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Five new limonoids isolated from *Walsura robusta*

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Abstract

Five new toosendanin limonoids with highly oxidative furan ring walsurobustones A-D (**1–4**), and one new furan ring degraded limonoid walsurobustone E (**5**) together with one known compound toonapubesic acid B (**6**) were isolated from the leaves of *Walsura robusta*. Their structures were elucidated by NMR and MS data. Especially, the absolute configuration of toonapubesic acid B (**6**) was confirmed by X-ray diffraction study. Compounds **1–6** exhibited good cytotoxicity against the cancer cell lines HL-60, SMMC-7721, A-549, MCF-7, and SW480.

Keywords Limonoids, Tetranortriterpenoids, *Walsura robusta*, Cytotoxicity

1 Introduction

Limonoids, well known as tetranortriterpenoids, were widely found in the families of Meliaceae and Rutaceae, which have attracted great interests from the chemical and biological research communities [1, 2]. The genus *Walsura* (Meliaceae), comprising about 16 species, distributes in subtropical regions such as Southern China, India, and Indonesia [3]. In previous literature, kinds of natural products such as triterpenoids, phenols, and steroids have been identified in this genus. Some triterpenoids and phenols exhibited cell protection, antioxidation and antimalarial activities [4–14]. However, the chemical constituents from *Walsura robusta* and their activities study are few. We reported herein the isolation, characterization as well as cytotoxic activity of these highly oxidized limonoids and a plausible biosynthesis pathway of **5** and **6**.

2 Results and discussion

The MeOH extract of *Walsura yunnanensis* was filtered and concentrated in *vacuo* to afford a residue, which was then defatted by petroleum ether and extracted with EtOAc. The EtOAc fraction was subjected to column chromatography on silica gel, ODS, HPLC, and Sephadex LH-20 to yield compounds **1–6** (detailed procedures see Extraction and Isolation part).

Walsurobustone A (**1**) was isolated as a white amorphous powder. Its molecular formula was determined to be $C_{28}H_{38}O_9$ by the $[M+Na]^+$ ion peak at *m/z* 541.2418 (calcd 541.2413 for $C_{28}H_{38}O_9Na$) in the HRESIMS, with 16 mass units less than that of the known compound yunnanol A, isolated from the congener plant

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W. yunnanensis [15]. The ^{13}C NMR data (Table 2) of **1** showed high similarity to those reported for yunnanol A, with the main difference is the absence of signals for the hydroxyl at C-11 (δ_H 1.81, 1H, m and 1.56, 1H, m; δ_C 19.2) in **1**, while δ_H 5.03 (1H, m) and δ_C 67.0 in yunnanol A. The proton at H-22 (δ_H 3.79), coupled with the proton at H-23 (δ_H 4.77) in the COSY, indicated the two hemiacetal carbons at C-21 (δ_C 109.5) and C-23 (δ_C 110.4). A combined analysis of HSQC and HMBC data showing 21-OCH_3 (δ_H 3.22, 3H, s), 22-OH (δ_H, 5.33, s) and 23-OCH_3 (δ_H 3.30, 3H, s) attached to C-21 (δ_C 109.5), C-22 (δ_C 77.5) and C-23 (δ_C 110.5) respectively revealed identical substituted furan ring when compared to yunnanol A. The HMBC correlations networks of 20-OH (δ_H 4.35, s) to C-20 (δ_C 80.4), C-21 (δ_C 109.5), C-17 (δ_C 46.8), and C-22 (δ_C 77.5) confirmed the furan ring attached at C-17. According to the above information, the planar structure of **1** was elucidated as shown.

The absolute stereochemistry of the C-17 was inferred by biosynthetic path as **1** was the homolog with compound **6** whose absolute configuration was determined by X-ray diffraction study. The relative stereochemistry of the tetrahydrofuran ring of **1** was achieved with the aid of ROESY experiment, in which, the correlations of H-21/OMe-23, and H-21/H-22 suggested these protons and the methoxy were homolateral of the tetrahydrofuran ring. The ROESY cross-peaks of H-23/OH-20 indicated that they are on the other face of the tetrahydrofuran ring. The structure of **1** was elucidated as shown in Fig. 1.

Walsurobustone B (**2**), a white amorphous powder, showed a molecular ion peak at *m/z* 641.2938 $[M+Na]^+$ in the HRESIMS (calcd for $C_{33}H_{46}O_{11}Na$ 641.2937), consistent with the molecular formula $C_{33}H_{46}O_{11}$, which revealed that **2** possessed five more carbon and two more oxygen than compound **1**. The difference part was identified as a 2-methylbutyric ester moiety by analysis of ^1H and ^{13}C NMR data (Tables 1 and 2). The correlations of H_3-5′/H_2-3′; H_2-3′/ H-2′; H_3-4′/H-2′ in ^1H–^1H COSY spectra confirmed the presence of 2-methylbutanoate moiety. The location of 2-methylbutyric ester moiety at C-11 was proved by COSY correlation of H-11 (δ_H 5.16, m)/ H-9 (δ_H 3.06, d, 11.5 Hz), as well as HMBC correlation from H-11 to C-1′ (δ_C 174.9). The relative configuration of **2** was established by NOESY experiment. The NOESY correlations H-17/H-21, H-17/ H-22, OH-22/H-23, and H-23/OH-20 indicated the former three protons were on the same side of the tetrahydrofuran ring, while the latter three protons were on another side. The strong cross-peaks of H-11/Me-19 and H-11/Me-30 demonstrated that H-11 was β-configuration. Accordingly, the structure of **2** was assigned as depicted in Fig. 1.

Walsurobustone C (**3**), a white amorphous powder, had the molecular formula of $C_{27}H_{32}O_7$ as established by the

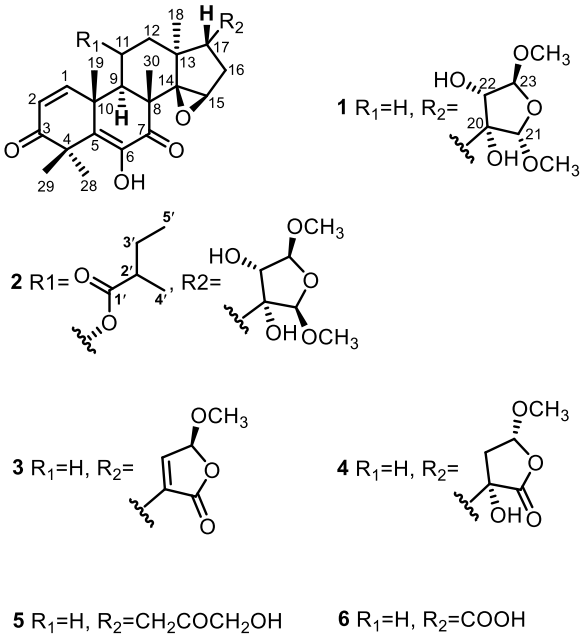


Fig. 1 The chemical structures of **1–6**

HRESIMS at *m/z* 491.2048 $[M+Na]^+$ (calcd. 491.2045). The ^1H and ^{13}C NMR data (Tables 1 and 2) suggested that the compound **3** was structurally related to walsunoid B [16] as the NMR data of both the compounds are almost similar. The main difference between **3** and walsunoid B is the absence of signals for the hydroxyl at C-11(δ_H 1.84, 2H, m; δ_C 19.6) in **3**, while C-11 (δ_H 5.05, 1H, d, 6.2 Hz; δ_C 66.5) in walsunoid B. Particularly, 23-OMe in **3** was assigned to be α-oriented by comparing the relevant NMR data with a reported compound walsunoid D [16] (δ_H 5.72 (1H, m) and δ_C 102.4 of CH-23 in **3**; δ_H 5.73 (1H, brs) and δ_C 102.5 of CH-23 in walsunoid D). Thus compound **3** was deduced as walsurobustone C (Fig. 1).

Walsurobustone D (**4**) also exhibited a molecular formula ion peak at *m/z* 509.2141 $[M+Na]^+$ (calcd for $C_{27}H_{34}O_8Na$ 509.2151) in its HRESIMS. The ^1H and ^{13}C NMR data of **4** is similar to that of isowalsuranolide [4] except for additional NMR signals (δ_C 56.5 and δ_H 3.40) due to a methoxy group and the hydrated double bond in the E ring. The location of the methoxy group was established by the HMBC correlation of methoxy methyl protons to the hemiacetal carbon signal at C-21 (δ_C 109.8). Furthermore, the HMBC correlations from δ_H 5.29 (s, –OH) to C-20 (δ_C 77.3), C-21 (δ_C 109.8), C-17 (δ_C 46.1) and C-22 (δ_C 38.6) indicated that the hydroxyl group δ_H 5.29 attached to the characteristic quaternary carbon C-20 (δ_C 77.3). The relative configuration of the tetrahydrofuran ring of **4** was established by analysis of the ROESY spectrum. ROESY correlation between H-17 and H-23 indicated that they were co-facial and arbitrarily assigned

Table 1 ^{1}H NMR spectroscopic data for **1**–**6**

Position	1[a]	2[a]	3[b]	4[b]	5[b]	6[b]
1	7.13, d (10.0)	7.51, d (10.0)	6.89, d (10.0)	7.13, d (10.0)	6.90, d (10.0)	6.91, d (10.0)
2	6.06, d (10.0)	6.10, d (10.0)	6.11, d (10.0)	6.08, d (10.0)	6.11, d (10.0)	6.11, d (10.0)
9	2.59, d (12.0)	3.06, d (11.5)	2.62, m	2.59, d (12.0)	2.63, m	2.60, d (10.6)
11	1.81, m 1.56, m	5.16, m	1.84, m	1.85, m 1.58, m	1.81, m	1.83, m
12	1.74, m 1.89, m	2.19, dd (13.4, 6.8) 1.71, m	2.39, m 1.67, m	1.73, m 1.66, m	1.85, m 1.54, m	2.15, m 1.83, m
15	3.56, s	3.64, s	3.77, s	3.62, s	3.69, s	3.73, s
16	1.94, m 1.76, m	1.94, m 1.77, m	2.25, dd (13.2, 6.0) 1.97, dd (13.6, 11.2)	1.91, m 1.82, m	2.23, t (6.4) 1.46, m	2.25, dd (14.1, 6.9) 2.11, m
17	1.77, m	1.79, m	2.67, m	1.82, m	2.06, m	2.54, dd (10.1, 7.1)
18	1.04, s	1.09, s	0.80, s	0.97, s	0.88, s	0.99, s
19	1.14, s	1.18, s	1.28, s	1.14, s	1.27, s	1.27, s
20					2.36, dd (10.0, 5.5) 2.27, t (10.0)	
21	4.48, s	4.49, s				
22	3.79, dd (7.2, 4.0)	3.72, dd (8.0, 4.4)	6.74, m	2.32, d (17.0) 2.65, d (17.0)		
23	4.77, d (4.0)	4.77, d (4.4)	5.72, d (1.7)	4.96, s	4.23, s	
28	1.45, s	1.45, s	1.57, s	1.45, s	1.48, s	1.56, s
29	1.37, s	1.37, s	1.48, s	1.37, s	1.57, s	1.48, s
30	0.93, s	1.00, s	1.10, s	0.94, s	1.07, s	1.08, s
21-OCH_3	3.22, s	3.23, s				
23-OCH_3	3.30, s	3.30, s	3.55, s	3.40, s		
6-OH	8.35, s	8.55, s	6.41, s	8.38, s	6.44, s	
20-OH	4.35, s	4.62, d (3.8)		5.29, s		
22-OH	5.33, d (8.0)	5.43, d (8.0)				
2′		2.39, m				
3′		1.60, m 1.44, m				
4′		1.09, d (1.5)				
5′		0.83, t (7.4)				

[a] Measured in DMSO, [b]measured in $CDCl_3$. Chemical shifts (δ) are in ppm from TMS

as β-oriented. The correlations of Me-18 with OH-20, OH-20 with OMe-23 supported the α-orientation of OH-20 and OMe-23. Thus, the structure of **4** has been determined as showed in Fig. 1.

Walsurobustone E (**5**) was isolated as a white amorphous powder, and the molecular formula $C_{25}H_{32}O_6$ was assigned through its HRESIMS, at *m/z* 451.2096 $[M+Na]^+$ (calcd for $C_{25}H_{32}O_6Na$, 451.2091). The ^{1}H and ^{13}C NMR spectra showed signals for five methyls (δ_H 0.88, 1.07, 1.27, 1.48, and 1.57, each 3H), five methylenes, five methines, four high-field quaternary carbons (δ_C 48.7, 46.8, 40.4 and 41.4), two double bonds (δ_C 152.5, 141.3, 127.4, and 134.0) and three carbonyl carbons (δ_C 208.9, 203.8, and 198.0). These data indicated that **5** has the same core structure as cedrelone [17], except the absence of furan ring signal feature in compound **5**. Based on the HSQC and HMBC data analysis, a hydroxyl acetone moiety was revealed by a hydroxylmethyl group C-23 (δ_C 68.5, δ_H 4.23, and hydroxyl δ_H 5.31) attached to carbonyl C-22 (δ_C 208.7) (Fig. 2). The carbonyl C-22 linked to C-17 via C-20 was established by the HMBC correlations from H-17 (δ_H 2.06) to C-20 (δ_C 37.7) and C-22 (δ_C 208.7), and H-16a (δ_H 1.46) to C-20. Accordingly, the structure of **7** was assigned as depicted in Fig. 1.

Toonapubesic acid B [18] (**6**) was obtained as a colorless crystal (recrystallized in $MeOH/CH_3COCH_3$) and the molecular formula $C_{23}H_{28}O_6$ was assigned through its HRESIMS, at *m/z* 423.1777 $[M+Na]^+$ (calcd for $C_{23}H_{28}O_6Na$, 423.1783), suggesting 10 degrees of unsaturation. The ^{13}C NMR spectrum (Table 2) of **6** were very close to those for **5**, except that the furan ring was oxidized to a carboxylic acid in compound **6**. The inferred

Table 2 ^{13}C NMR spectroscopic data for **1**–**6**

Position	1[a]	2[a]	3[b]	4[b]	5[b]	6[b]
1	154.0	155.9	152.5	154.0	152.5	152.4
2	126.2	125.6	127.5	126.3	127.4	127.5
3	203.3	203.3	203.7	203.4	203.8	203.8
4	47.9	48.5	48.7	47.9	48.7	48.7
5	132.7	131.9	134.3	132.8	134.0	134.2
6	142.1	141.8	141.2	142.2	141.3	141.2
7	197.2	195.8	198.1	197.1	198.0	197.8
8	46.7	46.2	46.9	46.7	46.8	46.7
9	42.3	44.3	43.3	42.1	43.5	43.2
10	39.6	40.1	40.4	39.5	40.4	40.4
11	19.2	69.3	19.6	19.2	19.5	19.5
12	35.0	43.1	35.2	35.5	34.9	35.3
13	41.6	40.9	42.2	41.6	41.4	42.5
14	69.1	68.7	69.9	68.8	69.4	69.1
15	54.0	55.2	54.8	54.3	55.1	55.0
16	28.2	27.8	31.9	27.4	33.5	29.6
17	46.8	46.9	42.3	46.1	40.9	51.0
18	22.8	22.5	23.3	23.1	22.4	22.9
19	23.6	24.2	24.1	23.7	24.0	24.0
20	80.4	80.2	138.1	77.3	37.7	178.8
21	109.5	109.3	171.0	175.6		
22	77.5	77.6	144.8	38.6	208.9	
23	110.5	110.3	102.4	109.8	68.5	
28	26.5	26.9	26.9	26.5	26.9	26.9
29	20.8	20.7	21.3	20.9	21.3	21.3
30	19.8	20.9	20.3	19.7	20.4	20.3
21-OCH_3	54.5	54.5				
23-OCH_3	55.4	55.6	57.1	56.5		
1′		174.9				
2′		41.0				
3′		26.0				
4′		16.6				
5′		11.5				

[a] Measured in DMSO, [b]measured in $CDCl_3$. Chemical shifts (δ) are in ppm from TMS

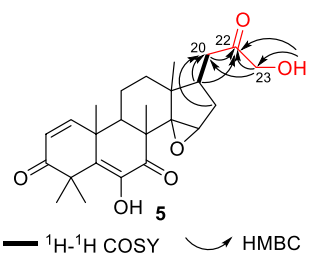


Fig. 2 Key ^{1}H–^{1}H COSY and HMBC (H → C) correlations of **5**

structure was further established through analysis of its MS and HMBC data. In the HMBC spectrum, H-17 (δ_H 2.54) and H-16β (δ_H 2.11) were correlated with the carbon resonance at δ_C 178.8, which was assigned to the C-20 carboxyl group. According to the above information, the planar structure of **6** was elucidated as shown (Fig. 3A).

The relative configuration of **6** was determined by ROESY spectrum (Fig. 3B). As shown in ROESY data, the correlations of H_3-18/H-9, H_3-18/H-16α, and H_3-18/H-11α indicated that they were co-facial, arbitrarily assigned as α-orientated. The ROESY correlations of H_3-30/H_3-19, H_3-19/H_3-29 revealed that H_3-30, H_3-19,

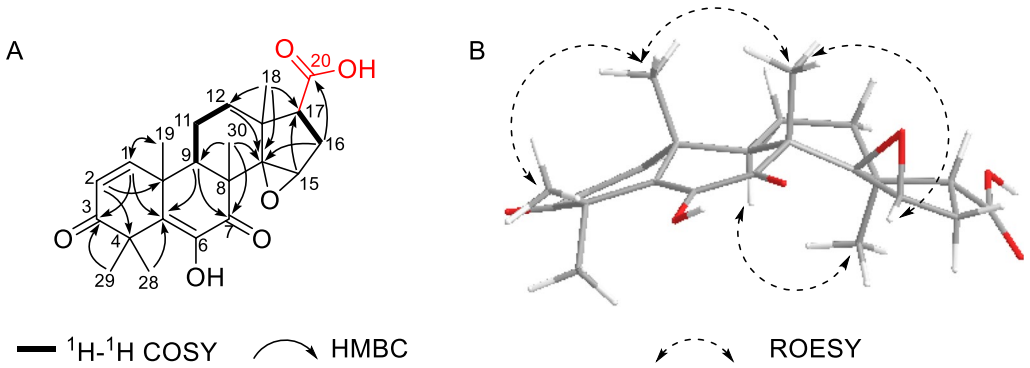


Fig. 3 Key ^{1}H–^{1}H COSY and HMBC (H → C) correlations (A), and selective ROESY correlations (B) of **6**

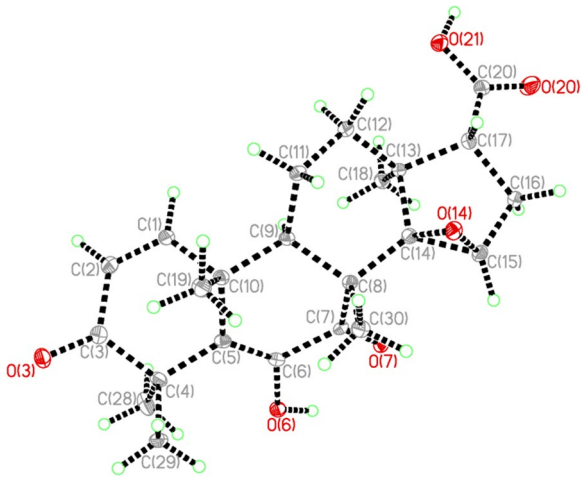
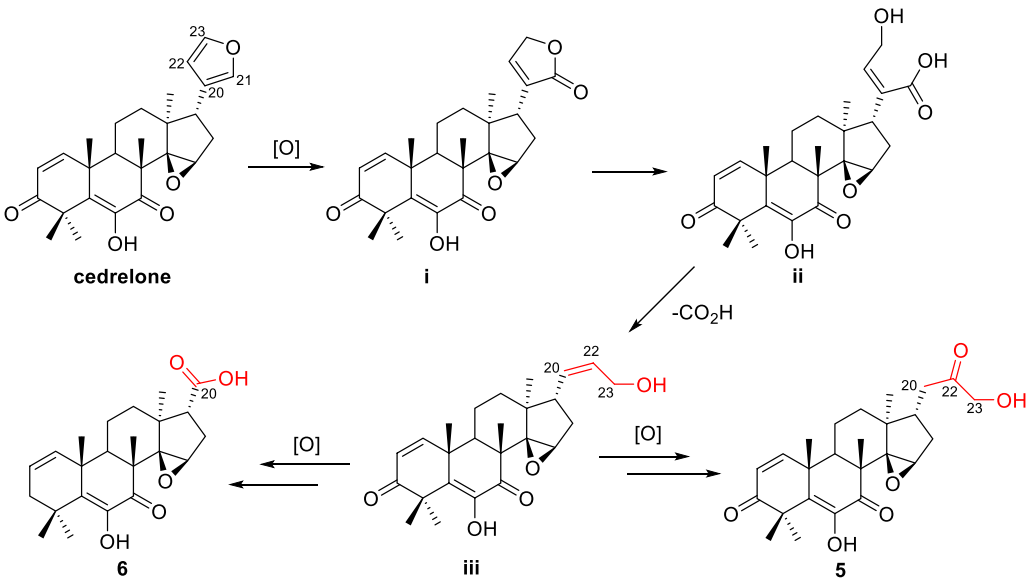


Fig. 4 Single-crystal X-ray structure of **6**

and H_3-29 were *β*-oriented, thus H_3-28 was *α*-orientated. The configuration of five methyls was the same as other reported limonoids [4]. In order to fix the orientation of the epoxide, **6** was recrystallized in methanol: acetone = 1: 1 mixture solvent and been structurally determined by X-ray diffraction analysis (Fig. 4). The X-ray diffraction data were collected by using CuK_α radiation and its absolute configuration has been determined as *8R*, *9R*, *10R*, *13S*, *14R*, *15R*, and *17R*. Although the structure of toonapubesic acid B (**6**) was reported in literature [18], while its NMR data was not available. Here we report the X-ray structure of toonapubesic acid B and its NMR data together to facilitate the community.

Hypothetic biosynthesis of *seco*-E ring derivatives **5** and **6** was proposed based on the common structural characteristics of discovered intermediates (Scheme 1).



Scheme 1 Hypothesis route of **5** and **6**

The furan ring of cedrelone was oxidized to form butenolactone, which was hydrolyzed to give free carboxyl and hydroxyl groups subsequently. After decarboxylation and a few steps oxidation, **5** and **6** formed respectively.

The similar patterns of Cotton Effects in the CD spectra of walsurobustones A-E (**1**–**5**) and toonapubesic acid B (**6**) (Fig. 5) indicated that the former's chiral centers in rings A, B, C and D have absolute configurations identical to the latter.

The cytotoxicity of **1**–**6** against the cancer cell lines (HL-60, SMMC-7721, A-549, MCF-7, and SW480) were evaluated by using the MTT method with taxol and cisplatin as the positive control. While compound **6** only showed moderate effects for all cell lines, other five compounds all showed obvious activity, especially to SMMC-7721, A-549 and MCF-7 (Table 3).

Table 3 Cytotoxicity Data for Compounds **1**–**6** against the cancer cell lines[a]

Compounds	HL-60	SMMC-7721	A-549	MCF-7	SW480
Walsurobustone A (**1**)	16.10	3.51	5.86	3.59	4.70
Walsurobustone B (**2**)	5.12	6.10	4.56	2.76	6.95
Walsurobustone C (**3**)	2.58	0.44	2.11	2.09	3.78
Walsurobustone D (**4**)	17.54	5.81	5.68	9.67	13.10
Walsurobustone E (**5**)	5.62	4.09	3.63	5.70	11.48
Toonapubesic acid B (**6**)	20.31	10.24	13.41	13.81	15.00
Cisplatin	1.81	8.86	11.68	15.92	16.65
Taxol	< 0.008	< 0.008	< 0.008	< 0.008	< 0.008

[a] Results are expressed as IC_{50} values in μM. HL-60 leukemia cancer; SMMC-7721 liver cancer; A-549 lung cancer; MCF-7 breast cancer; SW480 colon cancer. All the compounds exhibited potential cytotoxicity

3 Experimental section

3.1 General experimental procedure

Optical rotations were measured with a Horiba SEPA-300 polarimeter. UV spectra were detected on a Shimadzu UV-2401 spectrophotometer. IR spectra were determined on a Tenor 27 spectrophotometer with KBr pellets, whereas CD spectra were recorded with an Applied Photophysics Chirascan spectrometer. ESIMS and HRESIMS were measured on a Finnigan MAT 90 instrument and VG Auto Spec-3000 spectrometer, respectively. 1D and 2D NMR spectra were recorded on Bruker AM-400, Bruker DRX-500 and Bruker Avance III 600 spectrometers with TMS as internal standard. Semipreparative HPLC was performed on an Agilent 1100 liquid chromatographer with a Zorbax SB-C18 (9.4 mm 25 cm) column. Column chromatography was performed with silica gel (300–400 mesh, Qingdao Marine Chemical, Inc., Qingdao, People's Republic of China), and MCI gel (75–150 μM, Mitsubishi Chemical Corporation, Tokyo, Japan). Fractions were monitored by TLC, and spots were visualized by heating silica gel plates sprayed with 10% H_2SO_4 in EtOH.

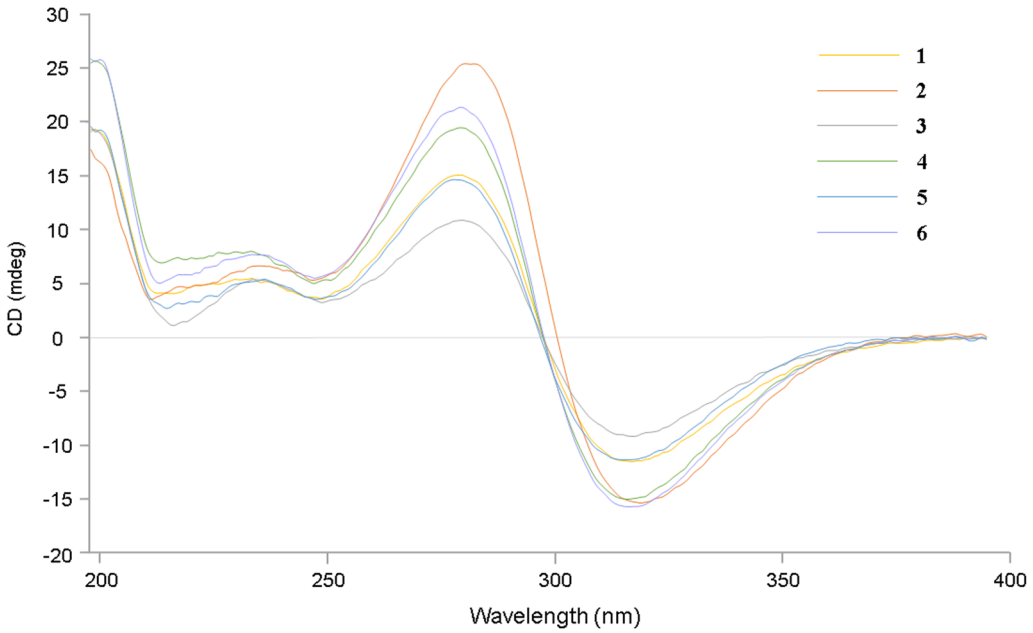


Fig. 5 CD spectra for walsurobustones A-E (**1**–**5**) and Toonapubesic acid B (**6**) (in MeOH)

3.2 Plant material

The leaves of *W. robusta* collected in Hainan Province, People's Republic of China in December 2010. The plant was authenticated by Dr. Guangwan Hu, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen (No. H20101202) was deposited in the State Key Laboratory of Photochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

3.3 Extraction and isolation

The dried and powdered leaves (12 kg) of *W. robusta* were extracted with MeOH three times under reflux, and the solvent was evaporated in *vacuo.* The residue was partitioned in H_2O and extracted successively with petroleum ether and EtOAc. The EtOAc fraction (200 g) was separated by silica gel column chromatography (CC) eluted with a gradient of petroleum ether/Me_2CO (50:1 to 1:1) and $CHCl_3$/MeOH in a gradient (15:1 to 3:1), eight fractions (Fr. A-H) were obtained according to TLC monitor. Fr. C (17 g) was subjected to MCI-gel column (MeOH/H_2O, 6:4 to 9:1) to give sixteen sub-fractions (C1–C16). C7 (4.1 g) was then chromatographed on a column of reversed-phase C18 silica gel eluted with MeOH/H_2O (5:5 to 9:1) to get eight parts (C7a–C7h). C7h was purified by CC over silica gel and then applied to a Sephadex LH-20 column using a solvent system acetone to provide **1** (5 mg), **3** (5 mg), **4** (11 mg), **5** (15 mg). C8 was further purified by preparative RP-8 HPLC using a solvent system 60% aqueous MeOH to provide compounds **2** (11 mg). Fr. D (60 g) was subjected to MCI-gel column (MeOH/H_2O, 4:6 to 9:1) to give twenty fractions (D1–D20), D15 (1 g) was subjected to silica gel column chromatography eluting sequentially with petroleum ether/EtOAc to afford 11 fractions, the second portion was purified by Sephadex LH-20 column to obtain **6** (11 mg).

Walsurobustone A (**1**), a white amorphous powder; $[\alpha]-30.6275$ (*c* 0.17, $CHCl_3$); UV ($CHCl_3$) λ_{max} (logε) 283 (3.10) nm; ^{1}H NMR (DMSO) and ^{13}C NMR (DMSO) (see Tables 1 and 2). IR ν_{max} cm^{-1}: 3430, 1630 cm^{-1}; HRESIMS at *m/z* 509.2141 $[M+Na]^+$ (calcd for $C_{27}H_{34}O_8Na$, 509.2151).

Walsurobustone B (**2**), a white amorphous powder, $[\alpha]-20.25$(*c* 0.16, $CHCl_3$); UV ($CHCl_3$) λ_{max} (logε) 283(3.10) nm; ^{1}H NMR (DMSO) and ^{13}C NMR (DMSO) (see Tables 1 and 2). IR ν_{max} cm^{-1}: 3426, 1682, 1630, 1030, 998 cm^{-1}; HRESIMS at *m/z* 641.2938 $[M+Na]^+$ in the HRESIMS (calcd for $C_{33}H_{46}O_{11}Na$, 641.2937).

Walsurobustone C (**3**), a white amorphous powder; $[\alpha]-21.1905$ (*c* 0.14, $CHCl_3$); UV ($CHCl_3$) λ_{max} (logε) 281 (3.30) nm; ^{1}H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) (see Tables 1 and 2). IR ν_{max} cm^{-1}: 3406, 2957, 2923, 1764, 1676, 1034 cm^{-1}; HRESIMS at *m/z* 491.2048 $[M+Na]^+$ (calcd for $C_{27}H_{32}O_7Na$, 491.2045).

Walsurobustone D (**4**), a white amorphous powder; $[\alpha]-68.6111$ (*c* 0.12, $CHCl_3$); UV ($CHCl_3$) λ_{max} (logε) 283 (3.12) nm; ^{1}H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) (see Tables 1 and 2). IR ν_{max} cm^{-1}: 3431, 1630 cm^{-1}; HRESIMS at *m/z* 509.2141 $[M+Na]^+$ (calcd for $C_{27}H_{34}O_8Na$, 509.2151).

Walsurobustone E (**5**), a white amorphous powder; $[\alpha]-54.5641$ (*c* 0.14, $CHCl_3$); UV ($CHCl_3$) λ_{max} (logε) 281 (3.28) nm; ^{1}H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) (see Tables 1 and 2). IR ν_{max} cm^{-1}: 3482, 3406, 2924, 2854, 1718, 1680, 1356, 1249, 1031 cm^{-1}; HRESIMS *m/z* 451.2103 $[M+Na]^+$ (calcd for $C_{23}H_{28}O_6Na$, 451.2096).

Toonapubesic acid B (**6**), a colorless crystal, deposited to CCDC with No.2235264; $[\alpha]-79.4872$ (*c* 0.13, $CHCl_3$); UV($CHCl_3$) λ_{max} (logε) 280 (3.26) nm; ^{1}H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) (see Tables 1 and 2). IR ν_{max} cm^{-1}: 3418, 2926, 1713, 1686, 1240, 1031 cm^{-1}; HRESIMS *m/z* 423.1777 $[M+Na]^+$ (calcd for $C_{23}H_{28}O_6Na$, 423.1783).

Supplementary Information

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Supplementary file 1

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Author contributions

Li Hou carried out the isolation and data curation at leading degree.Cui-Xuan Mei conducted the writing of original draft.Chun-Mao Yuan contributed to investigation, and validation at supporting degree.Gui-Hua Tang contributed to investigation, and validation at supporting degree.Duo-Zhi Chen contributed to data curation and analysis at supporting degree.Qing Zhao contributed to project administration at supporting degree.Hong-Ping He contributed to project administration at leading degree.Mingming Cao contributed to guiding of the writing and data proof reading.Xiao-Jiang Hao contributed to funding acquisition and project administration at leading degree. All authors read and approved the final manuscript.

Declarations

Competing interests

The authors declare there is no competing interests.

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