

Insect Antifeedant Activity of Three New Tetranortriterpenoids from *Trichilia pallida*

Monique S. J. Simmonds,*[†] Philip C. Stevenson,^{‡,†} Elaine A. Porter,[†] and Nigel C. Veitch[†]

Jodrell Laboratory, Royal Botanic Gardens, Kew, Richmond, Surrey, TW9 3DS, U.K., and Natural Resources Institute, University of Greenwich, Chatham Maritime, Kent, ME4 4TB, U.K.

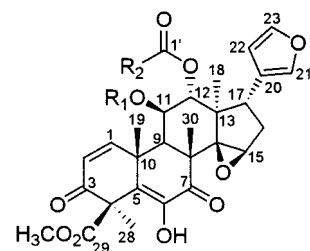
Received April 13, 2001

Three new tetranortriterpenoids, methyl 6-hydroxy-11 β -acetoxy-12 α -(2-methylpropanoyloxy)-3,7-dioxo-14 β ,15 β -epoxy-1,5-meliacadien-29-oate (**3**), methyl 6,11 β -dihydroxy-12 α -(2-methylpropanoyloxy)-3,7-dioxo-14 β ,15 β -epoxy-1,5-meliacadien-29-oate (**4**), and methyl 6-hydroxy-11 β -acetoxy-12 α -(2-methylbutanoyloxy)-3,7-dioxo-14 β ,15 β -epoxy-1,5-meliacadien-29-oate (**5**), have been isolated from the roots of *Trichilia pallida*. The related compounds hirtin (**1**) and deacetylhirtin (**2**) were also obtained. Compound **4** had the greatest antifeedant activity of **1–5** when tested against larvae of four species of Lepidoptera.

Extracts of the genus *Trichilia* L. (Meliaceae) are reported to have a variety of biological properties, including antiviral,¹ analgesic,² insecticidal,³ and insect growth-inhibition activity.⁴ Their anti-insect activity has been attributed to a group of tetranortriterpenoids that includes hirtin⁴ and the trichilins.^{3,5} The current report describes the isolation and structural elucidation of three new tetranortriterpenoids from *Trichilia pallida* Sw. and two related compounds, hirtin (**1**) and deacetylhirtin (**2**). A binary-choice bioassay was used to test the antifeedant activity of the compounds against four species of Lepidoptera: *Spodoptera littoralis*, *S. exigua*, *Heliothis virescens*, and *Helicoverpa armigera*.

An acetone extract of the roots of a five-year-old *T. pallida* tree grown under glasshouse conditions was analyzed by HPLC coupled to a photodiode-array detector. Five major apolar components (**1–5**) were detected with UV-vis spectra similar to that of the tetranortriterpenoid limonin,⁶ which shows distinctive UV maxima at 217 and 276 nm. Milligram quantities of **1–5** sufficient for structure elucidation were obtained only by repetitive isolation using an analytical HPLC column, because of the loss of resolution experienced on semipreparative columns.

The ¹H and ¹³C NMR spectra of **1** recorded in CDCl₃ contained a number of resonances typical of tetranortriterpenoids including four quaternary methyl groups (δ_{H} 0.79, 1.40, 1.43 and 1.82), a methyl ester (δ_{H} 3.76; δ_{C} 53.0 and 170.0), and a β -substituted furan (δ_{H} 6.08, 7.11, and 7.30; δ_{C} 111.1, 121.7, 140.5, and 142.7). Many examples of this class of compound have been reported previously from *Trichilia* spp.⁷ Other distinctive resonances included those for an acetyl group (δ_{H} 2.19; δ_{C} 21.1 and 169.4), a propanoyl side chain (δ_{H} 1.02, 2.19, and 2.27; δ_{C} 8.9, 27.7, and 172.2), and two α,β -unsaturated carbonyls (δ_{H} 7.01 and 6.16; δ_{C} 150.7, 126.8, and 195.6; δ_{C} 129.4, 141.9, and 196.2) located at C1–C3 and C5–C7, respectively, according to HMBC correlations. A molecular formula of C₃₂H₃₆O₁₁ was obtained for **1** by HRMS. Analysis of both 1D and 2D NMR data (1D ¹H and ¹³C, DEPT, DQF-COSY, HSQC, and HMBC) confirmed the molecular structure of **1** to be that of hirtin, a known tetranortriterpenoid isolated previously from *T. hirta*.⁸ Resonance assignments are summarized in



	R ₁	R ₂
1	Ac	CH ₂ CH ₃
2	H	CH ₂ CH ₃
3	Ac	CH(CH ₃)CH ₃
4	H	CH(CH ₃)CH ₃
5	Ac	CH(CH ₃)CH ₂ CH ₃

Tables 1 and 2, and long-range correlations obtained from HMBC data are listed in Table 1S (Supporting Information). The ¹H NMR assignments for **1** are in agreement with a partial set available from the literature,⁸ but ¹³C NMR assignments for this compound have not been reported previously (Table 2).

The ¹H and ¹³C NMR spectra of **2** were similar to those of **1**, the only significant difference being the absence of resonances corresponding to the 11-OAc group of **1** (Tables 1 and 2). The chemical shift value of H-11 in **2** (δ_{H} 4.21) was shifted upfield compared to that of **1**, consistent with the absence of the acetyl group. HRMS of **2** gave a molecular formula of C₃₀H₃₄O₁₀ (42 amu less than **1**) and confirmed its identity as deacetylhirtin, a compound also known from *T. hirta*.⁸ A full set of ¹H and ¹³C NMR resonance assignments for **2** are presented in Tables 1 and 2, respectively.

The NMR spectra of **3–5** were also similar to those of **1** but contained additional resonances in the aliphatic regions. Two of the compounds (**3** and **5**) were found to be acetylated at C-11, as in **1**. Comparison of the spectra of **3** and **1** indicated that the propanoyl side chain at C-12 of the latter was replaced by a 2-methylpropanoyl side chain (Tables 1 and 2). The two methyl resonances of **3** at δ_{H} 0.97 (d, $J = 7.1$ Hz) and δ_{H} 1.07 (d, $J = 7.1$ Hz) showed cross-peaks in the DQF-COSY spectra to the septet at δ_{H} 2.44,

* To whom correspondence should be addressed. Tel: 44-20-8332-5328. Fax: 44-20-8332-5340. E-mail: m.simmonds@rbgkew.org.uk.

[†] Royal Botanic Gardens, Kew.

[‡] Natural Resources Institute.