PERGAMON

Phytochemistry 52 (1999) 709–714

PHYTOCHEMISTRY

Limonoids from *Melia toosendan*

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Received 8 October 1998; received in revised form 7 April 1999

Abstract

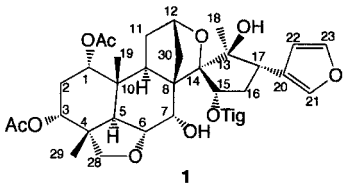
Four limonoids were isolated from *Melia toosendan* together with two known limonoids, nimbolinin B and its 1-deacetyl derivative. Among the new limonoids included one skeletal spiro-, one ring- C-seco nimbolinin-type, and two trichilinin-type apo-euphol-triterpenoids derivatives. Their structures were determined on the basis of spectroscopic data. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: *Melia toosendan*; Meliaceae; Limonoids; Spirosendan; Nimbolinins; Trichilinins; Antifeedant activity

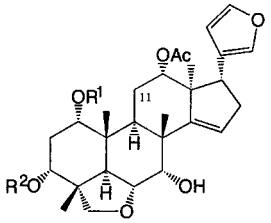
1. Introduction

Limonoids from *Melia* species are attracting considerable interest because of their biological activities and variety of structures (Champagne, Koul, Isman, Scudder & Towers, 1992). In previous studies of Meliaceae plants, several types of limonoids have been isolated as insect antifeedants from *Trichilia roka* (Nakatani & Nakanishi, 1993) and *Melia azedarach* (Huang et al., 1996). *Melia toosendan*, closely related to *M. azedarach*, is a large tree native to China. The extract of the bark of this tree is used as an antihelmintic in China. Thirty-six limonoids including eighteen new compounds have been isolated as antifeedant constituents from the stem (Zhou, Okamoura, Iwagawa & Nakatani, 1996) and root bark (Zhou et al., 1998) of *M. toosendan* collected in China.

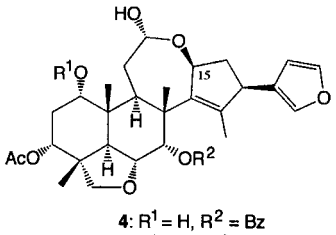
In further studies, the limonoid spirosendan (**1**), possessing a new skeleton with a spiro-structure, was isolated from the ether extract of the root bark along with six limonoids of known meliacarpinins A (Nakatani, Huang, Okamura & Iwagawa, 1993), B and D (Nakatani et al., 1995), and the new compounds 1-*O*-acetyltrichilin H and neoazedarachins A and B (Zhou et al., 1998). Additionally three new limonoids were obtained from the fruit, two of which possessed an intact carbon skeleton and were named trichilinins D (**2**) and E (**3**); the third, a C-seco nimbolinin type,



1



2: R^1 = Cin, R^2 = H
3: R^1 = Bz, R^2 = H
7: R^1 = Cin, R^2 = Ac



4: R^1 = H, R^2 = Bz
5: R^1 = Ac, R^2 = Tig
6: R^1 = H, R^2 = Tig

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PII: S0031-9422(99)00332-5

was named 1-deacetylnimbolinin A (**4**). The known nimbolinin B (**5**) and 1-deacetylnimbolinin B (**6**) (Kraus & Bokel, 1981) were also isolated from the fruit. All of the known limonoids have been previously isolated from *M. azedarach*. In this paper, we report structural studies and antifeedant activity of these limonoids.

2. Results and discussion

A precipitate insoluble in 50% hexane–ether from the ethereal extract of the air-dried root bark of *M. toosendan* was fractionated by DCCC. After a combination of successive silica gel flash chromatography, preparative TLC and reversed-phase HPLC separations, a limonoid fraction gave **1** together with six limonoids, meliacarpinins A, B and D, 1-*O*-acetyltrichilin H and neoazedarachins A and B. The previously uninvestigated fruits of *M. toosendan* gave five limonoids. The hexane-soluble fraction of the acetone extract from the fruits was flash chromatographed on silica gel affording a mixture of limonoids, which was further purified by reversed-phase HPLC to give three new limonoids **2**, **3** and **4** together with two known ring C-seco limonoids, nimbolinin B (**5**) and its 1-deacetyl derivative (**6**). Compounds **4**, **5** and **6** having a 12-hemiacetal structure were observed as a mixture of epimers in a MeOH–H_2O HPLC solvent.

Compound **1**, named spirosendan, was obtained as an amorphous powder. Its molecular formula $C_{35}H_{46}O_{11}$ (13 unsaturations) was determined by HRFAB-MS (*m/z* 643.3129 $[M+1]^+$; $\Delta+1.1$ mmu). The UV maximum at 219 nm and IR absorption at 3550–3250, 1735, 1705, 1640 and 1618 cm^{-1} showed the presence of carbon–carbon double bonds, hydroxyl groups and carbonyl (ester) moieties. From the ^1H and ^{13}C NMR spectral data, it was evident that six units of unsaturation were present as double bonds, three carbon–carbon (two as a furan ring and the other as a part of a conjugated ester) and three CO (esters). Thus, the molecule is heptacyclic. It was also clear from the NMR spectral data that **1** contained seven CH_3 (three tertiary, two vinylic and two acetyl), five CH_2, twelve CH (four olefinic), eleven carbons (two olefinic) not bonded to hydrogen, and two protons in OH groups. The presence of a furan ring at C-17 as well as one tigloyl and two acetyl groups, was also apparent from the spectra.

All protons directly bonded carbon atoms were assigned by a ^1H-^{13}C NMR shift-correlated measurement (HSQC) (Tables 1 and 2), and two major molecular fragments were deduced from the ^1H-^1H COSY spectrum, decoupling experiments, NOE measurements (Fig. 1) and the ^1H-^{13}C HMBC spectrum. Thus, H-7β (δ 4.42, *d, J* = 3.9 Hz), sharpened by the addition of D_2O, was coupled with H-6β (δ 3.87, *dd, J* = 12.5 and 3.9 Hz) attached to a carbon bearing an oxygen function, which in turn showed a coupling to H-5 (δ 2.61, *d, J* = 12.5 Hz) and a NOE correlation with 4β-Me (29) at δ 1.19. 4β-Me (29) showed NOEs to H-2β (δ 2.06, *dt, J* = 4.0 and 2.9 Hz), H-3β (δ 4.84, *t, J* = 2.8 Hz) and H-28β (one of methylene AB, *d, J* = 7.5 Hz) at δ 3.56 and 10β-Me (19) at δ 0.91, which also showed a NOE with H-1β (δ 4.64, *t, J* = 2.9 Hz), H-2β and 6β. This 2β-H NOE signal and its small couplings ($J = \sim 2.9$ Hz) with the H-1β and 3β showed that the A ring was in the chair form. Further W-shape long range couplings of 4β-Me with H-28α (*br d, J* = 7.5 Hz) at δ 3.59 and 10β-Me with H-9 at δ 3.02 clearly defined the first molecular fragment, C-1–C-10 in the A/B ring system including 10β-/4β-Me and an oxide bridge between 4α-methylene and C-6. These assignments were unambiguously confirmed from the HMBC correlations (Fig. 2). Couplings of H-17 (δ 2.84, *dd, J* = 12.8 and 7.0 Hz) with H_2-16 (δ 1.50, *m*, and 2.30, *ddd, J* = 12.8, 12.0 and 7.7 Hz) and H_2-16 with H-15 (δ 5.37, *t, J* = 7.7 Hz), as well as a W-shaped long range coupling of H-17 with 13α-Me (18) at δ 1.29 characterized a second fragment of the molecule, C-15–C-17 of the D-ring in the limonoid skeleton. The fact that a β-substituted furan ring and a tigloyl ester group were attached to C-17 and C-15, respectively, was also confirmed by the HMBC spectrum.

Three tertiary methyls at 4β (29), 10β (19) and 13α (18) and one methylene group (28) at C-4α in the basic limonoid skeleton were confirmed by the HMBC spectrum, and both the absence of a methyl group at C-8 and the presence of a methylene group directly attached to the 12-methine carbon in **1**, were also confirmed. The methine proton (H-12: δ 4.35, *br s*) attached to a carbon bearing an oxy-function was coupled with H-11β at δ 1.65 (*br dd, J* = 13.5 and 5.2 Hz) and a proton (*m*,H-$30_{pro\ R}$) at δ 1.85, which in turn was coupled with H-9 at δ 3.02 and the ^1H signal at δ 1.47 (*m*, H-$30_{pro\ S}$), respectively. Actually the ^1H-^1H couplings from these proton resonances could not be interpreted unambiguously due to signal overlapping. The HMBC spectrum of **1** permitted these connections, especially the C_{30}—C_{12} carbon linkage, to be solved. Thus long-range ^1H-^{13}C couplings from H-7 and 9 to C-30 and between H_2-30 and C-8, 9, 11, 12 and 14, as well as between H_3-18 and C-14 and between H-12 and C-14, clearly established the C-12 to C-13 fragment through C-30, 8 and 14. In a similar manner, the structure of the C-13–C-17 fragment was also established.

Assignment of the relative configuration at the five chiral centers of the right half of **1** was established from the NOESY experiment. NOE correlation of H-$30_{pro\text{-}R}$ with H-12 and 15β, suggested a spatial proxi-

Table 1
^{1}H NMR spectral data for compounds **1**–**4** (400 and 500 MHz, $CDCl_3$)

H	**1**[a]	**2**	**3**	**4**
1	4.64 *t*(*br*) (2.9)	4.94 *t*(*br*) (2.8)	5.06 *t*(*br*) (2.9)	3.70 *m*
2α	2.05 *dt* (4.0, 2.9)	2.09 *ddd* (16.5, 2.8, 2.6)	2.22 *dt* (16.3, 2.6)	2.25 *dt* (16.5, 3.2)
β	2.06 *dt* (4.0, 2.9)	1.30 *dt* (16.5, 2.8)	2.34 *dt* (16.3, 3.1)	2.20 *dt* (16.5, 2.7)
3	4.84 *t*(*br*) (2.8)	3.87 *m*	3.88 *m*	4.97 *dd* (3.2, 2.7)
5	2.61 *d* (12.5)	2.70 *d* (12.1)	2.85 *d* (12.3)	2.92 *d* (12.8)
6	3.87 *dd* (12.5, 3.9)	4.21 *dd* (12.1, 2.9)	4.23 *dd* (12.3, 3.1)	4.19 *dd* (12.8, 3.0)
7	4.42 *d* (3.9)	4.25 *d* (2.9)	4.26 *d* (3.1)	5.92 *d* (3.0)
9	3.02 *dd* (9.7, 5.2)	2.81 *dd* (12.5, 7.3)	2.87 *dd* (12.7, 7.5)	3.11 *dd* (7.9, 2.0)
11α	1.55 *m*	1.11 *ddd* (15.1, 7.3, 6.5)	1.12 *dt*(*br*) (14.5, 7.2)	1.82 *m*
11β	1.65 *dd*(*br*) (13.5, 5.2)	2.18 *m*	2.19 *m*	1.94 *m*
12	4.35 *s*(*br*)	5.05 *dd* (9.1, 6.5)	5.03 *dd* (9.1, 6.7)	5.37 *m*
15	5.37 *t* (7.7)	5.70 *m*	5.70 *dd*(*br*) (3.1, 1.6)	5.19 *d*(*br*) (7.2)
16α	1.50 *m*	2.55 *ddd* (15.6, 10.6, 1.4)	2.51 *ddd* (16.4, 10.9, 1.6)	1.95 *ddd* (14.1, 9.5, 7.2)
β	2.30 *ddd* (12.8, 12.0, 7.7)	2.45 *ddd* (16.2, 7.9, 3.4)	2.42 *ddd* (16.4, 7.7, 3.4)	1.41 *d(br)* (14.1)
17	2.84 *dd* (12.8, 7.0)	3.00 *dd* (10.6, 8.3)	2.96 *dd* (10.9, 7.8)	3.20 *d(br)* (9.5)
18	1.29 *s*	0.95 *s*	0.70 *s*	1.82 *s*
19	0.91 *s*	1.04 *s*	1.08 *s*	0.97 *s*
21	7.16 *m*	7.16 *t*(*br*) (0.7)	7.12 *s*(*br*)	7.20 *s*(*br*)
22	6.36 *d* (1.3)	6.18 *m*	6.14 *m*	6.34 *m*
23	7.30 *dd* (1.7, 1.3)	7.27 *m*	7.25 *t*(*br*) (1.8)	7.28 *t*(*br*) (1.5)
28α	3.59 *d*(*br*) (7.5)	4.14 *d*(*br*) (7.4)	4.18 *d*(*br*) (7.4)	3.42 *d*(*br*) (9.2)
β	3.56 *d* (7.5)	3.66 *d* (7.4)	3.67 *d* (7.4)	3.48 *d* (9.2)
29	1.19 *s*(*br*)	1.17 *s*	1.20 *s*	1.16 *s*
$30_{Pro\text{-}R}$	1.85 *m*	1.13 *s*	1.15 *s*	1.51 *s*
Pr0-S	1.47 *m*			
Ac	1.96 *s*, 2.03 *s*	1.86 *s*		1.99 *s*
OH	2.58 *s*, 3.10 *s*	2.21 *m*, 2.35 (*br*)		3.55 *m*, 4.00 (*br*)
Tig				
3′	6.90 *qq* (7.2, 1.1)			
2′-Me	1.82 *dq* (1.4, 1.1)			
3′-Me	1.77 *dq* (7.2, 1.1)			
Cin				
1′		6.34 *d* (16.1)		
2′		7.71 *d* (15.8)		
4′, 6′, 8′		7.40 *m*		
5′, 7′		7.50 *m*		
6′		7.40 *m*		
Bz				
3′, 7′			8.03 *dd* (8.4, 1.1)	8.10 *d*(*br*) (7.9)
4′, 6′			7.43 *dd* (8.4, 7.4)	7.44 *t* (7.8)
5′			7.57 *dt* (7.4, 1.1)	7.56 *t*(*br*) (7.7)

[a] 500 MH_Z.

mity of the H-30 proton to H-15β. In addition, H-15β showed a cross peak with H-17β, suggesting α- orientation of the furan ring. On the other hand, the NOE correlation from Me-18 at C-13α with H-9, 7-OH and H-22 suggested that these protons were present on the same α side of the molecule, another hydroxyl group at C-13 was β, which was confirmed from an NOE with H-17β. Consequently, the above evidence indicated *R*-configuration at C-14 spiro-center.

Compound **2**, $C_{37}H_{44}O_8$, named trichilinin D, showed the presence of hydroxyl (3500–3250 cm^{-1}), ester (1735 cm^{-1}) and conjugated ester (1710 cm^{-1}) groups and olefinic double bond (1637 cm^{-1}) in the IR spectrum. The ^{1}H and ^{13}C NMR spectra showed the presence of an acetyl and a tigloyl group, along with a furan ring. These NMR spectral data strongly suggested that **2** had a trichilinin-type structure observed in the constituents from the root bark of the same tree. The ^{1}H NMR spectrum of **2** is similar to that of 1-*O*-cinnamoyltrichilinin (**7**) isolated from the fruits of *M. volkensii* (Rajab & Bentley, 1988), particularly with respect to the presence of a trisubstituted olefinic proton at δ 5.70 (*m*, H-15) and an isolated AB-type methylene due to the C-28/C-6 oxymethylene bridge at δ 3.66 (*d*, J = 7.4 Hz, H-28β) and δ 4.14 (*br d*, J = 7.4 Hz, H-28α), weakly coupled to 4β-Me (29) at δ 1.17. These data suggested that **2** differed from **7** only in the lack of one acetyl group of the A-ring of **2**.

Table 2
^{13}C NMR data of compounds **1**–**4** (100 and 125 MHz, $CDCl_3$)

C	**1**[a]	**2**	**3**	**4**	C	**1**[a]	**2**	**3**	**4**
1	72.2 *d*	71.2 *d*	71.1 *d*	71.3 *d*	30	42.6 *t*	15.8 *q*	15.4 *q*	20.7 *q*
2	28.4 *t*	30.4 *t*	30.5 *t*	29.3 *t*	*CH*$_3$CO	21.3 *q*	20.8 *q*	21.3 *q*	21.1 *q*
3	71.8 *d*	73.9 *d*	74.0 *d*	72.5 *d*	*CH*$_3$CO	21.9 *q*	21.8 *q*		
4	43.0 *s*	43.8 *s*	43.8 *s*	42.5 *s*	CH$_3$*CO*	170.7 *s*	169.7 *s*	170.3 *s*	170.2 *s*
5	39.4 *d*	38.6 *d*	38.6 *d*	39.3 *d*	CH$_3$*CO*	170.7 *s*	170.0 *s*		
6	74.9 *d*	73.8 *d*	73.9 *d*	72.6 *d*	Tig				
7	67.3 *d*	72.7 *d*	72.7 *d*	75.4 *d*	1′	167.6 *s*			
8	60.3 *s*	45.2 *s*	45.3 *s*	45.3 *s*	2′	129.3 *s*			
9	35.9 *d*	34.8 *d*	34.6 *d*	36.0 *d*	3′	138.5 *d*			
10	39.3 *s*	39.7 *s*	39.9 *s*	41.1 *s*	2′-Me	12.5 *q*			
11	34.0 *t*	24.5 *t*	24.6 *t*	31.1 *t*	3′-Me	15.0 *q*			
12	76.6 *d*	77.2 *d*	77.1 *d*	92.0 *d*	Cin				
13	81.6 *s*	51.4 *s*	51.3 *s*	142.4 *s*	1′		165.3 *s*		
14	96.7 *s*	157.1 *s*	157.2 *s*	143.0 *s*	2′		117.1 *d*		
15	80.7 *d*	122.8 *d*	122.7 *d*	77.9 *d*	3′		146.4 *d*		
16	32.6 *t*	36.6 *t*	36.6 *t*	38.0 *t*	4′		133.9 *s*		
17	45.2 *d*	50.5 *d*	50.5 *d*	46.7 *d*	5′, 9′		128.3 *d*		
18	20.7 *q*	26.8 *q*	26.9 *q*	16.4 *q*	6′, 8′		129.0 *d*		
19	16.9 *q*	15.3 *q*	15.3 *q*	16.2 *q*	7′		130.8 *d*		
20	123.9 *s*	124.4 *s*	124.5 *s*	128.1 *s*	Bz				
21	142.7 *d*	140.2 *d*	140.2 *d*	142.7 *d*	1′			165.3 *s*	164.9 *s*
22	111.4 *d*	111.6 *d*	111.7 *d*	110.3 *d*	2′			130.5 *s*	130.5 *s*
23	139.9 *d*	142.0 *d*	142.0 *d*	138.9 *d*	3′, 7′			129.6 *d*	129.4 *d*
28	79.1 *t*	78.2 *t*	78.2 *t*	78.0 *t*	4′, 6′			128.8 *d*	128.5 *d*
29	20.8 *q*	20.0 *q*	20.2 *q*	18.8 *q*	5′			133.7 *d*	132.9 *d*

[a] 125 MH$_z$.

The substitution pattern of 1α-cinnamoyloxy and 3α-OH groups around the A-ring was deduced from a W-type long range coupling between H-1β and 3β at δ 4.94 (*br t, J* = 2.8 Hz) and 3.87 (*m*) and the significant upfield shift for H-11α at δ 1.11 (*ddd, J* = 15.1, 7.3 and 6.5 Hz), when compared with H-11β at δ 2.18 (*m*), indicating that the cinnamoyl group and H-11α are close to each other (Henderson, McCrindle, Melera & Overton, 1968; Rajab & Bentley, 1988). The presence of a 3α-OH was also confirmed by NOE enhancement of the H-3β signal by irradiation of the 4β-Me signal.

Compound **3**, $C_{35}H_{42}O_8$, named trichilinin E, showed very similar IR and NMR spectra with **2** except for the change of a cinnamoyl group in **2** to a benzoyl group in **3**. The presence of a 1α-benzoyloxy group was deduced from the chemical shift of H-1β at δ 5.06 (*br t, J* = 2.9 Hz), weakly coupled with H-3β at δ 3.88 (*m*), and by the shielded resonance observed for H-11α at δ 1.12 (*br dt, J* = 14.5 and 7.2 Hz), as observed for **2**.

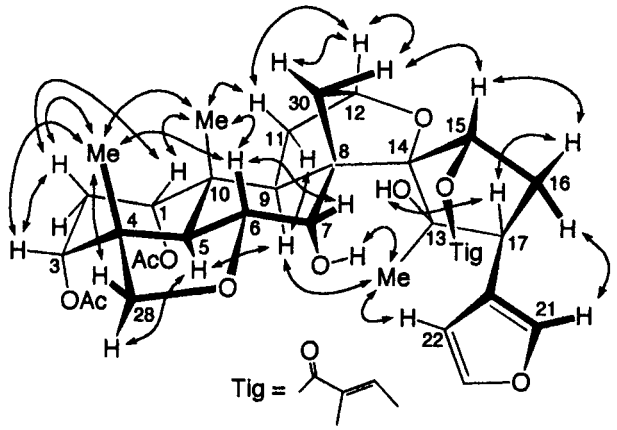


Fig. 1. NOE correlations of **1**.

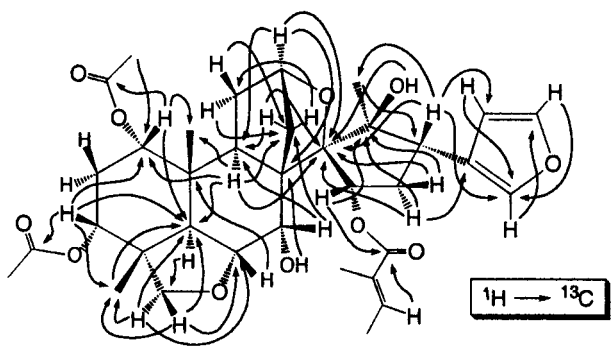
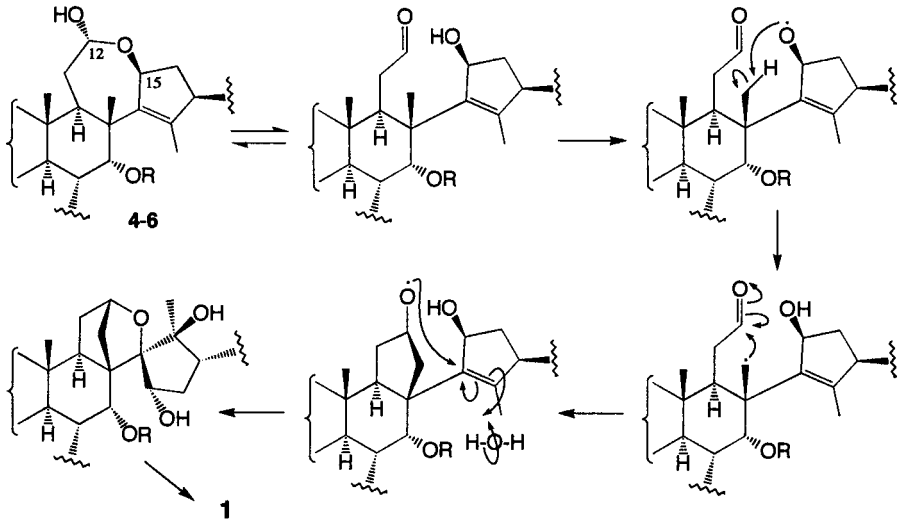


Fig. 2. Significant HMBC correlations observed for compound **1**.



Scheme 1. Proposed biogenetic pathway to spirosendan (**1**) from nimbolinins **4**–**6**.

Compound **4**, $C_{35}H_{42}O_9$, named 1-deacetylnimbolinin A, also showed the presence of hydroxyl (3600–3250 cm^{-1}), ester (1735 cm^{-1}) and conjugated ester (1710 cm^{-1}) groups, and olefinic double bonds (1655–1630, 1600 and 1585 cm-1) in the IR spectrum. The ^1H NMR spectrum indicated that **4** contained one each of acetyl and monosubstituted phenyl groups, along with a furan moiety. The ^1H and ^{13}C NMR spectra of **4** were superimposable on those of 1-deacetylnimbolinin B (**5**) isolated from the same specimen (first reported from *M. azedarach* (Nakatani et al., 1993)) except that a tigloyl group in **5** was replaced by a benzoyl group in **4**.

The presence of a benzoyloxy group at C-7α was deduced from the downfield shift of H-7β to δ 5.92 in **4** from δ 5.78 in **5**. The substitution pattern around the A-ring, namely, that **4** has 1α-hydroxyl and 3α-acetoxy groups, was deduced from a W-type long range coupling between H-1β at δ 3.70 (*m*) and H-3β at δ 4.97 (*dd, J* = 3.2 and 2.7 Hz) and a NOE between H-3β and 4β-Me (29) at δ 1.16. The *S*-configuration at C-15 and the presence of the 12α-OH group were also elucidated from NOE correlations between H-7β and the vinylic 13-Me (18) at δ 1.82, and between the 12β-H at δ 5.37 (*m*) and 8β-Me (30) at δ 1.51, respectively.

Some spiro limonoids have been isolated from Meliaceae plants (Bilton et al., 1985; Ayafor et al., 1994). In addition to the spiro structure in **1**, C-30 forms a carbon bridge between C-8 and C-12, which is, to the best of our knowledge, the first such occurrence in a limonoid. A possible pathway leading to the formation of spirosendan (**1**) can now be proposed by modifying that proposed by Taylor (1983) for the biosynthesis of the phragmalin limonoid having a bicyclo[2.2.1] system. An inspection of the structure of **1** suggests a derivation from **4**–**6**, whose cyclic hemiacetal/alcohol and aldehyde equilibrium yields an oxygen radical, which can then oxidize Me-30 to a radical. This can attack the aldehyde C-12, giving a second oxygen radical which finally attacks the 14,15-double bond, giving a bicyclo[$2^{11,9}.2^{14,O}.1^{12,8}$]-heptane-spiro^{14}[4.5]-decane system, as shown in Scheme 1.

The antifeedant activity of the isolated limonoids **1**–**5** against the third-instar larvae of the pest insect *Spodoptera littoralis* (Boisduval) were tested by a conventional leaf disk method (Wada & Munakata, 1968). All of the compounds **1**–**5** showed only a weak activity at 1000 ppm, corresponding to a concentration of ca 20 $\mu g/cm^2$.

3. Experimental

^1H NMR and ^{13}C NMR; with 400 and 500 MHz and 100 and 125 MHz, respectively, in $CDCl_3$, (Tables 1 and 2). $[\alpha]_D$, CD and UV: MeOH. IR: with KBr.

3.1. Plant materials

The root bark of *Melia toosendan* was collected in December 1992 at Xiangtan, China and the fruits were collected in July 1995 at Guangzou, China. The plant materials were identified by Dr. Wen Xue and voucher specimens are deposited in the herbarium of the Department of Biology, Normal University of Xiangtan, Peoples Republic of China.

3.2. Extraction and isolation

(i) The air-dried root bark (1.5 kg) was first extracted with hexane (20 l) and then with Et_2O (20 l) to yield 12.8 g of an ether extract, which was dissolved

in 50 ml of Et_2O and then added to the same vol. of hexane to give 3.5 g of a precipitate. The ppt was fractionated by DCCC using CH_2Cl_2–MeOH–H_2O (5:5:3 v/v) in ascending mode to give 7 frs. The sixth fr (277 mg) was flash chromatographed on silica gel with a hexane–Et_2O solvent system. Each of the limonoid frs eluting with Et_2O was purified through HPLC using μ-Bondapak C_{18} with 25–50% H_2O–MeOH as the solvent to give **1** (2.2 mg) and six limonoids, meliacarpinin C (5.2 mg), 1-*O*-acetyltrichilin H (0.8 mg), meliacarpinin D (6.2 mg), neoazedarachins B (0.9 mg) and A (3 mg) and meliacarpinin A (2.1 mg) (Zhou et al., 1998), successively. (ii) The fresh fruit (1.4 kg) was extracted with acetone (20 l) to give an extract (127 g). A hexane soluble-part (11.5 g) of the extract (31 g) was flash chromatographed on silica gel with a MeOH–CH_2Cl_2 solvent system. Each of the limonoid frs eluting with 1% MeOH–CH_2Cl_2 was purified through HPLC using μ-Bondapak C_{18} with 10–35% H_2O–MeOH as the solvent to give **6** (1.5 mg), **2** (4.6 mg), **3** (2.9 mg), **4** (2.8 mg) and **5** (0.5 mg).

3.3. Spirosendan (*1*)

Amorphous powder, $[\alpha]_D$ −2°(*c* 0.07), $C_{35}H_{46}O_{11}$; HRFAB-MS *m/z* 643.3129 $[M+H]^+$ (Δ+1.1 mmu), 543 $[M+H\text{-tiglic acid}]^+$, 525 $[543\text{-}H_2O]^+$ and 419; UV λ_{max} nm (ε): 219 (9000); IR ν_{max} cm^{-1}: 3550–3250, 1735, 1705, 1640 and 1618; CD: $\Delta\epsilon_{215}$ −5.7.

3.4. Trichilinin D (*2*)

Amorphous powder, $[\alpha]_D$ +96° (*c* 0.14), $C_{37}H_{44}O_8$; HRFAB-MS *m/z* 639.2928 $[M+Na]^+$ (Δ−0.6 mmu); UV λ_{max} nm (ε): 217 (15,000); IR ν_{max} cm^{-1}: 3600–3250, 1735, 1710 and 1637.

3.5. Trichilinin E (*3*)

Amorphous powder, $[\alpha]_D$ +45° (*c* 0.03), $C_{35}H_{42}O_8$; HRFAB-MS *m/z* 613.2781 $[M+Na]^+$ (Δ+0.4 mmu); UV λ_{max} nm (ε): 227 (12,000) and 204 (12,000); IR ν_{max} cm^{-1}: 3550–3250, 1740, 1715 and 1653.

3.6. 1-Deacetylnimbolinin A (*4*)

Amorphous powder, $[\alpha]_D$ −7°(*c* 0.15), $C_{35}H_{42}O_9$; HRFAB-MS *m/z* 629.2734 $[M+Na]^+$ (Δ+0.8 mmu); UV λ_{max} nm (ε): 225 (11,000) and 207 (12,000); IR ν_{max} cm^{-1}: 3500–3250, 1735, 1710, 1637-1630, 1600 and 1580.

3.7. Nimbolinin B (*5*)

Amorphous powder, $C_{35}H_{46}O_{10}$; SI-MS *m/z* 627 $[M+1]^+$; UV λ_{max} nm (ε): 217 (11,000); IR ν_{max} cm^{-1}: 3500–3250, 1740, 1720 and 1655.

3.8. 1-Deacetylnimbolinin B (*6*)

Amorphous powder, $[\alpha]_D$ −42° (*c* 0.095), $C_{33}H_{44}O_9$; SI-MS *m/z* 685 $[M+1]^+$; UV λ_{max} nm (ε): 217 (11,000); IR ν_{max} cm^{-1}: 3500–3250, 1740, 1720 and 1655.

3.9. Antifeedant activity

The antifeedant potential of the isolated compounds was tested by a conventional leaf disk method (Wada & Munakata, 1968) using Chinese cabbage (*Brassica campestris* L. var *chinensis*) against the third-instar larvae of *S. littoralis* (Boisduval).

Acknowledgements

We would like to thank Mr K. Takezaki (Kagoshima Prefectural Agricultural Experiment Station) for the supply of insects.

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