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Research Article

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A new 5-deoxyflavonol from *Tephrosia tinctoria*

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ABSTRACT

*A new flavonol, 2′-hydroxy-7-methoxyflavonol (**1**) together with three known flavonoids, 7-O-methylglabranin (**2**), tephrowatsin C (**3**), and kaempferol-3-O-β-D-glucopyranoside (**4**), and a known dehydrorotenoid, dehydrodeguelin (**5**) were isolated from the flowers of Tephrosia tinctoria. The structure of the new as well as known compounds have been elucidated by extensive 2D NMR, ESI-TOFMS and chemical studies.*

Keywords: *Tephrosia tinctoria*, Fabaceae, flowers, flavonol

INTRODUCTION

The genus *Tephrosia* Pers. (Fabaceae) is a large tropical and subtropical genus estimated to contain about 300 species of which 35 species occur in India [1]. Some species of this genus have fish poision, piscicidal, repellent, insecticidal, antibacterial, antifungal and anticancer properties [2-5]. *Tephrosia tinctoria* Pers. is a perennial undershrub widely distributed in the Talakona forest ranges of Tirumala-Tirupati Hills, Andhra Pradesh, South India [6]. Earlier investigations on different parts of this species has resulted in the isolation of flavonoids, isoflavonoids and rotenoids [7,8]. As part of our ongoing studies on this species, we have investigated the flowers of *T. tinctoria* and report herein the isolation of a new flavonol, 2′-hydroxy-7-methoxyflavonol (**1**), together with three known flavonoids, 7-*O*-methylglabranin (**2**), tephrowatsin C (**3**), kaempferol-3-*O*-β-D-glucopyranoside (**4**), and a known dehydrorotenoid, dehydrodeguelin (**5**).

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were determined using a Kofler hot stage apparatus and are uncorrected. UV spectra were measured in MeOH on a Shimadzu UV-1800 spectrophotometer. IR spectra were recorded on a Bruker Alpha Eco ATR-FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 600 and 400 spectrometers operating at 600.19 and 400.13, and 150.93, 100.61 MHz, respectively using DMSO with TMS as internal standard. ^{1}H-^{1}H COSY, HSQC, HMBC and NOESY spectra were obtained using standard pulse sequences. ESI-TOFMS was recorded in positive mode on an API Q-STAR PULSA of Applied Biosystem. Column chromatography (CC) was performed on silica gel (Acme) finer than 200 mesh (0.08 mm). TLC was performed on silica gel 60 F_{254} precoated plates (Merck).

Plant Material

The flowers of the *T. tinctoria* were collected from Talakona forest ranges of Tirumala-Tirupati Hills, Andhra Pradesh, South India in January 2011. A voucher specimen (DG-112) has beeen deposited in the Herbarium of the Department of Botany, Sri Venkateswara University, Tirupati, India.

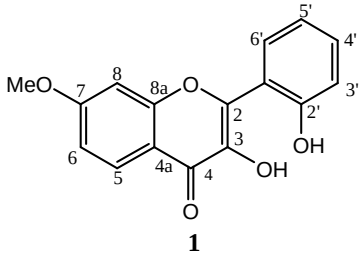
Extraction and Isolation

Air-dried and powdered flowers (3 kg) of *T. tinctoria* were extracted successively with *n*-hexane, Me_2CO and MeOH at room temperature. The *n*-hexane extract (18 g) on purification over a silica gel column using *n*-hexane-ethyl acetate step gradient (6:4) yielded **1** (16 mg). The concentrated Me_2CO extract (38 g) was segregated into EtOAc soluble and EtOAc insoluble fractions. The EtOAc soluble fraction (21 g) on purification over a silica gel column using *n*-hexane-ethyl acetate step gradient (7:3 and 1:1) yielded **2** (14 mg) and **3** (13 mg). The MeOH extract (36 g) was defatted with *n*-hexane and the residue (24 g) obtained was purified over a silica gel column using *n*-hexane-ethyl acetate step gradient (4:6 and 7:3) to yield **4** (20 mg) and **5** (14 mg).

RESULTS AND DISCUSSION

Compound 1 was obtained as yellow amorphous solid (16 mg) from methanol, mp 162-163°C. The positive ESI-TOFMS spectrum showed the presence of $[M+H]^+$ ion at *m/z* 285.0801 consistent with the molecular formula $C_{16}H_{12}O_5$. This was corroborated by the ^{13}C NMR spectrum which showed resonances for all the carbons present in the molecule. Positive ferric chloride test and two strong IR absorption bands at 3243 (-OH) and 1618 (>C=O) cm^{-1} along with the UV absorption maxima at 246, 312 and 341 nm suggested compound 1 to be a 5-deoxyflavonol derivative [9,10]. A bathochromic shift of 62 nm in band I UV absorption maximum with $AlCl_3$ and $AlCl_3$/HCl revealed the presence of a chelated hydroxyl group in **1**. The addition of NaOAc didn't cause any bathochromic shift in band II UV absorption maximum, indicating the absence of a free hydroxyl at C-7 position.

The ^1H NMR spectrum of compound 1 showed a downfield signal at δ 13.25, assigned to the chelated hydroxyl group at C-3 of a flavonol derivative. It also showed a signal for a non-chelated hydroxyl group at δ 9.65 and three aromatic proton signals at δ 8.02, 7.12 and 7.02. The aromatic proton signal appearing as an *ortho*-coupled doublet (J = 8.6 Hz) at δ 8.02 was assigned to H-5 of a 5-deoxyflavonol derivative [11] as it showed ^3J correlations with C-4 (δ 172.3), C-7 (δ 163.8) and C-8a (δ 157.4) in the HMBC spectrum (Figure 1). The aromatic signal appearing as broad singlet at δ 7.12 was assigned to H-8 as it showed HMBC correlations with C-6 (δ 114.9), C-7 (δ 163.8), C-4a (δ 116.1) and C-8a (δ 157.4). A broad aromatic proton doublet (J = 8.6 Hz) appearing at δ 7.02 was assigned to H-6 as it showed HMBC correlations with C-7 (δ 163.8), C-8 (δ 100.6) and C-4a (δ 116.1). It also showed a signal for a methoxyl group at δ 3.88 and is placed at C-7 as it showed ^3J correlation with this carbon at δ 163.8 in the HMBC spectrum, and two strong NOE correlations with H-6 (δ 7.02) and H-8 (δ 7.12) in the NOESY spectrum (Figure 1). It exhibited characteristic signal pattern of a 2′-oxygenated ring B at δ 7.49 (1H, m), 7.29 (1H, m) and 6.90 (2H, m) assigned to 6′, 4′ and 3′, 5′ protons based on HMBC correlations studies (Figure 1). The non-chelated hydroxyl group at δ 9.65 was placed at C-2′ (δ 156.6) as it showed cross correlations with H-3′ (δ 6.90) and H-6′ (δ 7.49) in the HMBC spectrum, further supported by NOE correlation of C-2′ hydroxyl proton (δ 9.65) with C-3 hydroxyl proton (δ 13.25) in the NOESY spectrum. From the foregoing spectral studies, the structure of 1 was established as 2′-hydroxy-7-methoxyflavonol.



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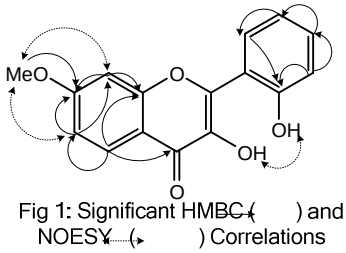

Fig 1: Significant HMBC (→) and NOESY (⇢) Correlations

2′-Hydroxy -7-methoxyflavonol (**1**)

Yellow amorphous solid (MeOH), m.p. 162-163°C; FT-IR ν_{max}: 3243 (-OH), 2920, 2850, 1618 (>C=O), 1572, 1505, 1454, 1439, 1411, 1257, 1205, 1169, 1108, 1026, 886, 831, 742, 625 cm^{-1}; UV (MeOH) λ_{max} nm (logε): 246 (4.52), 312 (4.46), 341 (3.52); (+$AlCl_3$): 260, 288, 403; (+ $AlCl_3$/HCl): 260, 288, 403; (+ NaOAc); 246, 312, 341;

^{1}H NMR (400.13 MHz, DMSO-d_6): δ 13.25 (1H, s, OH-3), 9.65 (1H, s, OH-2′), 8.02 (1H, d, J = 8.6 Hz, H-5), 7.49 (1H, m, H-6′), 7.29 (1H, m, H-4′), 7.12 (1H, br s, H-8), 7.02 (1H, br d, J = 8.3 Hz, H-6), 6.90 (2H, m, H-3′,5′), 3.88 (3H, s, OMe-7); ^{13}C NMR (DMSO-d_6, 100.61 MHz): δ 172.3 (>C=O), 163.8 (C-7), 157.4 (C-8a), 156.6 (C-2′), 147.1 (C-2), 144.2 (C-3), 131.6 (C-4′), 130.6 (C-6′), 126.6 (C-5), 119.5 (C-5′), 118.9 (C-3′), 117.4 (C-1′), 116.1 (C-4a), 114.9 (C-6), 100.6 (C-8), 56.5 (OMe-7); ESI-TOFMS (positive mode): *m/z* 569.1534 $[2M+H]^+$, 285.0801 $[M + H]^+$ (calcd for $C_{16}H_{12}O_5$+H, 285.0759).

By comparison of the spectral data with literature values, the known compounds were identified as 7-*O*-methylglabranin (**2**) [12], tephrowatsin C (**3**) [13], kaempferol-3-*O*-β-D-glucopyranoside (**4**) [14], and dehydrodeguelin (**5**) [15].

CONCLUSION

Incidentally, the isolation of compound 1 constitutes the rare occurrence of a 2′-oxygenated 5-deoxyflavonol derivative from a natural source.

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