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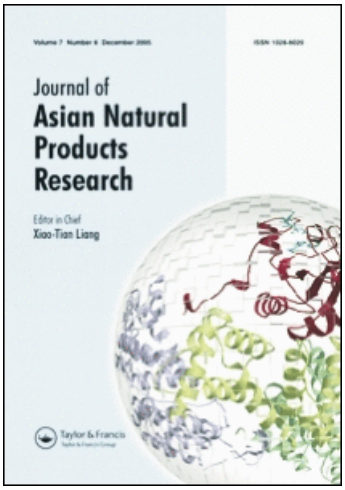

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A new di-*O*-prenylated isoflavone from *Tephrosia tinctoria*

Shaik Ibrahim Khalivulla[a], Bandi Anil Kumar Reddy[a], Duvvuru Gunasekar[a]*, Alain Blond[b], Bernard Bodo[b], Madugula Marthanda Murthy[c] and Tadikimalli Prabhakar Rao[d]

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A new di-*O*-prenylated isoflavone, 5,7-di-*O*-prenylbiochanin A (**1**), together with three known compounds, 7-*O*-methylglabranin (**2**), tephrowatsin C (**3**) and flemichapparin B (**4**), were isolated from the stems of *Tephrosia tinctoria*. The structures of these compounds were elucidated by extensive 2D NMR spectral studies.

Keywords: *Tephrosia tinctoria*; leguminosae; prenylated isoflavone; 5,7-di-*O*-prenylbiochanin A

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1. Introduction

The genus *Tephrosia* (Leguminosae, Papilionoideae) is known to elaborate a rich variety of flavonoids and isoflavonoids [1]. Some species of the genus *Tephrosia* have fish poison, piscicidal, repellent, insecticidal, antibacterial, antifungal, and anticancer properties [2–6]. *Tephrosia tinctoria* Pers. is an erect undershrub found widely in Talakona forest, Andhra Pradesh, South India [7]. Earlier investigation on the roots of this species [8] has resulted in the isolation of 7-*O*-geranylbiochanin A, a new *O*-geranylated isoflavone. As part of our ongoing studies on this species, we investigated the stems of *T. tinctoria* and report here the isolation and characterization of a new di-*O*-prenylated isoflavone, 5,7-di-*O*-prenylbiochanin A (**1**) together with two known flavanones, 7-*O*-methylglabranin (**2**)[9] and tephrowatsin C (**3**) [10], and a known pterocarpene, flemichapparin B (**4**) [11,12].

2. Results and discussion

Compound **1**, obtained as viscous oil, showed $[M + H]^+$ peak at *m/z* 421.1977 in the positive ESITOF mass spectrum consistent with the molecular formula $C_{26}H_{28}O_5$. This was corroborated by ^{13}C NMR spectrum which showed signals for all the 26 carbons of the molecule. The UV absorption maxima at 265 and 322 (sh) nm suggested that **1** was an isoflavone derivative [13]. It was further supported by the ^1H NMR spectrum, which showed a sharp one-proton singlet at δ 7.72 correlated with the carbon at δ 149.8 (C-2) in the HSQC spectrum, ascribed to H-2 of an isoflavone moiety [14]. The addition of $AlCl_3$ and NaOAc caused no shift in its UV spectrum, indicating the absence of free hydroxyl groups at C-5 and C-7 positions, respectively. The IR spectrum exhibited absorption bands at 2923 and 1647 cm^{-1} due to methoxyl and carbonyl functionalities, respectively.

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The ^{1}H NMR spectrum also showed a pair of meta-coupled doublets ($J = 2.3$ Hz) at δ6.37 and 6.42, integrating for one proton each, assigned to H-6 and H-8, respectively. A pair of *ortho*-coupled doublets ($J = 8.7$ Hz) at δ 7.45 and 6.92, integrating for two protons each, were attributed to the 2′, 6′ and 3′, 5′ protons, respectively, of *p*-disubstituted ring B. A sharp three-proton singlet at δ 3.82 was ascribed to a methoxyl group and was placed at C-4′ as it showed ^3J correlation with this carbon at δ 159.8 in its HMBC spectrum and two strong NOE correlations with H-3′ and H-5′ (δ6.92) in its NOESY spectrum (Figure 1). The ^{1}H NMR spectrum of **1** further revealed two sets of peaks at δ4.62 (2H, d, $J = 6.4$ Hz, CH_2-1″), 5.58 (1H, t, $J = 6.4$ Hz, H-2″), 1.82 (3H, s, Me-4″) and 1.75 (3H, s, Me-5″), and 4.57 (2H, d, $J = 6.9$ Hz, CH_2-1‴), 5.50 (1H, t, $J = 6.9$ Hz, H-2‴), 1.78 (3H, s, Me-4‴), and 1.71 (3H, s, Me-5‴), characteristic of two prenyloxy (γ,γ-dimethylallyloxy or 3-methylbut-2-enyloxy) moieties [15]. These two prenyloxy moieties were found to be attached to C-5 and C-7 positions of the isoflavone nucleus as the prenyloxy methylene protons at δ 4.62 (CH_2-1″) and 4.57 (CH_2-1‴) were correlated to C-5 (δ 160.6) and C-7 (δ 162.9), respectively, in its HMBC spectrum. NOE interactions of CH_2-1″ with H-6, and CH_2-1‴ with H-6 and H-8 in the NOESY spectrum also support the presence of prenyloxy moieties at C-5 and C-7 positions, respectively. From the foregoing spectral studies, the structure of **1** was established as 5,7-di-*O*-prenylbiochanin A.

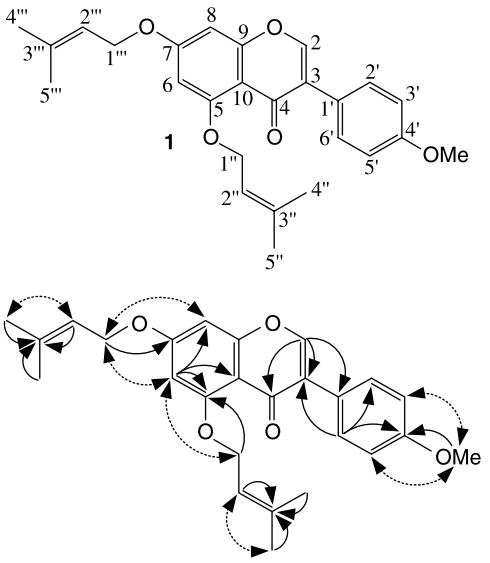

Figure 1. Significant HMBC (→) and NOESY (↔) correlations for **1**.

Incidentally, the isolation of compound **1** constitutes the first report of the occurrence of an isoflavonoid having an *O*-prenyl residue at C-5 position of ring A.

3. Experimental

3.1 General experimental procedures

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Optical rotations were measured in MeOH at 25°C on a Perkin-Elmer 241 polarimeter. UV spectra were recorded on a Shimadzu UV-550 spectrophotometer. IR spectra were recorded on Perkin-Elmer 283 and Thermo Nicolet Nexus 670 double beam spectrophotometers with KBr and NaCl optics. ^{1}H and ^{13}C NMR spectra were recorded on Varian Unity 400, Bruker Avance 400 and Bruker AM 300 spectrometers in $CDCl_3$ and Me_2CO-d_6 using TMS as an internal standard. ^{1}H–^{1}H COSY, HSQC, HMBC, and NOESY (with 500 ms mixing time) spectra were recorded using standard pulse sequences. ESITOFMS was recorded on an API Q-STAR PULSA of Applied Biosystem. Column chromatography separations were carried out by using Acme silica gel (100–200 mesh).

3.2 Plant material

The stems of *T. tinctoria* Pers were collected from Talakona forest, Andhra Pradesh, South India in December 2005. A voucher specimen (DG-058) has been deposited in the Herbarium of the Department of Botany, Sri Venkateswara University, Tirupati, India.

3.3 Extraction and isolation

The shade-dried and powdered stems (3 kg) of *T. tinctoria* were sequentially extracted

with *n*-hexane, Me_2CO, and MeOH at room temperature. The hexane extract (28 g) on purification over a silica gel column using *n*-hexane–EtOAc (8:2 and 1:1) as eluents yielded **2** (15 mg) and **3** (12 mg). The Me_2CO (20 g) and MeOH (27 g) extracts were found to be similar on paper and thin layer chromatograms and hence they were combined. The combined extracts (47 g) on purification over a silica gel column employing *n*-hexane–EtOAc (7:3 and 4:6) as eluents yielded **1** (12 mg) and **4** (8 mg), respectively.

3.4 5,7-Di-O-prenylbiochanin A (1)

Viscous oil; UV (MeOH) λ_{max} (nm) ($\log \varepsilon$): 265 (4.43), 322 (sh) (3.73); IR (neat) ν_{max} (cm^{-1}): 2923 (–OMe), 1647 (> C=O), 1608, 1568, 1511, 1433, 1289, 1246, 1209, 1180, 1067, 950, 871, 830; ^{1}H NMR ($CDCl_3$) δ (ppm): 7.72 (1H, s, H-2), 7.45 (2H, d, $J = 8.7$ Hz, H-2′, 6′), 6.92 (2H, d, $J = 8.7$ Hz, H-3′, 5′), 6.42 (1H, d, $J = 2.3$ Hz, H-8), 6.37 (1H, d, $J = 2.3$ Hz, H-6), 5.58 (1H, t, $J = 6.4$ Hz, H-2″), 5.50 (1H, t, $J = 6.9$ Hz, H-2‴), 4.62 (2H, d, $J = 6.4$ Hz, CH_2-1″), 4.57 (2H, d, $J = 6.9$ Hz, CH_2-1‴), 3.82 (3H, s, OMe-4′), 1.82 (3H, s, Me-4″), 1.78 (3H, s, Me-4‴), 1.75 (3H, s, Me-5″), 1.71 (3H, s, Me-5‴); ^{13}C NMR ($CDCl_3$) δ (ppm) 175.2 (C-4), 162.9 (C-7), 160.6 (C-5), 159.8 (C-4′), 159.3 (C-9), 149.8 (C-2), 139.2 (C-3″), 137.2 (C-3‴), 130.4 (C-2′, 6′), 126.0 (C-3), 124.5 (C-1′), 119.4 (C-2″), 118.6 (C-2‴), 113.7 (C-3′, 5′), 106.4 (C-10), 97.7 (C-6), 93.2 (C-8), 66.4 (C-1″), 65.2 (C-1‴), 55.2 (OMe-4′), 18.3 (C-5″), 18.2 (C-5‴), 25.8 (C-4″), 25.7 (C-4‴); ESITOFMS: 841.3973 $[2M + H]^+$, 443.1879 $[M + Na]^+$, 421.1977 $[M + H]^+$ (calcd for $C_{26}H_{29}O_5$, 421.2015).

References

[1] H.M.A. Al-Hazimi, N.A. Al-Jaber, and M.R.H. Siddiqui, *J. Saudi Chem. Soc.* **9**, 597 (2005).

[2] H. Fukami and M. Nakajima, in *Naturally Occurring Insecticides*, edited by M. Jacobson, D.G. Crosby, (Marcel Dekker, New York, 1971), p. 71.

[3] Y.L. Chen, Y.S. Wang, Y.L. Lin, K. Munakata, and K. Ohta, *Agric. Biol. Chem.* **42**, 2431 (1978).

[4] R.K. Kole, C. Satpathi, A. Chowdhury, M.R. Ghosh, and N. Adityachaudhury, *J. Agric. Food Chem.* **40**, 1208 (1992).

[5] A.K. Bashir, E.S.S. Hassan, M.H. Amiri, and A.A. Abdalla, *Fitoterapia* **63**, 371 (1992).

[6] J.P.S. Sarin, S. Singh, H.S. Garg, N.M. Khanna, and M.M. Dhar, *Phytochemistry* **15**, 232 (1976).

[7] K. Thammanna, K. Narayana Rao, and K. Madhava Chetty, *Angiospermic Wealth of Tirumala*, (TTD Press, Tirupati, 1994), p. 49.

[8] B.A.K. Reddy, S.I. Khalivulla, and D. Gunasekar, *Ind. J. Chem.* **46B**, 366 (2007).

[9] I. Jayaraman, A. Ghanim, and H.A. Khan, *Phytochemistry* **19**, 1267 (1980).

[10] F. Gomez, L. Quijano, J.S. Calderon, C. Rodriquez, and T. Rios, *Phytochemistry* **24**, 1057 (1985).

[11] N. Adityachaudhury and P.K. Gupta, *Phytochemistry* **12**, 425 (1973).

[12] E. Dagne, A. Bekele, and P.G. Waterman, *Phytochemistry* **28**, 1897 (1989).

[13] T.J. Mabry, K.R. Markham, and M.B. Thomas, *The Systematic Identification of Flavonoids*, (Springer-Verlag, New York, 1970), p. 165.

[14] T.J. Mabry, K.R. Markham, and M.B. Thomas, *The Systematic Identification of Flavonoids*, (Springer-Verlag, New York, 1970), p. 267.

[15] M. Ahsan, J.A. Armstrong, S. Gibbons, A.I. Gray, and P.G. Waterman, *Phytochemistry* **37**, 259 (1994).

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