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Original Article

Plectraterpene, a new ursane-type triterpene ester and other steroids from the aerial parts of *Plectranthus montanus*

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ABSTRACT

A new ursane-type triterpene ester, plectraterpene [3β-(decanoyloxy)-19-hydroxy-urs-12-ene] and four known steroidal compounds have been isolated from the aerial parts of *Plectranthus montanus* Benth. (syn. *Plectranthus cylindraceus* Hochst. ex Benth.), Lamiaceae. The known compounds were stigmasterol, sitosteryl ferulate, cholest-5-en-3-*O*-β-D-glucopyranoside and stigmasterol-3-*O*-β-D-glucopyranoside. Compounds plectraterpene, sitosteryl ferulate and stigmasterol-3-*O*-β-D-glucopyranoside are reported for the first time from this plant whereas compound cholest-5-en-3-*O*-β-D-glucopyranoside first time from the genus. The structures of these compounds were determined through spectral analysis, including extensive 2D NMR data as well as chemical methods and comparison with literature.

Introduction

Genus *Plectranthus* belonging to family Lamiaceae includes more than 300 species (Retief, 2000). The therapeutic, nutritional, and horticultural values of this genus are attributed to its aromatic nature and essential oil producing capability (Lukhoba et al., 2006; Grayer et al., 2010; Alasbahi and Melzig, 2010). *Plectranthus montanus* Benth. (syn. *Plectranthus cylindraceus* Hoechst. Ex. Benth.) is a strongly aromatic, succulent and highly branched herb or shrub, known as Al-Shar and Zefubrek in Saudi Arabia and Oman, respectively (Orabi et al., 2000; Asresa et al., 2013). It is used to treat sore throats, skin, digestive, respiratory, and inflammatory diseases (Orabi et al., 2000; Rahman et al., 2004). Its oil possessed antibacterial and antifungal activities (Marwah et al., 2007; Asresa et al., 2013). Previously, sesquiterpenes and flavonoids have been reported from this plant (Orabi et al., 2000). As a part of our ongoing search for new constituents from Saudi medicinal plants, a new ursane-type triterpene ester, plectraterpene (**1**), together with four known compounds were isolated from the aerial parts of *P. cylindraceus*. Their structures were verified by various spectroscopic and chemical methods.

Materials and methods

General experimental procedure

Optical rotations were measured on a Perkin-Elmer Model 341 LC polarimeter (Perkin-Elmer, Waltham, MA, USA). IR spectra were measured with a Shimadzu Infrared-400 spectrophotometer (Shimadzu, Kyoto, Japan). EIMS spectra were recorded on JEOL JMS-SX/SX102A mass spectrometer (Joel, Peabody, MA, USA). ESIMS spectra were recorded on an Agilent 6320 Ion trap mass spectrometer (Agilent technologies, USA). HRESIMS spectra were obtained using an LTQ Orbitrap mass spectrometer (Thermo Fisher, Waltham, MA, USA). NMR spectra were measured on a Bruker DRX 700 spectrometer (Bruker, Rheinstetten, Germany). Vacuum liquid chromatography (VLC) was performed using silica gel 60 (0.04–0.063 mm; 500 g; Merck, Darmstadt, Germany). Column chromatographic separations were performed on silica gel 60 (0.04–0.063 mm, Merck, Darmstadt, Germany), RP_{18} (0.04–0.063 mm, Merck, Darmstadt, Germany), and six ml standard LiChrolut extraction tube (RP_{18}, 40–63 μm, Merck, Darmstadt, Germany). TLC analyses were conducted on pre-coated silica gel F_{254} aluminum sheets (Merck, Darmstadt, Germany). Compounds were detected by spraying the sheets with *p*-anisaldehyde/H_2SO_4 reagent followed by heating at 110 °C for 1–2 min.

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Table 1
NMR spectral data of compounds **1** and **2** ($CDCl_3$, 700 and 176 Hz).

Position	**1**		Position	**2**	
	δ(H) (mult., *J* [Hz])	δ(C) (mult.)		δ(H) (mult., *J* [Hz])	δ(C) (mult.)
1	1.56–1.58 (*m*)1.01–1.04 (*m*)	38.8 CH_2	1	1.85–1.87 (*m*)1.11–1.13 (*m*)	37.2 CH_2
2	2.21–2.24 (*m*)1.86–1.88 (*m*)	28.8 CH_2	2	1.88–1.90 (*m*)1.31–1.33 (*m*)	28.0 CH_2
3	4.31 (*dd*, *J* = 11.0, 5.0)	79.0 CH	3	4.26–4.29 (*m*)	78.4 CH
4	–	39.6 C	4	2.45–2.47 (*m*)2.28–2.30 (*m*)	38.3 CH_2
5	1.53–1.56 (*m*)	55.2 CH	5	–	141.0 C
6	1.61–1.63 (*m*)1.46–1.48 (*m*)	18.4 CH_2	6	5.40 (*brs*)	121.4 CH
7	1.64–1.66 (*m*)1.23–1.26 (*m*)	32.9 CH_2	7	1.95–1.98 (*m*)1.57–1.59 (*m*)	31.7 CH_2
8	–	40.0 C	8	0.94–0.96 (*m*)	45.9 CH
9	1.69 (*dd*, *J* = 13.1, 3.9)	47.7 CH	9	0.91–0.93 (*m*)	50.3 CH
10	–	36.9 C	10	–	36.5 C
11	1.94–1.96 (*m*)1.83–1.85 (*m*)	23.7 CH_2	11	1.59–1.61 (*m*)1.50–1.53 (*m*)	20.8 CH_2
12	5.14 (*t*, *J* = 3.5)	124.4 CH	12	2.05–2.07 (*m*)1.21–1.24 (*m*)	39.7 CH_2
13	–	139.6 C	13	–	42.1 C
14	–	42.8 C	14	1.05–1.07 (*m*)	56.8 CH
15	2.18–2.20 (*m*)1.10–1.13 (*m*)	27.3 CH_2	15	1.25–1.27 (*m*)	25.7 CH_2
16	2.04–2.06 (*m*)1.90–1.92 (*m*)	25.8 CH_2	16	1.92–1.94 (*m*)1.63–1.65 (*m*)	29.3 CH_2
17	–	33.1 C	17	1.17–1.19 (*m*)	56.1 CH
18	1.93 (*d*, *J* = 7.2)	59.1 CH	18	1.06 (*s*)	18.4 CH_3
19	–	72.9 C	19	0.75 (*s*)	11.9 CH_3
20	1.20–1.22 (*m*)	42.1 CH	20	1.54–1.56 (*m*)	31.9 CH
21	1.34–1.36 (*m*)1.27–1.29 (*m*)	31.3 CH_2	21	0.98 (*d*, *J* = 6.8)	18.0 CH_3
22	1.97–1.99 (*m*)1.67–1.68 (*m*)	39.7 CH_2	22	1.41–1.46 (*m*)1.07–1.09 (*m*)	33.7 CH_2
23	0.83 (*s*)	28.2 CH_3	23	1.66–1.68 (*m*)1.12–1.15 (*m*)	23.9 CH_2
24	0.89 (*s*)	15.9 CH_3	24	1.47–1.49 (*m*)	36.1 CH_2
25	1.02 (*s*)	16.9 CH_3	25	1.25–1.27 (*m*)	29.0 CH
26	1.03 (*s*)	17.6 CH_3	26	0.87 (*d*, *J* = 6.3)	21.8 CH_3
27	1.14 (*s*)	23.5 CH_3	27	0.86 (*d*, *J* = 6.3)	21.9 CH_3
28	0.81 (*s*)	28.4 CH_3	1′	4.40 (*d*, *J* = 7.0)	101.0 CH
29	1.15 (*s*)	26.6 CH_3	2′	3.18–3.20 (*m*)	73.7 CH
30	0.98 (*d*, *J* = 6.3)	21.4 CH_3	3′	3.27–3.29 (*m*)	76.5 CH
1′	–	170.3 C	4′	3.29–3.31 (*m*)	70.3 CH
2′	2.34 (*t*, *J* = 6.8)	33.8 CH_2	5′	3.35–3.38 (*m*)	76.7 CH
3′	1.78–1.80 (*m*)	25.2 CH_2	6′	3.85–3.87 (*m*)3.67–3.70 (*m*)	61.4 CH_2
$(CH_2)_{4'\text{-}8'}$	1.27–1.30 (*m*)	29.2–29.9 CH_2	–	–	–
9′	1.23–1.25 (*m*)	22.7 CH_2	–	–	–
10′	0.81 (*t*, *J* = 6.5)	14.1 CH_3	–	–	–

Plant material

The aerial parts of *Plectranthus montanus* Benth. (syn. *Plectranthus cylindraceus* Hoechst. Ex. Benth.), Lamiaceae, were collected in March 2011 from Abha, Saudi Arabia. The plant was identified by Dr. Mohamed Yousef, Prof. of Pharmacognosy, College of Pharmacy, King Saud University, Saudi Arabia. A voucher specimen (P-5-2011) was deposited at the herbarium of the Department.

Extraction and isolation

The air-dried powdered aerial parts (1 kg) was extracted with MeOH (4 × 3 l). The combined MeOH extract was concentrated under reduced pressure to yield a dark green viscous residue (19.2 g). The latter was subjected to VLC using hexane, EtOAc, and MeOH. Each fraction was concentrated to give hexane (2.9 g), EtOAc (5.6 g), and MeOH (9.8 g) fractions. The EtOAc fraction (5.6 g) was subjected to VLC using hexane:EtOAc gradient to afford ten subfractions: P-1 to P-10. Subfraction P-3 (718 mg) was chromatographed over SiO_2 column (50 g, 50 × 3 cm) using hexane:EtOAc gradient to give stigmasterol (82.1 mg, colorless needles). Subfraction P-4 (560 mg) was similarly treated as subfraction P-3 to give impure plectraterpene (**1**). Purification of **1** was achieved on RP_{18} column chromatography (30 g, 50 × 2 cm) using MeOH:H_2O gradient to afford **1** (15.9 mg, white amorphous powder). Subfraction P-5 (610 mg) was subjected to SiO_2 column (55 g, 50 × 3 cm) using hexane:EtOAc gradient to afford sitosteryl ferulate (37.5 mg, white amorphous powder). Subfraction P-6 (380 mg) was subjected to SiO_2 column (35 g, 50 × 2 cm) using hexane:EtOAc gradient to afford impure sitosteryl ferulate which was purified on LiChrolut EN/RP_{18} solid phase extraction tube using H_2O:acetonitrile gradient to yield cholest-5-en-3-*O*-β-D-glucopyranoside (**2**) (11.5 mg, white amorphous powder). Subfraction P-7 (508 mg) was subjected to SiO_2 column (45 g, 50 × 3 cm) using *n*-hexane:EtOAc gradient gave stigmasterol-3-*O*-β-D-glucopyranoside (89 mg, white amorphous powder).

Plectraterpene (3β-(decanoyloxy)-19-hydroxy-urs-12-ene; **1**): white amorphous powder; $[\alpha]_D$ +39 (*c* = 0.1, MeOH); IR (KBr): 3436, 2951, 1729, 1619, 1248 cm^{-1}; ^1H ($CDCl_3$, 700 MHz) and ^{13}C NMR data ($CDCl_3$, 176 MHz) see Table 1; HR-ESI-MS *m*/*z* 597.5242 (calcd for 597.5247 $[M+H]^+$, $C_{40}H_{69}O_3$).

Cholest-5-en-3-*O*-β-D-glucopyranoside; **2**: white amorphous powder; $[\alpha]_D$ +56 (*c* = 0.5, MeOH); IR (KBr): 3396, 2945, 1635 cm^{-1}; ^1H ($CDCl_3$, 700 MHz) and ^{13}C NMR data ($CDCl_3$, 176 MHz)see Table 1; HR-ESI-MS *m*/*z* 549.4159 (calcd for 549.4155 $[M+H]^+$, $C_{33}H_{57}O_6$).

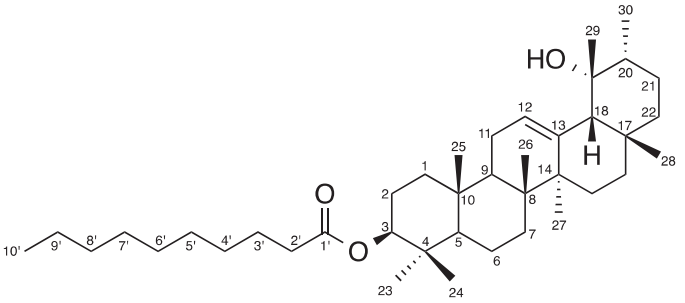
*Alkaline hydrolysis of compound **1***

A solution of **1** (7 mg) in 3% KOH/MeOH (5 ml) was left to stand for 15 min at room temperature then neutralized with 1 N HCl/MeOH. The solution was extracted with $CHCl_3$. The solvent was evaporated and the residue obtained was chromatographed on SiO_2 column, using hexane:EtOAc gradient to furnish the methyl ester of decanoic acid, which was identified by GC-MS using Clarus 500 GC/MS (*Perkin-Elmer*, Shelton, CT) as previously outlined (Al-Musayeib et al., 2013; El-Shanawany et al., 2015; Ibrahim et al., 2016a,b).

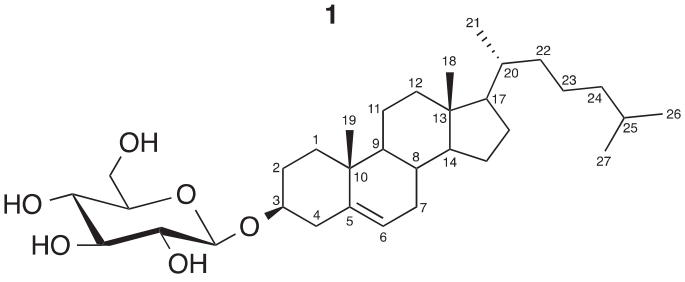
Results and discussion

The dried-powdered aerial parts were extracted with MeOH. The concentrated MeOH extract was subjected to vacuum liquid chromatography (VLC) using hexane, EtOAc, and MeOH. The EtOAc fraction was separated on VLC, silica gel, and Rp_{18} CC to yield one new (**1**) and four known compounds.

Compound **1** was obtained as white amorphous powder. It gave a positive Liebermann-Burchard's reaction (Gołembiewska et al., 2013), indicating its triterpenoidal nature. Its molecular formula was determined as $C_{40}H_{68}O_3$ based on the HRESIMS pseudo-molecular ion peaks at *m/z* 597.5242 (calcd for $C_{40}H_{69}O_3$, 597.5247 $[M+H]^+$), requiring seven degrees of unsaturation. These degrees of unsaturation can be accounted for five rings system, one olefinic double bond, and one ester carbonyl group. Its IR spectrum showed characteristic absorption bands for hydroxyl (3436 cm^{-1}), ester carbonyl (1729 cm^{-1}), and double bond (1619 cm^{-1}). The ^{13}C and HSQC spectra showed the presence of 40 carbons, consisting of nine methyls, seventeen methylenes, six methines one of them for oxymethine at δ(C) 79.0 C(3) and one for a tri-substituted olefinic double bond at δ(C) 124.4 C(12), and eight quaternary carbons including one carbonyl at δ(C) 170.3 C(1′) and oxygen-bonded quaternary carbon δ(C) 72.9 C(19). Detailed 1D and 2D NMR analysis of **1** suggested that it is an ursane type pentacyclic triterpene (Ibrahim et al., 2012; Ibrahim et al., 2016a,b). The ^1H NMR spectrum of **1** exhibited six singlet methyls at δ(H) 0.83 H-C(23), 0.89 H-C(24), 1.02 H-C(25), 1.03 H-C(26), 1.14 H-C(27), 0.81 H-C(28), and 1.15 H-C(29), and one doublet methyl group at δ(H) 0.98 (d, *J* = 6.3 Hz, H-C(30)), establishing the ursane-type carbon framework of **1** (Ibrahim et al., 2012; Khedr et al., 2016). They correlated to the carbons resonating at δ(C) 28.2, 15.9, 16.9, 17.6, 23.5, 28.4, 26.6, and 21.4, respectively in the HSQC spectrum. Their positions were confirmed by the observed HMBC cross peaks of H-C(23) and H-C(24) to C(3), C(4), and C(5), H-C(25) to C(1), C(9), and C(10), H_3-26 to C(7), C(8), C(9), and C(14), H-C(27) to C(8), C(13), C(14), and C(15), H-C(28) to C(17), C(18), and C(22), H-C(29) to C(18), C(19), and C(20), and H-C(30) to C(19), C(20), and C(21) (Fig. 1). An oxymethine signal was observed at δ(H) 4.31 (dd, *J* = 11.5, 5.0 Hz, H-C(3)), showing HSQC cross peak to the carbon signal at δ_C 79.0 C(3). This assignment was established by the ^1H–^1H COSY correlations of H-C(3) with H-C(2) and proved by the HMBC cross peaks of H-C(1), H-C(23), and H-C(24) to C(3) (Fig. 1). Furthermore, the ^1H and ^{13}C NMR spectra of **1** revealed signals at δ(H) 5.14 (d, *J* = 3.5 Hz, H-C(12))/δ(C) 124.4 C(12) and 139.6 C(13), indicating the presence of a tri-substituted olefinic double bond (Table 1). Its presence at C(12)/C(13) was secured based on the ^3J HMBC correlations of H-C(9) and H-C(18) to C(12) and H-C(27) to C(13). The oxygen-bonded quaternary carbon at δ_C 72.9 was assigned to C(19). This assignment was established by the cross peaks of H-C(18), H-C(20), H-C(21), and H-C(30) to C(19) observed in HMBC. Additionally, the signals for primary methyl at δ(H) 0.81 (t, *J* = 6.5 Hz, H-C(10′))/δ(C) 14.1 C(10′), aliphatic methylenes cluster at δ(H) 1.27–1.30 (m, H-C(4′-8′))/δ(C) 29.2–29.9 C(4′-8′), and carbonyl at δ(C) 170.3 C(1′) indicated the presence of fatty acyl moiety in **1** (Mohamed et al., 2013; Mohamed, 2014; El-Shanawany et al., 2015). Alkaline hydrolysis of **1** gave a methyl ester of decanoic acid, which was identified by GC–MS molecular ion peak at *m/z* 186 $[M]^+$. This was further confirmed by the ESIMS fragment ion peak at *m/z* 442 $[M+H\text{-}OC_{10}H_{19}]^+$. Its connectivity at C(3) was established based on the HMBC correlation of H-C(3) to C(1′) and confirmed by the downfield shift of H-C(3) (δ(H) 4.31) (Al-Musayeib et al., 2013). The relative stereochemistry at C-3 and C-19 was assigned based on the comparison of the coupling constant values as well as ^1H and ^{13}C chemical shift with those of related triterpenes (Mahato and Kundu, 1994; Akbar and Malik, 2002; Kim et al., 2012). On the basis of these findings and by comparison with the literature, the structure of **1** was assigned as 3β-(decanoyloxy)-19-hydroxy-urs-12-ene and named plectraterpene.



1



2

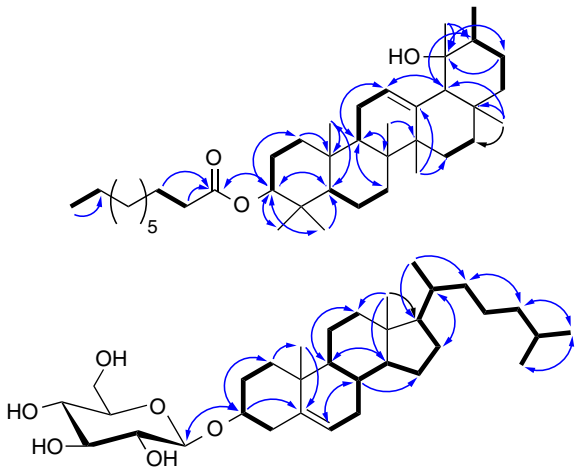


Fig. 1. Some key ^1H–^1H COSY (—) and HMBC (H → C) correlations of **1** and **2**.

Compound **2** was obtained as white amorphous powder. It gave a positive Liebermann-Burchard's test, suggesting its steroidal nature (Gołembiewska et al., 2013). Its HRESIMS spectrum showed a pseudo-molecular ion peak at *m/z* 549.4159 (calcd for 549.4155 $[M+H]^+$), which was compatible with the molecular formula $C_{33}H_{56}O_6$, representing six degrees of unsaturation. The IR spectrum of **2** showed characteristic absorption bands, indicating the presence of hydroxyl group (3396 cm^{-1}), unsaturation (1635 cm^{-1}), and aliphatic C-H (2945 cm^{-1}). The ^1H and ^{13}C NMR spectra exhibited two tertiary methyls [δ(H) 1.06 and 0.75 for H-C(18)/C(18) and H-C(19)/C(19), respectively], three secondary methyls [0.98 (d, *J* = 6.8 Hz, H-C(21)), 0.87 (d, *J* = 6.3 Hz, H-C(26)), and 0.86 (d, *J* = 6.3 Hz, H-C(27))], a double bond at δ(H) 5.40 (brs, H-C(6))/δ(C) 121.4 C(6) characteristic for cholesteryl derivative (Plouguerné et al., 2006). The placement of the double bond at C(5)-C(6) was assigned based on the observed ^1H–^1H COSY and HMBC correlations (Fig. 1). The geometry of the double bond was deduced to be *Z* based on the coupling constant value (Plouguerné et al., 2006; Elkhayat et al., 2015; Ibrahim et al., 2015). The ^{13}C

and HSQC spectra displayed 33 signals, 27 of them were attributed to cholesteryl moiety with olefinic carbons at δ(C) 141.0 C(5) and 121.4 C(6) and the remaining six carbons for glucose moiety. This was confirmed by the observed signals at δ(H) 4.40 (d, J = 7.0 Hz, H-C(1′)/δ(C) 101.0 C(1′) characteristic for the β-glucopyranose moiety (Mohamed et al., 2014). In the HMBC, the cross peak of H-C(1′) to C(3) (δ(C) 78.4) confirmed the attachment of glucose moiety at C-3 (Fig. 1). On the basis of the previous mentioned data, **2** were identified as cholest-5-en-3-*O*-β-D-glucopyranoside and in agreement with the literature (Mustafa and Ali, 2011).

The other isolated compounds were identified as stigmasterol (Mohamed and Ibrahim, 2007; Ibrahim et al., 2016a,b), sitosteryl ferulate (Jaiswal et al., 2015), and stigmasterol-3-*O*-β-D-gluco (Ibrahim, 2010) by the analysis of the spectroscopic data (1D, 2D NMR, and MS) and comparison of their data with those in the literature.

Authors' contributions

MA and NAM designed the study, performed extraction, isolation and characterization of isolated constituents. GAM and SRMI participated NMR interpretation, manuscript preparation and also contributed to critical reading of manuscript. All the authors have read the final manuscript and approved the submission.

Conflicts of interest

The authors declare no conflicts of interest.

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