

TRICHILININS B AND C, TWO NEW LIMONOIDS FROM *MELIA TOSENDAN*

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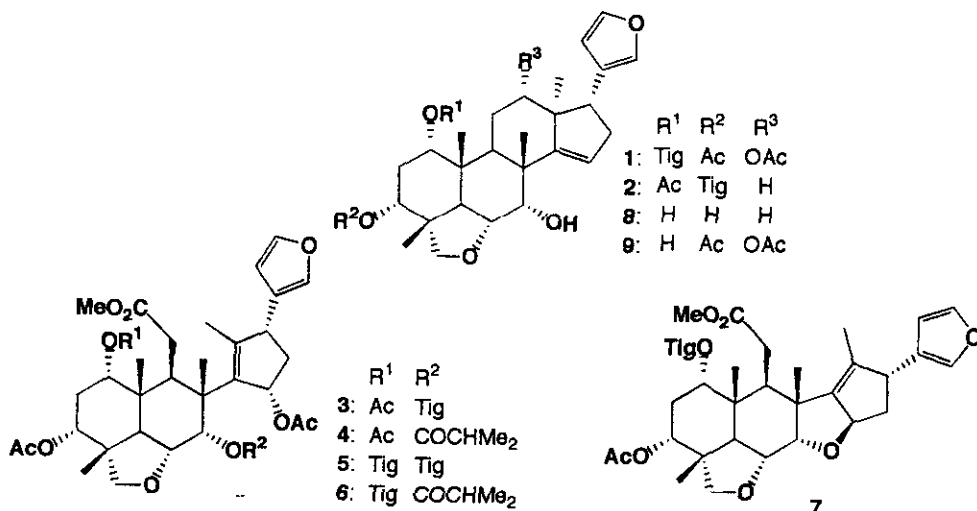
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Abstract—Two new limonoids, trichilinins B and C, were isolated
along with four nimbolidins and salannin from the root bark of
Melia toosendan.

Meliaceae plants are a rich source of limonoids and attracting considerable interest, because the limonoids from them showed several interesting biological activities, in which an insect antifeedant activity has been well studied.¹ We have isolated several types of limonoids as insect antifeedant from a typical plant *Melia azedarach* Linn and a related plant *M. toosendan*: i.e. meliacarpinins,^{2,3} trichilins⁴⁻⁶ and azedarachins.^{7,8}

In the continuous study of limonoids from *M. toosendan*, we isolated two new limonoids, named trichilinins B (1) and C (2), along with four nimbolidins (3)–(6)⁹ and salannin (7)¹⁰ from the hexane extract of the dried root bark.



Their structures were elucidated by spectroscopic means and the trichilinins were considered to be biogenetic precursors of ring-C cleaved limonoids such as 3-7. We report here the isolation and structures of trichilinins B(1) and C(2) and the anti-feedant activity of the isolated limonoids against the larvae of *Spodoptera eridania* (Boisduval).

Trichilin B (1), $[\alpha]_D^{19} +56^\circ$ (c 0.13, MeOH), exhibited following spectral data. Negative FABms: m/z 609[M-H]⁻; HRFABms: m/z 551.3002[M+H-AcOH]⁺ ($\Delta -0.7$ mmu); uv: 221nm (ϵ 11400); ir: 3600-3220, 1738, 1712 and 1655 cm⁻¹. The ms and ¹³C nmr (Table 2) data revealed the molecular formula as C₃₅H₄₆O₉ (13 unsaturations). In the ¹H nmr spectrum, the presence of four tertiary methyls and a β -furyl moiety were observed along with a trisubstituted olefinic proton signal at δ 5.69 (dd, J=3.3 and 1.5 Hz, 15-H) and a typical AB quartet at δ 3.60 (J=7.6 Hz, 28 β -H) and 3.63 (br, J=7.6 Hz, 28 α -H), weakly coupled to 4 β -Me signal. One methine proton at δ 4.21 (d, J=2.9 Hz, 7-H) under hydroxyl, coupling with a methine proton at δ 4.16 (dd, J=12.5 and 2.9 Hz, 6-H) linked to an ether oxygen, was also observed along with three protons under acyloxy groups at δ 4.66 (dd, J=2.9 and 2.6 Hz, 1-H), 4.93 (dd, J=2.9 and 2.6 Hz, 3-H) and 5.05 (dd, J=9.2 and 7.0 Hz, 12-H).

These data strongly suggested that 1 was a hexacyclic structure similar to vilasinin (8)¹¹ and trichilin (9),¹² and the ¹H nmr spectrum of 1 was very similar to that of 9 except for the addition of one tigloyl group. The substitution pattern around the A-ring with 1 α -tigloyloxy and 3 α -acetoxy groups, was deduced from the long range coupling between 1 β - and 3 β -H signals and the high field shift to δ 1.08 (dt, J=14.3 and 7.0 Hz) of the 11 α -H signal, attributable to a shielding effect of the 1 α -tigloyl group,¹⁰ compared to δ 1.49 in 9. The presence of 1 α -tigloyl was also confirmed by a nOe enhancement of the 9-H signal by irradiation at the 2'-methyl signal of tig-

Table 1. ¹H Nmr data for 1 and 2

H	1	2	H	1	2
1	4.66 dd(2.9, 2.6)	4.77 dd(3.0, 2.6)	18	1.03 s	1.02 s
2 α	2.14 dt(16.7, 2.7)	2.12 m	19	0.94 s	0.96 s
β	2.21 dt(16.7, 2.9)	2.23 m	21	7.20 br s	7.35 br s
3	4.93 dd(2.9, 2.6)	4.96 dd(3.3, 2.6)	22	6.23 d(1.1)	6.56 br s
5	2.75 d(12.5)	2.81 d(12.5)	23	7.32 dd(1.5, 1.3)	7.35 br s
6	4.16 dd(12.5, 2.9)	4.19 dd(12.8, 2.9)	28 α	3.63 br d(7.6)	3.66 br d(7.7)
7	4.21 d(2.9)	4.26 d(2.9)	β	3.60 d(7.6)	3.63 d(7.7)
9	2.80 dd(12.3, 7.6)	3.18 dd(13.5, 5.9)	29	1.21 br s	1.23 br s
11 α	1.08 dt(14.3, 7.0)	2.22 m	30	1.11 s	1.07 s
β	2.13 m	2.28 m	Ac	1.88 s	1.93 s
12	5.05 dd(9.2, 7.0)	2.18 m		1.90 s	
		2.36 m	Tig		
15	5.69 dd(3.3, 1.5)	5.71 dd(3.3, 1.8)	2'-Me	1.83 br s	1.79 br d(1.1)
16 α	2.55 ddd(16.1, 10.9, 1.5)	2.59 ddd(15.7, 10.7, 1.8)	3'	6.96 qq(7.2, 1.5)	6.95 qq(7.2, 1.5)
β	2.45 ddd(16.1, 7.9, 3.0)	2.51 ddd(15.6, 7.8, 3.3)	3'-Me	1.75 dd(7.3, 1.1)	1.70 dd(7.2, 1.4)
17	3.01 dd(10.6, 7.7)	3.46 dd(10.6, 7.7)			

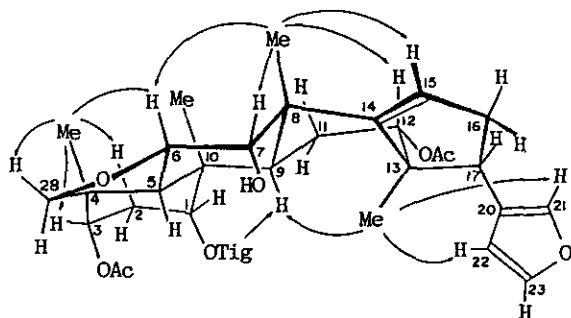


Figure 1. Selected nOe connectivities for 1.

Table 2. ^{13}C Nmr data for 1

C		C	
1	71.9 d	19	15.2 q
2	27.4 t	20	124.5 s
3	73.9 d	21	140.3 d
4	42.4 s	22	111.7 d
5	39.6 d	23	142.1 d
6	72.4 d	28	78.0 t
7	71.7 d	29	19.7 q
8	45.4 s	30	15.3 q
9	34.3 d	Ac	20.9 q
10	39.5 s		21.3 q
11	24.2 t		170.2 s
12	77.2 d		170.9 s
13	51.4 s	1'	166.5 s
14	157.4 s	2'	128.7 s
15	122.7 d	2'-Me	11.9 q
16	36.6 t	3'	138.0 d
17	50.3 d	3'-Me	14.4 q
18	26.9 q		

loyl. The α configuration of the 12-OAc group was apparent from the couplings of the 12 β -H signal and also from the high field shift of the acetyl signal to δ 1.88 in 1 from δ 2.13 in 9, attributable to the effect of the 1 α -tigloyl group. Another stereochemistry of 1 was confirmed by nOe experiments (Figure 1).

The ^1H nmr spectrum of trichilin C (2), $[\alpha]_D^{19} +22^\circ$ (c 0.09, MeOH); $\text{C}_{33}\text{H}_{44}\text{O}_7$, was superimposable on that of 1 except for the lack of one acetoxy group and some differences in the chemical shifts. The fact that the 12-OAc group in 1 is missing in 2, was apparent from the presence of 12-methylene signals at δ 2.18 and 2.36. On the other hand, the substitution pattern of the A-ring with 1-acetoxy and 3-tigloyloxy groups was deduced from the large low field shifts of the 11 α - and 9-H signals from δ 1.08 and 2.80 in 1 to δ 2.22 and 3.18 in 2. These shifts would result in the cancellation of the effect due to 1 α -tigloyl and a conformational change of the ring C, which was deduced from a large low field shift of the 17-H signal.

Vilasinin and trichilins appear to be biogenetic precursors of nimbolidins and salannin class ring-C cleaved limonoids, that is, a Grob type olefin-forming fragmentation¹³ of a 12-hydroxy 14,15-epoxyvilasinin class compound and subsequent ether ring formation between C-7 and C-15 hydroxyl groups would yield nimbolidins and salannin. Insect antifeedant activity of the isolated limonoids was tested by a leaf disk method¹⁴ against the larvae of a Japanese pest insect *Spodoptera eridania* (Boisduval). Nimbolidins (3-6) showed the activity at 500 ppm, whereas trichilins B (1) and C (2) and salannin (7) were all active at 1000 ppm. The activities of these compounds were not so strong compared to those of the azedarachins, 200-400 ppm, and trichilins, 200-400ppm, isolated from the same plant.

EXPERIMENTAL

^1H and ^{13}C Nmr were measured in CDCl_3 on a JEOL FX-400 spectrometer. Ir (KBr) and uv (in MeOH) were recorded on JASCO FT/IR 5300 and Shimadzu UV-210A spectrophotometers. Optical rotation was measured in MeOH using a JASCO J-20 A spectrometer.

Plant material. The root bark was collected in December 1992 at Xiangtan, China.

Extraction and isolation. The air-dried root bark (1.5 kg) was extracted with hexane (20 l), 15 °C, 2 weeks, to yield 9.3 g of an extract, which was flash chromatographed on silica gel with a hexane-ether solvent system. Each limonoid fractions eluted with Et_2O was purified by prep-tlc using Et_2O to give three limonoid fractions. Each fraction was further separated and purified through hplc using μ -Bondapac C_{18} with 20-45% $\text{H}_2\text{O}/\text{MeOH}$ as the solvent to give 1 (3.8 mg), 2 (0.9 mg), 3 (0.9 mg), 4 (6.6 mg), 5 (4.4mg), 6 (5.0 mg), and 7 (4.2 mg).

Trichilin B (1). An amorphous powder, $\text{C}_{35}\text{H}_{46}\text{O}_9$; $[\alpha]_{\text{D}}^{19} +56^\circ$ (c 0.13); uv 221 nm (ϵ 11400); ir 3600-3220, 1738, 1712 and 1655 cm^{-1} ; negative FABms m/z 609 $[\text{M}-\text{H}]^-$, HRFAB ms m/z 551.3002 $[\text{M}+\text{H}-\text{Ac}]^+$ (Δ -0.7 mmu).

Trichilin C (2). An amorphous powder, $\text{C}_{33}\text{H}_{44}\text{O}_7$; $[\alpha]_{\text{D}}^{19} +22^\circ$ (c 0.09); uv 217 nm (ϵ 9000); FABms m/z 553 $[\text{M}+\text{H}]^+$.

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