D^{25} -22.5^\circ$  (*c* 1.0, MeOH); UV (MeOH)  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 252sh (3.83), 310sh (3.99), 365 (4.15);  $[\text{NaOAc}$  252sh, 309sh, 365;  $-\text{AlCl}_3$  270, 408;  $+\text{AlCl}_3 \cdot \text{HCl}$  270, 408 nm; IR (KBr)  $\nu_{\text{max}}$  3341 ( $-\text{OH}$ ), 1616 ( $\text{>C=O}$ ), 1535, 1384, 1338, 1293, 1202, 1160, 1077, 1051  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  13.55 (1H, s, OH-6'), 10.17 (1H, s, OH-2), 8.07 (1H, d,  $J = 16.0$  Hz, H- $\alpha$ ), 8.0 (1H, d,  $J = 16.0$  Hz, H- $\beta$ ), 7.79 (1H, dd,  $J = 8.0, 1.5$  Hz, H-6), 7.25 (1H, ddd,  $J = 8.0, 8.0, 1.5$  Hz, H-4), 6.91 (1H, dd,  $J = 8.0, 1.5$  Hz, H-3), 6.84 (1H, ddd,  $J = 8.0, 8.0, 1.5$  Hz, H-5), 6.33 (1H, d,  $J = 2.3$  Hz, H-3'), 6.17 (1H, d,  $J = 2.3$  Hz, H-5'), 5.13 (1H, d,  $J = 7.0$  Hz, H-1''), 3.82 (3H, s, OMe-4'), 3.10–3.80 (6H, m, sugar protons);  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-}d_6$ )  $\delta$  192.8 ( $\text{>C-O}$ ), 165.3 (C-6'), 165.2 (C-4'), 159.7 (C-2'), 157.0 (C-2), 137.8 (C- $\beta$ ), 131.9 (C-4), 127.9 (C-6), 126.0 (C- $\alpha$ ), 121.7 (C-1), 119.7 (C-5), 116.2 (C-3), 106.9 (C-1'), 100.5 (C-1''), 95.2 (C-5'), 93.8 (C-3'), 77.5 (C-3''), 76.8 (C-5''), 73.6 (C-2''), 69.7 (C-4''), 60.7 (C-6''), 55.6 (OMe-4'); HRFABMS  $m/z$  471.1266  $[\text{M} + \text{Na}]^+$  ( $\text{C}_{22}\text{H}_{24}\text{O}_{10}\text{Na}$  requires 471.1267); FABMS  $m/z$  471  $[\text{M} + \text{Na}]^+$ , 449  $[\text{M} + \text{H}]^+$ , 287  $[\text{M} + \text{H}-162]^+$ .

***Echioidinin 5-O-β-D-glucopyranoside (2)***

Pale yellow needles from MeOH, m.p. 245–246°C. The physical and spectral data were consistent with literature values [4].

***Acetylation of 1***

A mixture of compound **1** (5 mg), Ac<sub>2</sub>O (2 ml) and C<sub>5</sub>H<sub>5</sub>N (1 ml) was kept at room temperature for 72 h and poured into crushed ice to yield the hexaacetate as colourless needles (7 mg) from CHCl<sub>3</sub>, m.p. 110°C. IR (KBr)  $\nu_{\max}$  2943, 1759 ( $\text{>C=O}$  of OAc), 1616, 1433, 1371, 1325, 1213 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (1H, dd,  $J = 8.0, 1.8$  Hz, H-6), 7.45 (2H, m, H-4, 5), 7.32 (1H, d,  $J = 15.0$  Hz, H- $\alpha$ ), 7.12 (1H, dd,  $J = 8.0, 1.8$  Hz, H-3), 6.90 (1H, d,  $J = 15.0$  Hz, H- $\beta$ ), 6.70 (1H, d,  $J = 1.8$  Hz, H-5'), 6.46 (1H, d,  $J = 1.8$  Hz, H-3'), 5.30 (1H, d,  $J = 7.0$  Hz, H-1''), 4.97–5.28 (4H, m, H-2'', 3'', 4'', 5''), 4.24 (2H, m, CH<sub>2</sub>-6''), 3.83 (3H, s, OMe-4'), 2.29 (3H, s, OAc-6'), 2.17 (3H, s, OAc-2), 1.97–2.10 (12H, m, 4 × OAc).

***Acid hydrolysis of 1***

A MeOH solution of **1** (10 mg) in 2 N HCl (4 ml) was heated at 100°C for 2 h. The acid hydrolysate was extracted with EtOAc and evaporated to dryness to yield a colourless solid which on crystallization from CHCl<sub>3</sub> afforded the aglycone as colourless needles (6 mg). It was characterized as the isomeric flavanone, dihydroechioidinin (**3**), m.p. 200–201°C as its physical and spectral data were very similar to the literature values [3]. The sugar in the aqueous layer was determined as D-glucose by paper chromatography.

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