Mexicanolides from the Seeds of a Krishna Mangrove, *Xylocarpus moluccensis*

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Two new mexicanolides, named xylomexicanolides A and B, were isolated from the seeds of an Indian mangrove, *Xylocarpus moluccensis*, together with four known limonoids, khayasin, angolensic acid methyl ester, khayasin T, and 2′*S*-methylbutanoylproceranolide. The structures of these limonoids were established on the basis of spectroscopic data. The ^{13}C-NMR data of khayasin were reported for the first time. Khayasin was found to exhibit marked insecticidal activity against the fifth instar larvae of *Brontispa longissima* (Gestro) at a concentration of 10 mg/l.

Key words mexicanolide; *Xylocarpus moluccensis*; insecticidal activity

Limonoids, derived from a precursor with a 4,4,8-trimethyl-17-furanylsteroid skeleton, are tetranortriterpenoids with a β-furyl ring substituent located at C-17. They are classified by the type of four rings, which are usually oxidized and designated as A, B, C, and D, in the intact triterpene nucleus. The mangroves *Xylocarpus moluccensis* and *X. granatum* are known for producing antifeedant limonoids, especially phragmalins and mexicanolides. Previous investigations on the mangrove, *X. moluccensis*, yielded a gedunin,[1)] a monoterpene,[2)] an andirobin,[3)] two phenolic acids,[4)] two phragmalins,[3,5)] and 15 mexicanolides.[1,3,5—7)] Previously, eight unique 8,9,30-phragmalin orthoesters and 13 limonoids with a new carbon skeleton were identified by us from the bark and seeds of a Chinese mangrove, *X. granatum*.[8—10)] In the continuing search for potential drug leads from mangrove plants, two new mexicanolides, named xylomexicanolides A and B (**1**, **2**), were isolated from the seeds of an Indian mangrove, *X. moluccensis* (Lam.) M. Roem. (Meliaceae), collected in the mangrove wetlands in Krishna estuary, Andhra Pradesh, together with four known limonoids, khayasin,[11)] angolensic acid methyl ester, khayasin T,[12)] and 2′*S*-methylbutanoylproceranolide.[13)] The complete assignments of NMR data for xylomexicanolides A, B and khayasin were achieved by means of 2D NMR techniques, including ^{1}H–^{1}H correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond correlation (HMBC), and nuclear Overhauser effect spectroscopy (NOSEY) spectra. The ^{13}C-NMR data of khayasin were reported for the first time.

Results and Discussion

Xylomexicanolide A (**1**) was obtained as a white, amorphous powder. Its molecular formula of $C_{31}H_{38}O_8$ was established by a *quasi*-molecular ion peak in the HR-time of flight (TOF)-MS at *m*/*z* 561.2491 (Calcd for $[M+Na]^+$ 561.2464), indicating that **1** had 13 degrees of unsaturation. From the ^{1}H- and ^{13}C-NMR data (Table 1) of **1**, it was clear that eight of the 13 elements of unsaturation came from a ketone, three ester functionalities, and four carbon–carbon double bonds. Therefore, the molecule was pentacyclic. The ^{13}C-NMR data and distortionless enhancement by polarization transfer (DEPT) experiments revealed that **1** had seven methyls (a methoxy, two secondary methyls, and four methyls of the mexicanolide nucleus), three methylenes, eleven methines (five olefinic) and ten quaternary carbons (four carbonyls). The NMR data of **1** (Table 1) and its 2D NMR studies (^{1}H–^{1}H COSY, HSQC, HMBC) (Fig. 1) indicated the presence of a ketone (δ_C 214.2 qC), a methoxycarbonyl group (δ_H 3.68 s, δ_C 52.0 CH_3, 173.7 qC), an isobutyryl group [δ_H 1.26 (d, J=7.0 Hz), 1.27 (d, J=7.0 Hz), 2.70 m; δ_C 19.2 CH_3, 19.1 CH_3, 34.2 CH, 176.1 qC], and a β-furyl ring [δ_H 6.47 br s, 7.42 br s, 7.51 br s; δ_C 110.2 CH, 143.1 CH, 141.4 CH, 120.2 qC] (Table 1).

An α,β-unsaturated δ-lactone ring D, characterized by NMR data [δ_H 5.14 s, 6.22 s; δ_C 79.8 CH, 112.1 CH, 164.9 qC, 160.7 qC, 37.5 qC], was confirmed by HMBC (Table 1) correlations between H-15/C-13, H-15/C-14, H-15/C-16, H-17/C-13, and H-17/C-16. The above NMR studies strongly suggested that **1** was a mexicanolide. An aliphatic methine group (δ_H 3.64 br d, δ_C 49.0 CH), having ^{1}H–^{1}H COSY correlations to H-3 and H-30, was attributed to CH-2. Another aliphatic methine group [δ_H 3.30 (dd, J=9.5, 2.0 Hz), δ_C 40.5 CH], showing a ^{1}H–^{1}H COSY correlation to H-6 and HMBC correlations to C-4, C-6, C-10 (Table 1), was assigned to CH-5. Two protons [δ_H 2.33 (d, J=2.0 Hz), 2.36 (d, J=9.5 Hz)], having HMBC correlations to C-5 and C-7, were attributed to H_2-6. An oxygenated methine group [δ_H 4.88 (d, J=9.0 Hz), δ_C 78.0 CH], exhibiting a ^{1}H–^{1}H COSY cross-peak to H-2 and HMBC correlations to C-2, C-4, and C-30 (Table 1), was assigned to CH-3. An olefinic methine group [δ_H 6.29 (dd, J=6.0, 3.0 Hz), δ_C 128.9 CH], showing a ^{1}H–^{1}H COSY correlation to H-2 and HMBC correlations to C-9 and C-14, was attributed to CH-30. The NMR data of **1** (Table 1) were similar to those of tigloylseneganolide A,[13)] except for the presence of a different substituted group at C-3. The strong HMBC correlation from H-3 to the carbonyl

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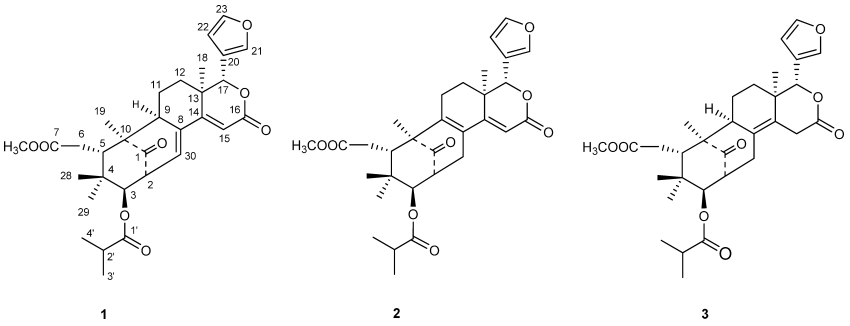
Table 1. ^{1}H- (HSQC), ^{13}C-NMR Data, HMBC and ^{1}H–^{1}H COSY Correlations for Xylomexicanolides A (**1**) (500 MHz for ^{1}H and 125 MHz for ^{13}C) and B (**2**) (400 MHz for ^{1}H and 100 MHz for ^{13}C) ($CDCl_3$)

Carbon No.	^{1}H-NMR [δH; mult.; J (Hz)]		^{13}C-NMR		HMBC correlations		^{1}H–^{1}H COSY correlations	
	A (**1**)	B (**2**)	A (**1**)	B (**2**)	A (**1**)	B (**2**)	A (**1**)	B (**2**)
1			214.2; qC	213.2; qC				
2	3.64 br d	3.14 t; 6.5	49.0; CH	46.6; CH	1,3,4,8,30	1,3,8,30	3,30	3,30α,30β
3	4.88 d; 9.0	5.11 d; 7.5	78.0; CH	78.0; CH	2,4,5,30,1′	2,4,5,30,1′	2	2
4			38.9; qC	37.7; qC				
5	3.30 dd; 9.5, 2.0	2.88 t; 6.0	40.5; CH	49.2; CH	4,6,10	4,6,10	6	6
6a	2.33 d; 2.0	2.31 d; 6.0	33.0; CH_2	32.2; CH_2	5,7	5,7	5	5
6b	2.36 d; 9.5				5,7	5,7	5	5
7			173.7; qC	173.9; qC				
8			136.0; qC	125.5; qC				
9	2.29 m		53.5; CH	151.9; qC	8,10,11		11α,11β	
10			51.8; qC	51.2; qC				
11α	1.77 m	2.59 m	21.4; CH_2	22.3; CH_2	8,9,12,13	8,9,12,13	9,11β,12α,12β	11β,12α,12β
11β	1.55 m	2.24 m			8,9,12,13	8,9,12,13	9,11α,12α,12β	11α,12α,12β
12α	1.29 m	1.89 m	32.5; CH_2	30.0;CH_2	9,11,13,14,17	9,11,13,14,17	11α,11β,12β	11α,11β,12β
12β	1.46 m	1.62 m			9,11,13,14,17	9,11,13,14,17	11α,11β,12α	11α,11β,12α
13			37.5; qC	36.8; qC				
14			160.7; qC	158.0; qC				
15	6.22 s	5.81 s	112.1; CH	109.9; CH	8,13,14,16	8,13,14,16		
16			164.9; qC	165.5; qC				
17	5.14 s	5.06 s	79.8; CH	80.8; CH	13,16,20,21,22	13,16,20,21,22		
18	1.04 s	0.97 s	22.3; CH_3	16.1; CH_3	12,13,14,17	12,13,14,17		
19	1.18 s	1.09 s	15.6; CH_3	16.9; CH_3	1,5,9,10	1,5,9,10		
20			120.2; qC	119.9; qC				
21	7.51 br s	7.49 br s	141.4; CH	141.2; CH	20,22,23	20,22,23	22,23	22,23
22	6.47 br s	6.44 br s	110.2; CH	110.0; CH	20,21,23	20,21,23	21,23	21,23
23	7.42 br s	7.44 br s	143.1; CH	143.1; CH	20,21,22	20,21,22	21,22	21,22
28	0.81 s	1.12 s	21.8; CH_3	25.9; CH_3	3,4,5,29	3,4,5,29		
29	0.74 s	0.90 s	21.2; CH_3	25.7; CH_3	3,4,5,28	3,4,5,28		
30α	6.29 dd; 6.0, 3.0	2.51 m	128.9; CH	30.6; CH_2	2,8,9,14	2,3,8,14	2	2,30β
30β		2.84 br d; 17.2				2,3,8,14		2,30α
7-OMe	3.68 s	3.69 s	52.0; CH_3	52.1; CH_3	7	7		
3-Acyl-1′			176.1; qC	175.9; qC				
2′	2.70 m	2.55 m	34.2; CH	34.3; CH	1′,3′,4′	1′,3′,4′	3′,4′	3′,4′
3′	1.26 d; 7.0	1.21 d; 7.0	19.2; CH_3	19.3; CH_3	1′,2′,4′	1′,2′,4′	2′	2′
4′	1.27 d; 7.0	1.21 d; 7.0	19.1; CH_3	19.0; CH_3	1′,2′,3′	1′,2′,3′	2′	2′



1 **2** **3**

Fig. 1. Structures of Compounds **1**—**3** with Relative Stereochemistry

carbon (δ_C 176.1 qC) of an isobutyryl group disclosed its location at C-3.

The relative configuration of **1** was established on the basis of NOE interactions (Fig. 2). The significant NOE interaction, observed in **1** from H-3 to H_3-29, but not from H-3 to H-5, helped to establish the 3α-H and the corresponding 3β-*O*-isobutyryl group. Similarly, NOE interactions between H-5/H-6a, H-5/H_3-28, and H-5/H-11β indicated the β-orientation of H-5, and those between H-17/H-11β, and H-17/H-12β suggested the β-orientation of H-17. Thus, the relative configuration of **1**, named xylomexicanolide A, was established as shown in Fig. 1.

The molecular formula of xylomexicanolide B (**2**) was established as the same as that of **1** by HR-TOF-MS (*m*/*z*: Calcd: 539.2639; Found: 539.2648 $[M+H]^+$). The NMR data of **2** were similar to those of **1**, except for the absence of a $\Delta^{8,30}$ double bound [δ_H 6.29 (dd, J=6.0, 3.0 Hz); δ_C 128.9 CH, 136.0 qC in **1**] and the presence of an additional $\Delta^{8,9}$ double bound [δ_C 125.5 qC, 151.9 qC in **2**] (Table 1). The existence of the above $\Delta^{8,9}$ double bound was confirmed by HMBC correlations between H_3-19/C-9, H_2-11/C-9, H_2-30/C-8, and H-15/C-8. Therefore, the structure of **2**, named

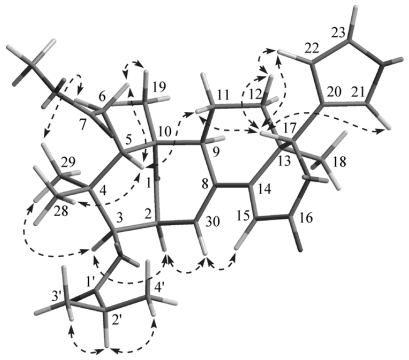


Fig. 2. Diagnostic NOE Interactions for Compound **1**

Table 2. ^{1}H- (HSQC), ^{13}C-NMR Data, HMBC and ^{1}H–^{1}H COSY Correlations for Khayasin (**3**) (500 MHz for ^{1}H- and 125 MHz for ^{13}C-NMR, $CDCl_3$)

Carbon No.	H-NMR [δ_H; mult.; J (Hz)]	^{13}C-NMR	HMBC correlations	^{1}H–^{1}H COSY correlations
1		217.9; qC		
2	3.13 m	48.0; CH	1,3,8,10,30	3,30α,30β
3	4.95 d; 10.0	78.0; CH	1,2,4,5,30,1′	2
4		38.4; qC		
5	3.21 dd; 9.0, 4.0	40.7; CH	4,6,10	6a,6b
6a	2.32 br s	33.4; CH_2	5,7	5
6b	2.36 d; 6.5		5,7	5
7		174.1; qC		
8		127.7; qC		
9	2.04 br s	52.2; CH	8,10,11	11α,11β
10		52.8; qC		
11α	1.79 m	18.7; CH_2	8,9,12,13	9,11β,12α,12β
11β	1.67 m		8,9,12,13	9,11α,12α,12β
12α	1.09 m	29.1; CH_2	9,11,13,14,17	11α,11β,12β
12β	1.76 m		9,11,13,14,17	11α,11β,12α
13		38.1; qC		
14		131.6; qC		
15α	3.44 d; 20.0	33.1; CH_2	8,13,14,16	9,15β
15β	3.73 d; 20.0		8,13,14,16	9,15α
16		169.6; qC		
17	5.64 s	80.6; CH	13,16,20,21,22	
18	1.03 s	17.7; CH_3	12,13,14,17	
19	1.13 s	16.5; CH_3	1,5,9,10	
20		120.6; qC		
21	7.52 br s	141.6; CH	20,22,23	22,23
22	6.45 br s	109.8; CH	20,21,23	21,23
23	7.38 br s	142.7; CH	20,21,22	21,22
28	0.78 s	20.5; CH_3	3,4,5,29	
29	0.70 s	23.1; CH_3	3,4,5,28	
30α	2.10 dd; 15.0, 6.0	33.1; CH_2	2,8,9,14	2,30β
30β	2.79 dd; 15.0, 2.0		2,8,9,14	2,30α
7-OMe	3.75 s	51.9; CH_3	7	
3-Acyl-1′		176.4; qC		
2′	2.60 m	34.3; CH	1′,3′,4′	3′,4′
3′	1.20 d; 7.0	19.8; CH_3	1′,2′,4′	2′
4′	1.21 d; 7.0	18.4; CH_3	1′,2′,3′	2′

xylomexicanolide B, was established as shown.

Khayasin (**3**) was isolated as a white, amorphous powder. Its molecular formula of $C_{31}H_{40}O_8$ was established by HR-TOF-MS (m/z 563.2625, Calcd for $[M+Na]^+$ 563.2621), indicating that **3** had twelve degrees of unsaturation. The NMR data of **3** were similar to those of **1**, except for the absence of two olefinic methine groups [δ_H 6.22 s, 6.29 (dd, J=6.0, 3.0 Hz); δ_C 112.1, 128.9; CH-15 and CH-30 in **1**] and the presence of two additional aliphatic methylene groups [δ_H 3.44 (d, J=20.0 Hz), 3.73 (d, J=20.0 Hz), 2.10 (dd, J=15.0, 6.0 Hz), 2.79 (dd, J=15.0, 2.0 Hz); δ_C 33.1, 33.1; CH_2-15 and CH_2-30 in **3**] (Table 2). A methylene group [δ_H 3.44 (d, J=20.0 Hz), 3.73 (d, J=20.0 Hz), δ_C 33.1 CH_2], having a HMBC correlation to C-16, was assigned to CH_2-15. Another methylene group [δ_H 2.10 (dd, J=15.0, 6.0 Hz), 2.79 (dd, J=15.0, 2.0 Hz), δ_C 33.1 CH_2], showing a ^{1}H–^{1}H COSY correlation to H-2, was attributed to CH_2-30. Moreover, the existence of a $\Delta^{8,14}$ double bound was corroborated by HMBC interactions between H-9/C-8, H_2-30/C-8, H_2-30/C-14, H_2-15/C-14, and H_3-18/C-14. Thus, the structure of **3** was identified as khayasin[11] (Fig. 1). Its ^{13}C-NMR data were reported for the first time.

The obtained mexicanolides were tested for insecticidal activity using a conventional leaf disk method against the fifth instar larvae of *Brontispa longissima* (Gestro). Khayasin exhibited potent insecticidal activity at a concentration of 10 mg/l, whereas other compounds showed less activities. Its lethal rates against the fifth instar larvae of *B. longissima* (Gestro) at exposure times of 24 and 48 h were 75.8% and 89.1%, respectively.

In summary, xylomexicanolides A, B and khayasin are rare mexicanolides possessing a $\Delta^{8,30}$ double bond, or $\Delta^{8,9}$, $\Delta^{8,14}$ double bonds inside their nucleus. Khayasin was found to exhibit potent insecticidal activity against the fifth instar larvae of *Brontispa longissima* (Gestro). This study demonstrated that mangrove plants of the xylocarpus genus are a new source for the production of limonoids with potent insecticidal activity.

Experimental

General Experiment Procedures Optical rotations were recorded on a Polaptronic HNQW5 automatic high-resolution polarimeter (Schmidt & Haensch Co., Ltd.). UV spectra were obtained on a Beckman DU-640 UV spectrophotometer and matrix assisted laser desorption/ionizatio (MALDI)-TOF-MS spectra were measured on a Bruker APEX II spectrometer in positive ion mode (spray voltage was set at 4.5 kV, drying gas flow was at 35 psi, and the temperature was at 275 °C). NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard using a Bruker AV-400 or AV-500 spectrometer. Preparative HPLC was carried out on ODS columns (250×10 mm i.d., YMC) with a Waters 2998 photodiode array detector. For CC, silica gel (200—300 mesh) (Qingdao Mar. Chem. Ind. Co., Ltd.) and RP C_{18} gel (Cosmosil C18-PREP 140 μm, Nacalai Tesque, Kyoto, Japan) were used.

Plant Material The seeds of *X. moluccensis* (Lam.) M. Roem. were collected in October 2007 at the mangrove wetlands in Krishna estuary, Andhra Pradesh, India. The identification of the plant was performed by one of the authors (T. S.). A voucher sample (No. IndianXM-01) is maintained in the Herbarium of the South China Sea Institute of Oceanology.

Extraction and Isolation The dried seeds (7.0 kg) of *X. moluccensis* were extracted five times with 95% ethanol at room temperature. The extract was concentrated under reduced pressure, followed by suspension in water and extraction with EtOAc. The resulting EtOAc extract (320 g) was chromatographed on silica gel CC and eluted using a $CHCl_3$–MeOH system (100 : 0—5 : 1) to yield 230 fractions. Fractions 70 to 80 were combined and further purified with RP C_{18} CC (MeCN–H_2O, 50 : 50—100 : 0) to afford 104 subfractions. Angolensic acid methyl ester (40 mg) was obtained in the subfraction 20. Subfractions 27 to 31 (2.0 g) were combined and further purified with preparative HPLC (YMC ODS-5-A, 250×10 mm, MeCN–H_2O, 50 : 50) to yield xylomexicanolides A (8 mg), B (4 mg), khayasin (17 mg), angolensic acid methyl ester (10 mg), khayasin T (6 mg), and 2′*S*-methylbutanoylproceranolide (10 mg).

Xylomexicanolide A (**1**): White, amorphous powder; $[\alpha]_D^{25}$ +8.9 (c=0.09, acetone); UV (MeCN) λ_{max} (log ε) 197.9 (3.76), 281.5 (3.59) nm; IR (film) ν_{max} 3441, 2976, 1728, 1639, 1260, 1158 cm^{-1}; ^{1}H- and ^{13}C-NMR data (see

Table 1); HR-TOF-MS *m*/*z* 561.2491 (Calcd for $C_{31}H_{38}O_8Na$ $[M+Na]^+$ 561.2464); CD (MeCN) 192 ($\Delta\varepsilon=-6.27$), 234 ($\Delta\varepsilon=+0.47$), 301 ($\Delta\varepsilon=+6.60$), and 339 nm ($\Delta\varepsilon=+0.37$).

Xylomexicanolide B (**2**): White, amorphous powder; $[\alpha]_D^{25}$ +129.2 ($c=0.13$, acetone); UV (MeCN) λ_{max} (log ε) 204.1 (4.16), 284.1 (4.34) nm; IR (film) ν_{max} 3445, 2975, 2929, 1729, 1606, 1260, 1158 cm^{-1}; ^1H- and ^{13}C-NMR data (see Table 1); HR-TOF-MS *m*/*z* 539.2648 (Calcd for $C_{31}H_{38}O_8$ $[M+H]^+$ 539.2639); CD (MeCN) 208 (De$\Delta\varepsilon=0.45$), 226 ($\Delta\varepsilon=+1.01$), 282 ($\Delta\varepsilon=+12.32$), and 312 nm ($\Delta\varepsilon=-1.16$).

Khayasin (**3**): White, amorphous powder; $[\alpha]_D^{25}$ −79.5 ($c=0.86$, acetone); UV (MeCN) λ_{max} 210.0 nm; ^1H- and ^{13}C-NMR data (see Table 2); HR-TOF-MS *m*/*z* 563.2625 (Calcd for $C_{31}H_{40}O_8Na$ $[M+Na]^+$ 563.2621).

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