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Phragmalin-type limonoids from the mangrove plant *Xylocarpus granatum*

Jianxin Cui [a], Zhiwei Deng [b], Jun Li [a], Hongzheng Fu [a], Peter Proksch [c], Wenhan Lin [a,*]

[a] *State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing 100083, China*
[b] *Analysis and Test Center, Beijing Normal University, Beijing 100073, China*
[c] *Institute of Pharmaceutical Biology, Heinrich-Heine University, 40225 Duesseldorf, Germany*

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Abstract

Five new phragmalin-type limonoids, xyloccensins Q–U (**1**–**5**), along with xyloccensin P were isolated from the stem bark of the mangrove plant *Xylocarpus granatum*. Their structures were elucidated on the basis of extensive 1D and 2D NMR as well as IR and MS spectroscopic data analyses.

Keywords: *Xylocarpus granatum*; Meliaceae; Phragmalin-type limonoids; Xyloccensins Q–U

1. Introduction

The marine mangrove plant *Xylocarpus granatum* Koenig (Meliaceae) is commonly distributed along the shores of Indian Ocean and South-East Asia, and local Indian people have used it for treatment of fever diseases such as malaria (Alvi et al., 1991). Since the first limonoid gedunin from *X. granatum* was reported by Taylor (1965), about 30 limonoids have hitherto been obtained from the *Xylocarpus* genus, in which 17 were isolated from the *X. granatum* involving two from fruit kernels (Alvi et al., 1991), six from seeds (Ahmed et al., 1978; Kokpol et al., 1996; Ng and Fallis, 1979; Okorie and Taylor, 1970), and five from stem bark (Wu et al., 2003, 2004a,b). In continuation of our studies on the chemical diversity of Chinese mangrove plants, the plant *X. granatum* was collected for re-examination, and from its stem bark six phragmalin-type limonoids, xyloccensin P–U (**1**–**6**) were obtained. The structures of the new limonoids, xyloccensin Q–U, were elucidated on the basis of IR, MS, ^{1}H and ^{13}C NMR, and 2D NMR spectroscopic, analyses.

2. Results and discussion

The 95% EtOH extract of the stem bark was partitioned between H_2O and CH_2Cl_2, and the CH_2Cl_2 fraction was subjected to repeated silica gel column chromatography followed by semi-preparative HPLC to afford xyoccensins P–U.

Xyloccensin Q (**1**) was isolated as a white amorphous powder, and its molecular formula was established to be $C_{33}H_{38}O_{15}$ from HRFABMS and ^{1}H and ^{13}C NMR data which indicated 15° of unsaturation. The IR absorptions at 3385, 1731, and 1646 cm^{-1} suggested the presence of hydroxyl and unsaturated lactone groups. The ^{1}H and ^{13}C NMR spectroscopic data (Table 1) were characteristic of a phragmalin orthoester (Wu et al., 2004a,b). The

* Corresponding author. Tel.: +86 10 62062210; fax: +86 10 82802724.
E-mail address: whlin@bjmu.edu.cn (W. Lin).

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Table 1
^{1}H NMR spectroscopic data of xyloccensins Q to U (**1**–**5**)

H	1	2	3	4	5
2					3.02, *dd* (2.5, 11.5)
3	5.13, *s*	5.17, *s*	5.19, *s*	5.27, *s*	5.36, *d* (11.5)
5	2.34, *brs*	2.53, *brs*	2.31, *brs*	2.17, *brd* (4.2)	2.97, *t* (6.5)
6	5.24, *brs*	6.36, *brs*	5.20, *brs*	2.31, *dd* (4.2, 16.5)	2.25, *d* (6.5)
				3.14 brd (16.5)	
9					2.14, *m*
11	2.05, *dd* (13.5, 14.0)	2.05, *dd* (13.5, 14.0)	2.02, *dd* (13.5, 14.0)	2.02, *dd* (13.5, 14.0)	1.97, *m*
	2.35, *dd* (4.0, 14.0)	2.35, *dd* (4.0, 14.0)	2.35, *dd* (4.2, 14.0)	2.24, *dd* (4.0, 14.0)	2.12, *m*
12	4.80, *dd* (4.0, 13.5)	4.93, *dd* (4.0, 13.5)	4.83, *dd* (4.2, 13.5)	4.80, *dd* (4.0, 13.5)	5.01, *brs*
14					2.43, *d* (8.5)
15	6.46, *s*	6.46, *s*	6.63, *s*	6.65, *s*	2.68, *dd* (8.5, 19.4)
					3.36, *d* (19.4)
17	5.88, *s*	5.97, *s*	5.86, *s*	5.95, *s*	5.80, *s*
18	1.61, *s*	1.62, *s*	1.61, *s*	1.61, *s*	1.03, *s*
19	1.56, *s*	1.33, *s*	1.59, *s*	1.32, *s*	1.09, *s*
21	7.41, *s*	7.47, *s*	7.43, *s*	7.52, *s*	7.51, *s*
22	6.56, *brs*	6.58, *brs*	6.56, *brs*	6.57, *brs*	6.41, *brs*
23	7.44, *brs*	7.43 *brs*	7.42, *brs*	7.44, *brs*	7.46, *brs*
28	0.94, *s*	0.96, *s*	0.92, *s*	0.77, *s*	0.88, *s*
29	1.77, *d* (10.5)	1.85, *d* (11.0)	1.70, *d* (11.0)	1.74, *d* (11.5)	2.01, *d* (10.5)
	2.30, *d* (10.5)	2.15, *d* (11.0)	2.41, *d* (11.0)	2.00, *d* (11.5)	2.46, *d* (10.5)
30	4.56, *s*	4.56, *s*	5.37, *s*	5.39, *s*	5.51, *d* (2.5)
32	1.73, *s*	1.72, *s*	1.73, *s*	1.72, *s*	
OMe	3.85, *s*	3.78, *s*	3.84, *s*	3.72, *s*	3.71, *s*
OAc-1					2.10, *s*
OAc-2			2.20, *s*	2.19, *s*	
OAc-3	2.06, *s*	2.07, *s*	2.09, *s*	2.11, *s*	2.17, *s*
OAc-6		2.23, *s*			
OAc-8					2.17, *s*
OAc-12	1.55, *s*	1.58, *s*	1.57, *s*		
OAc-30					2.09, *s*
OH-1	3.48, *s*	3.48, *s*	3.41, *s*	3.39, *s*	
OH-2	3.60, *s*	3.57, *s*			
OH-6	2.56, *brs*		2.56, *brs*		
OH-12					4.43, *brs*

^{1}H NMR spectrum exhibited the signals for a β-substituted furanyl ring [δ 7.41 (1H, *s*, H-21), 6.56 (1H, *brs*, H-22), and 7.44 (1H, *brs*, H-23)], a trisubstituted olefinic proton [δ 6.46 (1H, *s*, H-15)], five oxymethines [δ 5.13 (1H, *s*, H-3), 5.24 (1H, *brs*, H-6), 4.80 (1H, *dd*, $J = 4.0$, 13.5 Hz, H-12), 5.88 (1H, *s*, H-17), and 4.56 (1H, *s*, H-30)], four angular methyls [δ 1.61 (3H, *s*, H-18), 1.56 (3H, *s*, H-19), 0.94 (3H, *s*, H-28), and 1.73 (3H, *s*, H-32)], and a methoxy group [δ 3.85 (3H, *s*)]. In addition, three D_2O exchangeable protons at δ 3.48 (1H, *s*), 3.60 (1H, *s*), and 2.56 (1H, *brs*) attributed to hydroxyl groups were observed. Two methyls at δ 1.55 (3H, *s*) and 2.06 (3H, *s*) showed HMBC correlations with carbonyl carbons at δ 169.6 (*s*) and 170.6 (*s*), respectively, indicating the presence of two acetyl groups. A quaternary carbon at δ 119.4 (*s*, C-31) showing a HMBC correlation with H_3-32 suggested the presence of an orthoacetate group. A pair of geminal doublets at δ 1.77 (*d*, $J = 10.5$ Hz) and 2.30 (*d*, $J = 10.5$ Hz) was assigned to H_2-29 of 4,29,1-bridge in ring A, the typical signals of phragmalins. The nature of oxygenated carbons assigned for C-8 (δ 84.2, *s*) and C-9 (δ 87.4, *s*) was comparable to those of xyoccensin P and taken together with the HMBC correlation observed between H-30 and C-31, suggested the location of the orthoacetate at C-8, C-9, and C-30, in contrast to 1,8,9-ortho esters as reported. This was further supported by the detection of the hydroxyl group at δ 3.48 (1H, *s*) which was assigned to C-1 due to the HMBC correlations observed from δ 3.48 (1H, *s*) to C-1 (δ 83.6, *s*), C-10 (δ 48.0, *s*), and C-29 (δ 40.3, t). Since two acetoxy groups were assigned to C-3 and C-12 according to the HMBC correlations of H-3 and H-12 with the carbonyl carbons at δ 169.4 (*s*) and δ 170.6 (*s*), respectively, the remaining two hydroxyl groups were obviously positioned at C-2 and C-6. These assignments are supported by the HMBC correlations of the D_2O exchangeable proton at δ 3.60 (1H, *s*) with C-1, C-2, and C-3 (δ 86.1, *d*) and of the proton at δ 2.56 (1H, *s*) with a carbonyl carbon at δ 174.5 (*s*, C-7) and an oxygenated methine at δ 71.0 (*d*, C-6). The methoxyl group at δ 3.85 (3H, *s*) correlated to C-7 in the HMBC spectrum thus indicates the presence of a methyl ester at C-7. In order to elucidate the stereochemistry of compound **1**, NOESY experiments were conducted. The results of

these experiments when viewed together with the relevant coupling constants allowed assignment of various chiral centers. The coupling constants of H-12 ($J = 4.0$, 13.5 Hz) are in agreement with an axial-orientation, and the singlet proton H-6 was ascribed to the dihedral angle with H-5 near 90°. The NOE correlations between H-12/H-17, H_3-28/H_2-29, H-3, and OH-6, H-5/H-12, OH-2/H-29b, and H-30/H-15 indicated the basic skeleton of **1** to be identical to that of xyloccensin O which had been unequivocally been elucidated by X ray analysis (Wu et al., 2004b). In the structure of xyloccensin O, all rings were shown to be *cis*-fused, and the two five-carbocyclic ring in ring A and the two dioxolane rings in the orthoacetate unit adopted envelope conformations. Since in all known phragmalins the configuration of H-17 exhibits exclusively a β-orientation (Wu et al., 2004b), H-12 and H-5 are suggested to have a β-orientation, and in turn H-3, Me-18 and Me-19 are assumed to be in the α-orientation. Since the absolute stereochemistry of xyloccensin P at C-6 was also determined as described in the literature (Wu et al., 2004b), the excellent agreement of the ^{1}H and ^{13}C NMR spectroscopic data at left side chain of **1** with those of xyloccensin P (Table 2), along with the NOESY correlation between OH-2 and H_3-28, enabled the assignment of the absolute configuration of C-6 in **1** as *R*.

The similarity of the IR, ^{1}H and ^{13}C NMR spectra of compounds **2**–**4** (Tables 1 and 2) when compared to those of **1** indicated that the former natural products posses the same phragmalin skeleton linked with an orthoacetate at C-8, C-9, and C-30 as **1**, but differing in their ring substituents.

The molecular formula of xyloccensin R (**2**) was determined as $C_{35}H_{40}O_{16}$ by HRFABMS, 42 amu higher than that of **1**. The ^{1}H and ^{13}C NMR spectra of **2** were very similar to those of **1**, with exception of the presence of an additional acetyl group resonating at δ 2.23 (3H, *s*), 21.0 (*q*), and 169.3 (*s*), and the signal of H-6 which was shifted downfield to δ 6.36 (1H, *brs*). This finding suggested that the acetyl group was located at C-6. This assumption was further supported by the HMBC correlation of H-6 with the carbonyl carbons at δ 169.3 (*s*, Ac) and 171.8 (*s*, C-7). The similar NOESY correlations and the comparable NMR spectroscopic data (Tables 1 and 2) between **2** and **1** were indicative of the same stereochemistry of the core skeleton of compound **2** compared to **1**. The key NOE correlations for compound **2** between H-6/H_3-19 (δ 1.33, *s*) and between H-3-28/Ac (δ 2.23) confirmed the configuration of C-6 as *R*.

Xyloccensin S (**3**) showed the same molecular formula as that of **2**, as determined by HRFABMS. The ^{1}H and ^{13}C NMR spectroscopic data of **3** also presented three acetyl groups (Tables 1 and 2). The proton signal at δ 5.20 (*brs*), assigned to H-6, showed a COSY correlation with a D_2O exchangeable proton at δ 2.56 (1H, *brs*, OH-6) thus indicating a free hydroxyl group positioned at C-6, identical to that of **1**. Two of the three acetoxy groups were determined to be located at C-3 and C-12 through the HMBC correlations between H-3 (δ 5.19, *s*) and the acetyl carbon at δ 168.9 (*s*) and between H-12 (δ 4.83, *dd*) and the other acetyl carbon at δ 170.6 (*s*). Therefore, the third acetoxy group had to be located at one of the quaternary carbons C-1 or C-2. The downfield signal at δ 84.2 (*s*), assigned to C-2, suggested that the last acetoxy group was attached to C-2 rather than C-1. The NOESY spectrum of **3** indicated that the stereochemistry of **3** was the same as that of **2**.

Xyloccensin T (**4**) possessed the molecular formula $C_{35}H_{40}O_{15}$ as determined by HRFABMS. Compound **4** thus had lost one oxygen atom when compared to **3**. The ^{1}H and ^{13}C NMR spectra of **4** resembled largely

Table 2
^{13}C NMR spectroscopic data of xyloccensins Q to U (**1**–**5**)

No.	1	2	3	4	5
1	83.6, *s*	83.6, *s*	83.9, *s*	83.8, *s*	88.2, *s*
2	75.3, *s*	75.2, *s*	84.2, *s*	83.6, *s*	46.5, *d*
3	86.1, *d*	85.7, *s*	85.6, *d*	85.0, *d*	75.5, *d*
4	44.1, *s*	44.3, *s*	44.4, *s*	44.7, *s*	45.3, *s*
5	45.8, *d*	45.3, *d*	45.2, *d*	39.8, *d*	38.1, *d*
6	71.0, *d*	71.2, *d*	70.9, *d*	32.9, *t*	33.3, *t*
7	174.5, *s*	171.8, *s*	174.5, *s*	174.3, *s*	173.0, *s*
8	84.2, *s*	84.1, *s*	83.6, *s*	84.2, *s*	73.5, *s*
9	87.4, *s*	87.1, *s*	86.4, *s*	86.0, *s*	48.5, *d*
10	48.0, *s*	48.1, *s*	48.7, *s*	48.0, *s*	46.3, *s*
11	32.4, *t*	32.3, *t*	32.6, *t*	32.6, *t*	28.1, *t*
12	68.8, *d*	68.3, *d*	68.9, *d*	68.7, *d*	71.7, *d*
13	42.9, *s*	43.0, *s*	42.9, *s*	42.9, *s*	39.3, *s*
14	153.2, *s*	153.1, *s*	152.8, *s*	152.8, *s*	46.4, *d*
15	123.6, *d*	123.7, *d*	124.0, *d*	124.0, *d*	28.0, *t*
16	163.3, *s*	163.4, *s*	163.4, *s*	163.5, *s*	169.7, *s*
17	78.8, *d*	78.9, *d*	78.9, *d*	78.8, *d*	76.8, *d*
18	14.4, *q*	14.4, *q*	14.4, *q*	14.4, *q*	18.8, *q*
19	17.1, *q*	16.4, *q*	17.1, *q*	15.4, *q*	22.8, *q*
20	121.1, *s*	121.0, *s*	121.1, *s*	121.1, *s*	120.7, *s*
21	141.8, *d*	142.1, *d*	141.8, *d*	142.0, *d*	140.6, *d*
22	110.2, *d*	110.2, *d*	110.2, *d*	110.2, *d*	109.2, *d*
23	143.1, *d*	143.1, *d*	143.1, *d*	143.0, *d*	143.7, *d*
28	15.4, *q*	15.5, *q*	15.3, *q*	14.3, *q*	15.1, *q*
29	40.3, *t*	40.3, *t*	40.8, *t*	40.1, *t*	39.7, *t*
30	78.1, *d*	78.0, *d*	74.1, *d*	74.3, *d*	70.1, *d*
31	119.4, *s*	119.4, *s*	119.6, *s*	119.8, *s*	
32	16.5, *q*	16.4, *q*	16.5, *q*	16.5, *q*	
MeO	53.1, *q*	53.4, *q*	53.1, *q*	52.2, *q*	52.0, *q*
OAc-1					169.8, *s*
					21.0, *q*
OAc-2			170.6, *s*	170.5, *s*	
			21.9, *q*	21.9, *q*	
OAc-3	168.6, *s*	169.7, *s*	168.9, *s*	170.5, *s*	169.8, *s*
	21.7, *q*	21.7, *q*	21.7, *q*	21.7, *q*	21.3, *q*
OAc-6		169.3, *s*			
		21.0, *q*			
OAc-8					168.5, *s*
					22.8, *q*
OAc-12	170.6, *s*	170.5, *s*	170.6, *s*	169.2, *s*	
	19.9, *q*	19.8, *q*	19.9, *q*	19.9, *q*	
OAc-30					170.6, *s*
					21.4, *q*

those of **3**, with exception of the left side chain at C-5 where the oxymethine C-6 of **3** was replaced by a methylene group [δ 2.31 (1H, *dd*, $J = 4.2$, 16.5 Hz, H-6a), 3.14 (1H, *d*, $J = 16.5$ Hz, H-6b), and 32.9 (*t*, C-6)]. The HMBC correlations between H_2-6 and carbons at δ 44.7 (*s*, C-4), 39.8 (*d*, C-5), 48.0 (*s*, C-10), and 174.3 (*s*, C-7), along with COSY correlation between H_2-6 and H-5 (δ 2.17, *brd*, $J = 4.2$ Hz) indicated **4** to be the 6-dehydroxylated derivative of xyloccensin S. The stereochemistry of **4** was identical to that of **3** due to the similar NOE correlations observed for the two compounds.

The molecular formula of xyloccensin U (**5**) was determined as $C_{35}H_{44}O_{14}$ on the basis of HRFABMS and exhibited 14° of unsaturation. The UV absorption at 221 nm and IR absorptions at 3406, 1730, 1700, and 1622 cm^{-1} suggested the presence of hydroxyl, carbonyl, and vinyl groups. The ^1H and ^{13}C NMR spectroscopic data were indicative of a phragmalin-type limonoid, but also indicated the absence of an orthoacetate group. The signals at δ 7.51 (1H, *brs*, H-21), 6.41 (1H, *brs*, H-22), and 7.46 (1H, *brs*, H-23) were attributable to a β-substituted furanyl ring. The ^1H NMR spectrum exhibited signals at δ 5.36 (1H, *d*, $J = 11.5$ Hz, H-3), 5.01 (1H, *brs*, H-12), 5.80 (1H, *s*, H-17), and 5.51 (1H, *d*, $J = 2.5$ Hz, H-30) for four oxymethines, and signals at δ 2.09 (3H, *s*), 2.17 (6H, *s*), 2.10 (3H, *s*), 1.03 (3H, *s*), 1.09 (3H, *s*), and 0.88 (3H, *s*) for seven methyl groups. The ^{13}C NMR spectrum displayed thirty five carbons involving six carbonyl carbons at δ 173.0 (*s*), 170.6 (*s*), 169.8 (*s*, 2C), 169.7 (*s*), and 168.5 (*s*), four of which were attributed to acetyl groups based on HMBC correlations. With exception of six unsaturation elements for esters and three for a furanyl ring, the remaining degrees of unsaturation were accounted for by the pentacyclic ring. All protons and their directly bonded carbons were assigned through the HMQC spectrum. The COSY, HMQC and HMBC spectroscopic analysis afforded a gross structure of **5**. A pair of geminal protons at δ 2.68 (1H, *dd*, $J = 8.5$, 19.4 Hz, H-15a) and 3.36 (1H, *brd*, $J = 19.4$ Hz, H-15b) showed a COSY correlation with a proton at δ 2.43 (1H, *brd*, $J = 8.5$ Hz, H-14), and also HMBC correlations with a carbonyl carbon at δ 169.7 (*s*, C-16), suggesting the double bond at C-14/C-15 of **4** to be hydrogenated. The other pair of geminal protons at δ 2.25 (2H, *d*, $J = 6.5$ Hz) coupled with δ 2.97 (*d*, $J = 6.5$ Hz, H-5), and having HMBC correlations with a methyl ester carbonyl carbon at δ 173.0 (*s*, C-7), was assigned to CH_2-6. The ^{13}C NMR spectroscopic data in association with HMQC and HMBC correlations led to the assignment of the oxygen-bearing positions at C-1, C-3, C-8, C-12, C-17, and C-30, of which C-17 was attributed to the δ-carbon of the lactone. The presence of HMBC correlations between H-3 and the acetyl carbon at δ 169.8 (*s*) and between H-30 and the acetyl carbon at δ 170.6 (*s*), as well as the absence of HMBC correlation between H-12 and the acetyl carbon, permitted location of the four acetyl groups to C-1, C-3, C-8, and C-30, respectively. The relative configuration of **5** could be established on the basis of the NOESY spectrum and the proton coupling constants. The NOE correlations between H-12/H-17, H-3/H-2 (δ 3.02, *dd*), H-3/H-29a (δ 2.64, *d*), H_3-18 (δ 1.03, *s*)/H-14 (δ 2.43, *d*), H-30/H-5, and H-5/H-11a (δ 1.98, *m*), in association with the evidence of equatorial coupling of H-12 and axial coupling of H-3, indicated a *cis*-conjugation between ring B/C and C/D, and an α-configuration of H-3, as well as a β-configuration of H-5, H-12, H-17, and H-30.

Since the first report of limonoids xyloccensins A–F isolated from *Xylocarpus moluccensis* (Connolly et al., 1976), these structurally unique metabolites from the Mangrove genus *Xylocarpus* attracted the interest of natural products chemists for further chemical investigation. So far limonoids belonging to the gedunin, andirobin, mexianolide and phragmalin groups and to the obacunol group have been isolated from *Xylocarpus* genus. It is of interest to note that phragmalin containing 1,8,9-orthoacetate was only discovered from *X. moluccensis*, whereas 8,9,30-orthoacetate phragmalin-type was found in *X. granatum*. This evidence may be a chemotaxonomic significance for the identification of the two species.

3. Experimental

3.1. General

Optical rotations were measured with a Perkin–Elmer 243B polarimeter. IR spectra were recorded on a Thermo Nicolet Nexus 470 FT-IR spectrometer and UV spectra were recorded on a Shimadzu UV-210A spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a Brucker Avance DRX 500 spectrometer using TMS as an internal standard. Chemical shifts (δ) expressed in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). ESIMS spectra were recorded on a PE Q-STAR ESI-TOF-MS/MS spectrometer, and HRFABMS spectra were obtained on a Bruker FT-ICRMS spectrometer. Column chromatography was carried out with Si gel (200–300 mesh), and GF_{254} Si gel for TLC was provided by Qingdao Marine Chemistry Co. Ltd. HPLC was performed on Alltech 426 pump employing a UV detector, and the Chromasil C_{18} column (semi-preparative) was purchased from Pharm Co.

3.2. Plant material

The fresh stem bark of mangrove plant *X. granatum* was collected from the mangrove garden at Hainan Island, Southern China, in October 2002, and the species was identified by Prof. Peng Lin from Xiamen

University. A voucher (HM-17) specimen has been deposited in the State Key Laboratory of Natural and Biomimetic Drugs, Peking University.

3.3. Extraction and isolation of xyloccensins

The air-dried stem bark of the plant (8.4 kg) was percolated with 95% EtOH, and the EtOH solution was concentrated in vacuo to get the extract (634 g). The EtOH extract was partitioned between 90% aqueous methanol and petroleum ether to remove lipids. The aqueous methanol fraction was concentrated and then partitioned between H_2O and CH_2Cl_2, and the CH_2Cl_2 layer was collected and concentrated to afford a residue (12 g). The CH_2Cl_2 residue was purified by CC on silica gel with petrol–EtOAc (2:1) as eluant to yield seven fractions (A–G). Fraction F (0.5 g) showed a main spot on TLC (petrol–EtOAc, 2:1), but displayed a mixture signals of limonoids, which was separated further on semi-preparative HPLC (ODS column) using MeOH/H_2O (7:3) as mobile phase to obtain **2** (3.5 mg), **1** (4.1 mg), **3** (4.2 mg), **4** (10.5 mg), **5** (2.2 mg), and xyloccensin P (11.5 mg).

3.4. Xyloccensin Q (*1*)

White amorphous powder; $[\alpha]_D^{20}$ + 73.7° (*c* 0.21; MeOH). UV (MeOH) λ_{max} nm: 221. IR ν_{max}^{KBr} cm^{-1}: 3385, 2954, 2929, 1731, 1646, 1421, 1370, 1237, 1161, 1093 and 1028. ESIMS (positive ion mode): *m/z* 675 $[M+H]^+$, 692 $[M+NH_4]^+$, 697 $[M+Na]^+$. HRFABMS *m/z*: 675.2276 $[M+1]^+$ (calcd for $C_{33}H_{39}O_{15}$, 675.2283). For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2 (Fig. 1).

3.5. Xyloccensin R (*2*)

White amorphous powder; $[\alpha]_D^{20}$ + 70.3° (*c* 0.175; MeOH). UV (MeOH) λ_{max} nm: 221. IR ν_{max}^{KBr} cm^{-1}: 3436, 2922, 2852, 1741, 1599, 1458, 1374, 1235 and 1028. ESIMS (positive ion mode): *m/z* 717 $[M+H]^+$, 739 $[M+NH_4]^+$. HRFABMS *m/z*: 717.2399 $[M+1]^+$ (calcd for $C_{35}H_{41}O_{16}$, 717.2389). For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

3.6. Xyloccensin S (*3*)

White amorphous powder; $[\alpha]_D^{20}$ + 77.6° (*c* 0.21; MeOH). UV (MeOH) λ_{max}: 221 nm. IR ν_{max}^{KBr} cm^{-1}: 3434, 2933, 1735, 1645, 1422, 1373, 1240 and 1029. ESIMS (positive ion mode) *m/z*: 717 $[M+H]^+$, 734 $[M+NH_4]^+$, 739 $[M+Na]^+$. HRFABMS *m/z*: 739.2200 $[M+Na]^+$ (calcd for $C_{35}H_{40}O_{16}Na$, 739.2208). For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

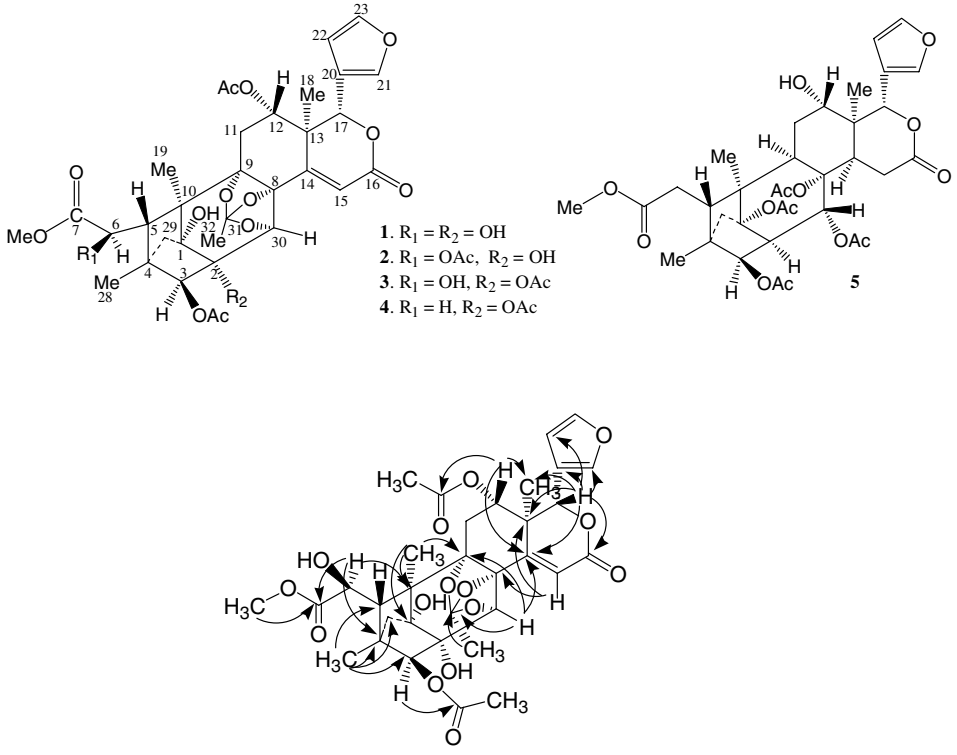

Fig. 1. Main HMBC correlations of **1**.

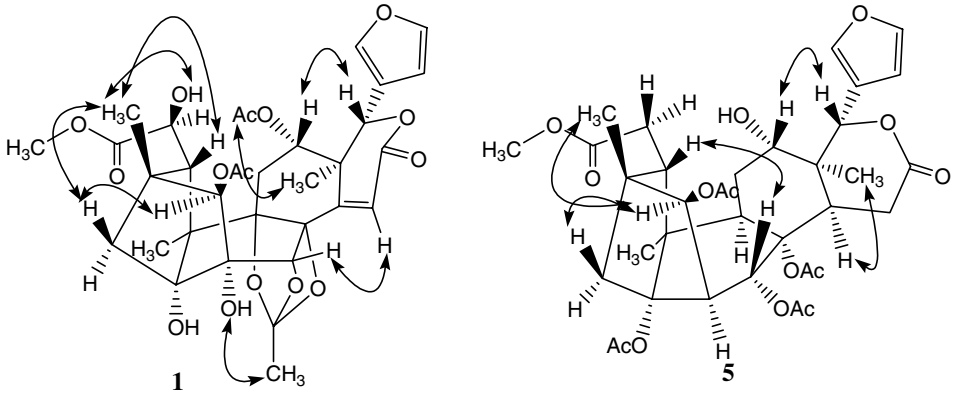

Fig. 2. Main NOESY correlations of **1** and **5**.

3.7. Xyloccensin T (*4*)

White amorphous powder; $[\alpha]_D^{20}$ + 81.0° (*c* 0.05, MeOH). UV (MeOH) λ_{max} nm: 221. IR ν_{max}^{KBr} cm^{-1}: 3410, 2927, 1735, 1605, 1422, 1384, 1239 and 1037. ESIMS (positive ion mode): *m/z* 701 $[M + H]^+$, 723.28 $[M + Na]^+$. HRFABMS *m/z*: 701.2436 $[M + 1]^+$ (calcd for $C_{35}H_{41}O_{15}$, 701.2439). For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2.

3.8. Xyloccensin U (*5*)

White amorphous powder; $[\alpha]_D^{20}$ +50.5° (*c* 0.1, MeOH). UV (MeOH) λ_{max} nm: 221. IR ν_{max}^{KBr} cm^{-1}: 3406, 2924, 1730, 1700, 1622, 1431, 1384 and 1145. ESIMS (positive ion mode): *m/z* 706 $[M + NH_4]^+$, 711 $[M + Na]^+$. HRFABMS *m/z*: 689.2782 $[M + 1]^+$ (calcd for $C_{35}H_{45}O_{14}$, 689.2803). For ^1H and ^{13}C NMR spectroscopic data, see Tables 1 and 2 (Fig. 2).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.phytochem.2005.06.020.

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