Xylomexicanins K-N: limonoids from the leaves and twigs of *Xylocarpus granatum*

Shao-Jing Li, Li-Kang Zhao, Jin-Jun Chen, Chun-Hua Zhou, Xin-Li Huang, Yi-Bing Wu, Françoise Sauriol, Yu-Cheng Gu and Hiromasa Kiyota

School of Pharmaceutical Sciences, Hebei Medical University, Shijiazhuang, Hebei Province, P. R. China; The First Hospital of Hebei Medical University, Shijiazhuang, P. R. China; Department of Pathophysiology, Hebei Medical University, Shijiazhuang, China; Department of Chemistry, Queen’s University, Kingston, Ontario, Canada; Syngenta Jealott’s Hill International Research Centre, Berkshire, UK; Graduate School of Environmental and Life Science, Okayama University, Okayama, Japan

**ABSTRACT**

Six new compounds, xylomexicanins K-N (1–4), granasteroid (5) and 5-methoxy-2-pentylbenzofuran-7-ol (6), along with nine known compounds were isolated from the leaves and twigs of *Xylocarpus granatum*. Among them, 1 was a biogenetic precursor of 1,8,9-phragmalin limonoid, and 4 represent the first example of degraded A-ring limonoid. The structures of them were elucidated on the basis of one- and two-dimensional NMR spectroscopic data (including 1H, 13C-NMR, DEPT, 1H-1H COSY, HSQC, HMBC, and NOESY) and confirmed by high-resolution mass spectrometry.

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1. Introduction

Limonoids are triterpene derivatives from a precursor of a 4,4,8-trimethyl-17-furanylstereoid skeleton (Mulholland and Taylor 1992). More than 50 limonoid derivatives have been isolated from Xylocarpus granatum, which was used as a folk medicine in Southeast Asia (Ng and Fallis 1979; Wu et al. 2005; Yin et al. 2006; Wu et al. 2007; Du et al. 2009; Lakshmi et al. 2012). Previous chemical studies on the seeds of X. granatum by our group have resulted in the isolation of limonoids with new skeletons (Wu et al. 2013; 2014; 2015; 2017). In the current study, six new compounds, including four limonoids, xylomexicanins K-N (1–4) and a steroid, granasteroid (5) and an aromatic compound, 5-methoxy-2-pentylbenzofuran-7-ol (6), along with nine known compounds, 16-en-isosteviol (Chaturvedula and Prakash 2012), granaxylocarpin B (Yin et al. 2007), 1-acetyl-2-deacetoxyxyloccensin V (Zhou et al. 2014), 6-deoxydestigloylswietenin acetate (Shao et al. 2015), 9,19-cycloergostan-24(28)en-3-ol (Kikuchi et al. 1985), 9,19-cycloergostan-3-ol (Nascimento and Morais 1995), 2-deacetoxyxyloccensin V (Zhou et al. 2014), xylocarpin I (Cui et al. 2007) and xylocarpin G (Cui et al. 2007) were isolated from the leaves and twigs of the same plant collected in the Hainan province of China. Among the new compounds, 1 could be a biogenetic precursor of 1,8,9-phragmalin type limonoid, and 4 represents the first example of separated A-ring limonoid type compound.

2. Results and discussion

Xylomexicanin K (1) was obtained as a white power. The molecular formula was deduced as C_{33}H_{40}O_{14} with fourteen degrees of unsaturation by HRTOFMS. The 13C-NMR spectral data (Table S1) revealed that 1 contains three C=C and five C=O groups. Therefore, the remaining six unsaturations indicated that 1 contains six rings. The 1H- and 13C-NMR spectral data exhibited signals of seven Me, three CH2, ten CH groups (four O-bearing and four olefinic ones), and thirteen quaternary C-atoms. Three tertiary Me groups \( \delta_H 1.63 \) (s), 1.33 (s), 0.77 (s); \( \delta_C 16.4, 13.4, 14.5 \), one MeO group \( \delta_H 3.71 \) (s); \( \delta_C 52.1 \) and a \( \beta \)-substituted furan ring \( \delta_H 7.38 \) (s), 6.53 (s), 7.38 (s); \( \delta_C 141.9, 110.2, 142.5, 120.6 \) were assigned. The 13C-NMR spectra implied a C=C bond at C14/15 (\( \delta_C 120.5, 169.9 \)). These spectroscopic data of 1 indicated the limonoid nature, thus the connectivity of the tetra carbocyclic core structure was elucidated following the literature data and confirmed by 2D NMR analyses (Figure S2), as detailed for compound 3. The HMBC correlations from Me protons to the respective 13C resonances explained the three tertiary Me groups located at C-18, C-19, and C-28. The 1H-NMR and HMBC spectra exhibited three acetyl Me groups at \( \delta_H 2.12 \) (s), 1.53 (s), 2.07 (s). In addition, the 1H-NMR spectra exhibited three OH proton signals at \( \delta_H 4.24 \) (s), 3.77 (s), 3.49 (s). The NOESY correlations between OH (\( \delta_H 4.24 \)/H-11, OH (\( \delta_H 4.24 \)/Me-19, OH (\( \delta_H 4.24 \)/OH (\( \delta_H 3.77 \); OH (\( \delta_H 3.77 \)/H-30, OH (\( \delta_H 3.77 \)/Me-18; OH (\( \delta_H 3.49 \)/H-11, OH (\( \delta_H 3.49 \)/Me-19 located OH groups at C-1 (\( \delta_C 78.6 \), C-8 (\( \delta_C 70.4 \) and C-9 (\( \delta_C 81.5 \)), respectively. Three AcO groups signals (\( \delta_H 2.12 \), \( \delta_C 20.8 \), \( \delta_C 171.2 \); \( \delta_H 1.53 \), \( \delta_C 19.8 \), \( \delta_C 170.6 \); \( \delta_H 2.07 \), \( \delta_C 21.5 \), \( \delta_C 170.6 \) were located also by the NOESY correlations between \( \delta_H 1.53 \)/H-22 and \( \delta_H 2.07 \)/H-15 located AcO group (\( \delta_H 1.53 \), \( \delta_C 19.8 \), \( \delta_C 170.6 \) at C-12 (\( \delta_C 68.2 \) and (\( \delta_H 2.07 \), \( \delta_C 21.5 \), \( \delta_C 170.6 \) at C-30 (\( \delta_C 68.0 \), meanwhile, the last
one ($\delta_H$ 2.12, $\delta_C$ 20.8, $\delta_C$ 171.2) located at C-3 ($\delta_C$ 76.8). This rather low chemical shift ($\delta_H$ 1.53) is observed for a similar limonoid, as in xylocardin I ($\delta_H$ 1.65) (Cui et al. 2007), probably due to a ring current effect by the furan ring. Detailed analysis of the $^1H$-$^1H$ COSY and HMBC correlations further established the structure of 1 is a typical limonoid with three rarely unbonded OH groups at C-1, C-8 and C-9.

The relative configuration of 1 was defined on the basis of the NOESY spectrum. H-12 exhibited a NOE with H-17, but not with Me-18; Me-18 displayed a NOE with H-22, indicating that the furan ring, Me-18 and 12-OAc were on the same side. The NOE between H-11b/H-18, H-11b/1-OH, H-11b/9-OH, H-19/1-OH, H-19/9-OH, 8-OH/9-OH, but without NOE between H-30/1-OH, H-30/9-OH confirmed that 1-OH, 8-OH, 9-OH, Me-19 and 30-OAc were on the same side. The NOE correlations from H-2 to H-29b, from H-3 to H-29b and from H-5 to H-12 evidenced H-29, H-2, H-3 were on the same side and H-5 on the other side. Based on the above results, the relative stereochemistry of 1 was elucidated as shown in Figure 1.

Xylomexicanin K (1) with three rarely unbonded OH groups might be the biogenetic precursor of 1,8,9-phragmalin type limonoids forming the corresponding orthoacetate.

Xylomexicanin L (2) was obtained as a white power. The molecular formula was deduced as C$_{33}$H$_{42}$O$_{16}$ with fifteen degrees of unsaturation by HRTOFMS. The $^{13}$C-NMR spectral data (Table S1) revealed that 2 contains one C=C and six C=O groups. Therefore, the remaining eight unsaturations indicated that 2 consisted eight rings. The $^1$H-NMR and $^{13}$C-NMR spectra exhibited signals of eight Me (one MeO and four tertiary Me), four CH$_2$, nine CH groups (five O-bearing and one olefinic), and fourteen quaternary C-atoms (four O-bearing, six ester, and one olefinic C-atoms). The spectroscopic data showed it is a phragmalin orthoester, characterized by a methyl singlet at $\delta_H$ 1.63 (s) and the HMBC correlation with a quaternary carbon at $\delta_C$ 119.0 for a 1,1,1-trioxyethyl moiety. Typical oxygenated carbon resonances at $\delta_C$ 83.4, 84.3, and 86.5 further substantiated this orthoester identification. The HMBC correlations well
supported the limonoid core framework (Figure S7). The $^1$H-NMR spectra exhibited three acetyl Me groups at $\delta_H$ 2.17 (s), 1.90 (s), 2.01 (s) as deduced by the HMBC correlation from Me protons to the respective C=O resonances located AcO groups at C-3, C-12, and C-30, respectively. The above analyses of the $^1$H-NMR, $^{13}$C-NMR spectra suggested that 2 was a phragmalin orthoester limonoid with an $\alpha,\beta$-unsaturated lactone ring [$\delta_H$ 6.25 (br. s), 7.24 (s); $\delta_C$ 97.0, 147.9, 134.6, 167.1] at C-17 by the HMBC correlation from H-17 to C-20. Detailed analysis of the $^1$H-$^1$H COSY and HMBC correlations further established the connectivities of 2.

The relative configuration of 2 was defined on the basis of the NOESY spectrum. The NOE correlations from H-6b to H-19 and H-28, from H-28 to H-3, from H-3 to H-29b, from H-29a to H-19 evidenced the configuration of the bicyclo[2.2.1]heptane ring. The NOE between H-17/H-12, H-17/H-30, H-17/H-23 indicated that the $\alpha,\beta$-unsaturated lactone ring, 23-OH, 12-OAc and 30-OAc were on the same side. Based on the above results, the relative stereochemistry of 2 was elucidated as shown in Figure 1.

Xylomexicanin M (3) was obtained as a white powder. The molecular formula was deduced as C$_{35}$H$_{42}$O$_{14}$ with fifteen degrees of unsaturation by HRTOFMS. The $^{13}$C-NMR spectral data (Table S1) revealed that 3 contains two C=O and five C=O groups. Therefore, the remaining eight unsaturations indicated that 3 consisted eight rings. The $^1$H-NMR and $^{13}$C-NMR spectra exhibited signals of eight Me, four CH$_2$, ten CH groups (four O-bearing and three olefinic ones), and thirteen quaternary C-atoms (four O-bearing, five ester, and one olefinic C-atoms). In addition, three Me groups ($\delta_H$ 1.21, 1.05, 0.92; $\delta_C$ 13.9, 15.5, 14.2), one MeO group ($\delta_H$ 3.74, $\delta_C$ 51.6), and a $\beta$-substituted furan ring [$\delta_H$ 6.43 (br. s), 7.38 (br. t), 7.46 (br. s); $\delta_C$ 109.8, 142.9, 140.9, 120.6] were assigned. The spectroscopic data indicated a phragmalin 1,1,1-trioxyethyl derivative as in 2. Typical oxygenated carbon resonances at $\delta_C$ 83.0, 84.5, and 86.2 further substantiated this orthoester identification. The structure information of the limonoid core was obtained as following according to 2D NMR analyses (Figure S12). The COSY and HMBC cross-peaks of H-2/H-3, H-5/H-6, H-2/C-1, H-2/C-3, H-2/C-4, H-3/C-5, H-3/C-30, H-5/C-10, H-19/C-5, H-28/C-3 and the COSY analysis revealed a bicyclo[2.2.1]heptane core for the A/B-rings. The cyclohexane D-ring was also elucidated by those of H-11/ H-12, H-11/C-8, H-11/C-13, H-14/C-13. The A/B- and D- rings are connected through the C-ring, which was shown by the corelations of H-2/H-30, H-3/C-30, H-11/C-10, H-14/C-30, H-19/C-9. The HMBC correlations of H-17/C-12, H-17/C-14, H-17/C-21, H-17/C-22 and H-15/C-8 indicated the connection of the lactone and furan rings. Thus, limonoid core carbon framework of 3 was elucidated. The $^1$H-NMR spectra exhibited 3 acetyl Me groups at $\delta_H$ 2.22 (s), 1.59 (s), 2.03 (s) as deduced by the HMBC correlations from Me protons to the respective C=O resonances. The HMBC correlations between H-3 ($\delta_H$ 4.88)/C=O ($\delta_C$ 171.6), H-12 ($\delta_H$ 4.64, dd)/C=O ($\delta_C$169.3), and H-30 ($\delta_H$ 6.10)/C=O ($\delta_C$ 168.9) located AcO groups at C-3, C-12, and C-30, respectively.

Compound 3 showed significant NOESY cross-peaks from H-28 to H-3, from H-29a to H-19, from H-29b to H-3, from H-5 to H-12 and H-30, from H-12 to H-17, to H-21, from H-17 to H-21 (Figure S12). Based on the above information, the relative stereochemistry of 3 was elucidated as shown in Figure 1.

Xylomexicanin N (4) was obtained as a colourless oil. The molecular formula was deduced as C$_{15}$H$_{24}$O$_{5}$ with four degrees of unsaturation by HRTOFMS. The $^{13}$C-NMR
spectrum revealed that 4 contains one C = C and two C = O carbons. Therefore, the remaining one unsaturation required 4 to be monocyclic. The $^1$H NMR, and $^{13}$C NMR spectra (Table S2) showed the presence of six Me, one CH$_2$, four CH groups (one oxygenated and one olefinic), and four quaternary carbons (one keto, one ester, and one olefinic carbon). In addition, two tertiary Me ($\delta_H$ 1.19 (s) and 1.05 (s); $\delta_C$ 28.1 and 20.3), three MeO ($\delta_H$ 3.69, 3.35 and 3.34; $\delta_C$ 51.9, 54.3 and 54.2), and one keto C = O ($\delta_C$ 199.0) groups were also observed in the $^{13}$C NMR spectrum. Furthermore, two geminal Me singlets resonated at $\delta_H$ 1.19 and 1.05 exhibited HMBCs to the quaternary carbon atom (C-4) and a saturated CH carbon C-5, which implied that C-4 was located between C-3 and C-5, bearing two Me groups. The mentioned spectroscopic data implied an A-ring of limonoid type feature of 4, the same numbering as limonoid were kept to show the similarity.

The relative stereochemistry of 4 was elucidated as 5,10-trans, considering the biogenetic origin and that no NOE correlation was observed between H$_2$-6ab to H-19. (Figure S18).

The biogenetic precursor of 4 might be xylomexicanin F (B-ring seco-limonoid), found also in this plant by us (Wu et al. 2014). The C-9-C-30 bond of B-ring may be ruptured to form 4.

Granasteroid (5) was obtained as a white powder. The molecular formula was deduced as C$_{29}$H$_{44}$O$_3$ with eight degrees of unsaturation by HRTOFMS. The $^{13}$C-NMR spectrum revealed that 5 contains two C = C and two C = O groups. Therefore, the remaining four unsaturations demonstrated that 5 consisting of four rings. The $^1$H- and $^{13}$C-NMR spectral data (Table S2) showed the presence of five Me [$\delta_H$ 1.17 (s), 0.77 (s), 0.78 (m), 0.80 (d), 0.85 (d); $\delta_C$ 17.3, 12.2, 12.1, 18.9, 21.0], nine CH$_2$, ten CH [three olefinic ones, $\delta_H$ 5.72 (s), 5.29 (dd), 5.33 (dd)] groups, five quaternary C-atoms [one C = O ($\delta_C$ 199.5), one COOH ($\delta_C$ 176.3) and one olefinic C-atom ($\delta_C$ 171.2)]. The $^{13}$C-NMR signals appearing at $\delta_C$ 199.5, 171.2, 123.8, 38.5, 35.7, and 33.9, elucidated 5 was to contain an $\alpha,\beta$-unsaturated carbonyl structural unit in ring A. The presence of a COOH group was also determined from the $^{13}$C-NMR chemical shifts $\delta_C$ 176.3. The HMBC spectra from H-20 to C-21 (Figure S23) allowed us to determine the position of the COOH group to be at C-20. The HMBCs from 18-Me to C-12, to C-13, to C-14 and to C-17; from 19-Me to C-1, to C-9 and to C-10; from 26-Me to C-24 and to C-25, from 27-Me to C-24, to C-25 and C-26; indicated that 5 was a typical steroid. On the basis of above findings and other detailed NOE correlations, the structure of 5 was fully established as a rare 21-carboxy steroid (Su et al. 2007, Chao et al. 2008).

5-Methoxy-2-pentylbenzofuran-7-ol (6) was obtained as a yellow viscous liquid. The molecular formula was deduced as C$_{14}$H$_{18}$O$_3$ with six degrees of unsaturation by HRTOFMS. The $^1$H-NMR and $^{13}$C-NMR spectra (Table S2) exhibited signals of two Me, four CH$_2$, three CH groups and five quaternary C-atoms. The $^1$H-NMR spectrum showed OH [$\delta_H$ 11.13 (s)], MeO [$\delta_H$ 3.86 (s)], and pentyl groups [$\delta_H$ 2.49 (t), 1.69 (quint), 1.36 (m), 1.36 (m), 0.91 (t)]. The HMBC correlations from $\delta_H$ 11.13 (s) to C-7a and C-6 implied that the OH was located at C-7; from H-1’ to C-1, C-2, C-10 and from H-5’ to C-3’, C-4’ implied that the pentyl group was assigned to C-2 (Figure S28). The NOSEY correlations from 5-OMe to H-6 and to H-4 allowed an assignment to a 5-OMe group.
On the basis of above findings and other detailed NOE correlations, the structure of 6 was fully established as a 5-methoxy-2-pentylbenzofuran-7-ol.

3. Experimental

3.1. General

Optical rotations were measured with a Jasco DIP-370. NMR analysis was performed using a Bruker AV-600; at 600 MHz (1H) and 151 MHz (13C) (δ in ppm rel. to Me₄Si as an internal standard, J in Hz). MS analysis was performed using a QStar XL QqTOF (ESI) from Applied Biosystems. Chromatography was carried out with silica gel 200-300 mesh (Qingdao Marine Chemical Factory, China). Semipreparative HPLC was performed using a Waters Delta Prep 3000 pump with a UV 2487 detector, and a Whatman Partisil 10 ODS-2 column (9.4 × 250 mm).

3.2. Plant material

Twigs and leaves of X. granatum were collected in March 2012 at Hainan Island, Southern China, dried at ambient temperature, and identified by Dr. Wen-Qing Wang, School of Life Sciences, Xia-Men University, China. Several voucher specimens (No. HEBNMC-2012-2) have been deposited in the herbarium of School of Pharmaceutical Sciences, Hebei Medical University, China.

3.3. Extraction and isolation

Dried twigs and leaves (7 kg) of X. granatum were extracted with 95% ethanol at room temperature. After evaporation of the solvent under reduced pressure, the residue was suspended in water and extracted with petroleum ether and ethyl acetate, successively. The ethyl acetate extract (160 g) was chromatographed on silica gel and eluted using a petroleum/ethyl acetate system (8:1 to 1:3) to yield 8 fractions. Fraction 1 (19.9 g) was subjected to silica gel column eluting with petroleum/acetone (30:1) to yield 6 subfractions (F₁-₁ to F₁-₆). F₁-₁ was purified by silica gel column chromatography and a semipreparative HPLC with acetonitrile/water (80:20) as a mobile phase to yield 6 (1 mg, tR = 16.68 min). Fraction 2 (17 g) was subjected to silica gel column eluting with petroleum/acetone (12:1) to yield 26 subfractions. F₂-₆ to F₂-₁₅ were purified by recrystallization to yield 9,19-cycloergostan-24(28)en-3-ol (12 mg) and 9,19-cycloergostan-3-ol (9 mg). Fraction 6 (2.5 g) was applied on silica gel column and eluted with CH₂Cl₂-acetone (40:1) to obtained ten subfractions (F₆-₁ to F₆-₁₀). 5 (2 mg, tR = 17.59 min) and 16-en-isosteviol (5 mg, tR = 4.8 min) were isolated from fraction F₆-₁₀ on a semipreparative HPLC column with acetonitrile/water (90:10) as a mobile phase. Fraction 7 (14 g) was fractionated by silica gel column using petroleum/acetone (5:1) as an eluent to give a new fraction (121 mg) and separated on a semipreparative HPLC column with acetonitrile/water (75:25) as a mobile phase to yield 1 (1 mg, tR = 3.47 min), 2 (3 mg, tR = 3.43 min), 3 (1 mg, tR = 4.49 min), granaxylocarpin B (6 mg, tR = 4.74 min), 1-acetyl-2-deacetoxyxyloccensin V (5 mg, tR = 5.07 min), 6-deoxydestigloylswietensin acetate (7 mg, tR = 4.80 min), 2-deacetoxyxyloccensin V (4 mg, tR = 9.03 min), xylocarpin I (3 mg, tR = 9.86 min) and xylocarpin G (7 mg, tR = 9.63 min). Fraction 8 (490 mg) was
purified by silica gel column and separated on a semipreparative HPLC column with methanol/water (55:45) as a mobile phase to yield 4 (2 mg, t\textsubscript{R} = 12.5 min).

### 3.4. Xylomexicanin K (1)
White powder, [\(\alpha\)]\textsubscript{24}D +17 (c 0.10, CHCl\textsubscript{3}); UV (CHCl\textsubscript{3}) \(\lambda\text{max} (\log \varepsilon) 220\) nm; IR (KBr) \(\nu\text{max} 3600-3210, 1740-1710\) cm\(^{-1}\);
HRTOFMS m/z 660.2414; calcd. for C\textsubscript{33}H\textsubscript{40}O\textsubscript{14} (M\textsuperscript{+}), 660.2418.

### 3.5. Xylomexicanin L (2)
White powder, [\(\alpha\)]\textsubscript{24}D-34 (c 0.10, CHCl\textsubscript{3}); UV (CHCl\textsubscript{3}) \(\lambda\text{max} \text{nm} 214\); IR (KBr) 3600-3200, 1740-1715 cm\(^{-1}\);
HRTOFMS m/z 718.2476; calcd. for C\textsubscript{35}H\textsubscript{42}O\textsubscript{16} (M\textsuperscript{+}), 718.2473.

### 3.6. Xylomexicanin M (3)
White powder, [\(\alpha\)]\textsubscript{24}D -31 (c 0.10, CHCl\textsubscript{3}); UV (CHCl\textsubscript{3}) \(\lambda\text{max} \text{nm} 214\); IR (KBr) 3600-3200, 1739-1715 cm\(^{-1}\);
HRTOFMS m/z 686.2572; calcd. for C\textsubscript{35}H\textsubscript{42}O\textsubscript{14} (M\textsuperscript{+}), 686.2575.

### 3.7. Xylomexicanin N (4)
Colourless oil, [\(\alpha\)]\textsubscript{24}D -25 (c 0.10, CHCl\textsubscript{3}); UV (CHCl\textsubscript{3}) \(\lambda\text{max} \text{nm} 219\); IR (KBr) 2957, 1668, 1437 cm\(^{-1}\);
HRTO-MS m/z 284.1620; calcd. for C\textsubscript{13}H\textsubscript{24}O\textsubscript{5} (M\textsuperscript{+}), 284.1624.

### 3.8. Granasteroid (5)
White powder, [\(\alpha\)]\textsubscript{24}D +59 (c 0.10, CHCl\textsubscript{3}); UV (CHCl\textsubscript{3}) \(\lambda\text{max} \text{nm} 240\); IR (KBr) 3374, 2932, 1703, 1676, 1372 cm\(^{-1}\);
HRTOFMS m/z 440.3294; calcd. for C\textsubscript{29}H\textsubscript{44}O\textsubscript{3} (M\textsuperscript{+}), 440.3290.

### 3.9. 5-Methoxy-2-pentylbenzofuran-7-ol (6)
White powder, [\(\alpha\)]\textsubscript{24}D -12 (c 0.10, CHCl\textsubscript{3}); HRTOFMS m/z 234.1253; calcd. for C\textsubscript{14}H\textsubscript{18}O\textsubscript{3} (M\textsuperscript{+}), 234.1256.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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ORCID

Yu-Cheng Gu http://orcid.org/0000-0002-6400-6167
Hiromasa Kiyota http://orcid.org/0000-0002-1330-6522

References

Chao CH, Wen ZH, Chen IM, Su JH, Huang HC, Chiang MY, Sheu JH. 2008. Anti-inflammatory steroids from the octocoral Dendronephthya griffini. Tetrahedron. 64:3554–3560.
Chaturvedula VSP, Prakash I. 2012. Spectral analysis and chemical studies of the sweet constituent, rebaudioside A. Eur J Med Plants. 2:57–65.
Cui J, Wu J, Deng Z, Proksch P, Lin W. 2007. Xylocarpins A-I, limonoids from the Chinese mangrove plant Xylocarpus granatum. J Nat Prod. 70:772–778.
Du S, Wang M, Zhu W, Qin Z. 2009. A new fungicidal lactone from Xylocarpus granatum (Meliaceae). Nat Prod Res. 23:1316–1321.
Kikuchi T, Kadota S, Suehara H. 1985. Studies on the constituents of orchidaceous plants. II. Isolation, structures, and stereochemistry of cyclonervilol, cyclohomonervilol, and dihydrocycloecucaleanol C-24 epimers, new triterpenes from Nervilia purpurea schlechter. Chem Pharm Bull. 33:1914–1929.
Lakshmi V, Srivastava S, Ishra SK, Srivastava MN, Srivastrava K, Pur SK. 2012. Antimalarial activity in Xylocarpus granatum (Koen). Nat Prod Res. 26:1012–1015.
Mulholland DA, Taylor DAH. 1992. Limonoids from Australian members of the meliaceae. Phytochemistry. 31:4163–4166.
Nascimento EA, Morais SAL. 1995. The composition of wood extracts form Spanish Pinus pinaster and Brazilian Pinus caribaea. J Brazil Chem Soc. 6:331–336.
Ng A, Fallis A. 1979. Comment: 7α-Acetoxydihydronomilin and mexicanolide: limonoids from Xylocarpus granatum (Koenig). Can J Chem. 57:3088–3089.
Shao K, Shen L, Wu J. 2015. Limonoids from Indian mangrove, seeds of Xylocarpus moluccensis. Chin Trad Herb Drugs. 46:2198–2205.
Su JH, Lin FY, Dai CF, Wu YC, Hsu CH, Sheu H. 2007. New steroids from the soft coral Nephthea chabrolii. Bull Chem Soc Jpn. 80:2547–2550.
Wu J, Zhang S. 2007. Xylogranatin E, a new phragmalin with a rare oxygen bridge between C1 and C29, from the fruit of a Chinese mangrove Xylocarpus granatum. Z Naturforsch. 62B:569–572.
Wu YB, Liu D, Liu PY, Yang XM, Liao M, Lu NN, Sauriol F, Gu YC, Shi QW, Kiyota H, et al. 2015. New limonoids from the seeds of Xylocarpus granatum. Helv Chim Acta. 98:691–698.
Wu YB, Ni ZY, Huo CH, Su J, Dong M, Sauriol F, Shi QW, Gu YC, Kiyota H. 2013. Xylomexicanins C and D, new mexicanolide-type limonoids from Xylocarpus granatum. Biosci Biotechnol Biochem. 77:736–740.
Wu YB, Qings X, Huo CH, Yan HM, Shi QW, Sauriol F, Gu YC, Kiyota H. 2014. Xylomexicanins E-H, new limonoids from Xylocarpus granatum. Tetrahedron. 70:4557–4562.
Wu YB, Wang YZ, Ni ZY, Qings X, Shi QW, Sauriol F, Vavricka CJ, Gu YC, Kiyota H. 2017. Xylomexicanins I and J: limonoids with unusual B/C rings from Xylocarpus granatum. J Nat Prod. 80:2547–2550.
Wu J, Zhang S, Song Y, Xiao Z, Xiao Q, Li Q. 2005. Two new mexicanolides from the fruit of the Chinese mangrove Xylocarpus granatum. Z Naturforsch. 60B:1291–1294.
Yin S, Fan CQ, Wang XN, Lin LP, Ding J, Yue JM. 2006. Xylogranatins A-D: novel tetranortriterpenoids with an unusual 9,10-seco scaffold from marine mangrove Xylocarpus granatum. Org Lett. 8:4935–4938.
Yin S, Wang XN, Fan CQ, Lin LP, Ding J, Yue JM. 2007. Limonoids from the seeds of the marine mangrove Xylocarpus granatum. J Nat Prod. 70:682–685.
Zhou ZF, Kong LY, Kurtan T, Liu HL, Mándi A, Li J, Gu YC, Guo YW. 2014. Four phragmalin orthoesters from the Chinese mangrove Xylocarpus granatum. Planta Med. 80:949–954.