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Triterpenoids and steroids from the lichen *Ramalina peruviana* Arch

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Abstract

Five known triterpenes, *β*-amyrone (**1**), isoarborinol acetate (**2**), hopane-6*α*,22-diol (**3**), hopane-22-ol (**4**), hopane-6*α*,16*β*,22-triol (**5**), along with two esgostane-type sterols, 5*α*,8*α*-esgosterol peroxide (**6**), brassicasterol (**7**) were isolated from the lichen *Ramalina peruviana* Ach. (Ramalinaceae). Their chemical structures were elucidated by spectroscopic data analysis and comparison with those reported in the literature. Except **2**, this is the first time these compounds are reported in *Ramalina* genus.

Keywords. *Ramalina peruviana*, triterpenes, esgostane-type sterols.

1. INTRODUCTION

In the researched species of the genus *Ramalina*, a diversity of chemical compounds was found, including depsides, depsidones, fatty acids, sterols, triterpenes and monocyclic aromatic compounds.[1] Our previous studies on the chemical constituents of *Ramalina peruviana* reported the presence of eight compounds from the chloroform extract,[2] but triterpenes have not been reported yet. Herein, we continuously report the isolation and structure elucidation of five known triterpenoids, *β*-amyrone (**1**), isoarborinol acetate (**2**), hopane-6*α*,22-diol (**3**), hopane-22-ol (**4**), hopane-6*α*,16*β*,22-triol (**5**), together with two known steroids, ergosterol-*5α,8α*-peroxide (**6**), brassicasterol (**7**). Their chemical structures were unambiguously determined by the analysis of 1D and 2D NMR and high resolution ESI mass spectroscopic data, as well as by comparison of their NMR data with the ones in the literature.

2. MATERIALS AND METHODS

2.1. General

The HR-ESI-MS were recorded on a Bruker microOTOF Q-II. The NMR spectra were measured on a Bruker Avance III spectrometer (500 MHz for 1H NMR and 125 MHz for 13C NMR). TLC was carried out on silica gel 60 F254 or silica gel 60 RP-18 F254S (Merck) and spots were visualized by spraying with a solution of 5 % vanillin in ethanol, followed by heating at 100 ^{o}C. Column chromatography was performed with silica gel 60 (0.040-0.063 mm, Merck).

2.2. Plant material

Thalli of the lichen *Ramalina peruviana* were separated from bark of teas at Cau Dat farm, Lam Dong province, Vietnam and authentified by Dr. Vo Thi Phi Giao, Faculty of Biology, University of Science, National University - Ho Chi Minh City.

2.3. Extraction and isolation

The clean, air-dried and ground material (1.3 kg) was extracted by maceration with acetone at ambient temperature, and the filtrated solution was evaporated under reduced pressure to afford the crude acetone extract (69.1 g). The rude acetone extract (69.1 g) was subjected to silica gel solid phase extraction to afford *n*-hexane extract (3.2 g), chloroform extract (49.8 g), acetone extract (11.8 g) and methanol extract (3.6 g).

The *n*-hexane extract (3.2 g) was applied to silica gel column chromatography, eluted with *n*-hexane and chloroform (10:0-5:5) to give 4 fractions from H1 to H4. Fraction H2 (0.8 g) was subjected to silica gel column chromatography using a gradient system of *n*-hexane-chloroform (10:0-5:5) to yield **1** (5.1 mg), and **2** (5.6 mg). Fraction H3 (1.3 g) was subjected to silica gel column chromatography using a gradient system of *n*-hexane-chloroform (10:0-5:5) to yield **3** (9.0 mg) and **4** (5.4 mg).

The chloroform extract (49.8 g) was applied to silica gel column chromatography, eluted with a mixture of *n*-hexane and chloroform (10:0-0-10) to give 10 fractions from C1 to C10. Fraction C3 (0.5 g) was applied to column chromatography, eluted with a gradient system of *n*-hexane-chloroform (9:1-5:5) to yield **5** (6.3 mg), **6** (5.2 mg) and **7** (9.3 mg).

***β*-Amyrone (1):** Colorless crystals, mp. 178 °C. HR-ESI-MS (positive mode) *m/z* 425.3797 $[M+H]^+$ (calcd. for $C_{30}H_{49}O^+$, 425.3786). The ^1H and ^{13}C-NMR ($CDCl_3$), see tables 1 and 2.

Isoarborinol acetate (2): Colorless crystals, mp. 296 °C. HR-ESI-MS (positive mode) *m/z* 469.4044 $[M+H]^+$ (calcd. for $C_{32}H_{53}O_2^+$, 469.4048). The ^1H and ^{13}C-NMR ($CDCl_3$), see tables 1 and 2.

Hopane-6*α*,22-diol (3): White powder mp. 236 °C. HR-ESI-MS (positive mode) *m/z* 467.3888 $[M+Na]^+$ (calcd. for $C_{30}H_{52}O_2Na^+$, 467.3868). The ^1H and ^{13}C-NMR ($CDCl_3$), see tables 1 and 2.

Hopane-22-ol (4): White powder. HR-ESI-MS (positive mode) *m/z* 429.4089 $[M+H]^+$ (calcd. for $C_{30}H_{53}O^+$, 429.4099). The ^1H and ^{13}C-NMR ($CDCl_3$), see tables 1 and 2.

Hopane-6*α*,16*β*,22-triol (5): White amorphous powder, mp. 335 °C. HR-ESI-MS (positive mode) *m/z* 443.3893 $[M-H_2O+H]^-$ (calcd. for $C_{30}H_{51}O_2^+$, 443.3892). The ^1H and ^{13}C-NMR ($CDCl_3$), see tables 1 and 2.

Ergosterol-5*α*,8*α*-peroxide (6): Colorless crystals, mp. 183 °C. HR-ESI-MS (positive mode) *m/z* 429.3351 $[M+H]^+$ (calcd. for $C_{28}H_{45}O_3^+$, 429.3371). The ^1H and ^{13}C-NMR ($CDCl_3$), see tables 1 and 2.

Brassicasterol (7): Colorless crystals, mp. 157 °C. HR-ESI-MS (positive mode) *m/z* 421.3416 $[M+Na]^+$ (calcd. for $C_{28}H_{46}ONa^+$, 421.3449). The ^1H and ^{13}C-NMR ($CDCl_3$), see tables 1 and 2.

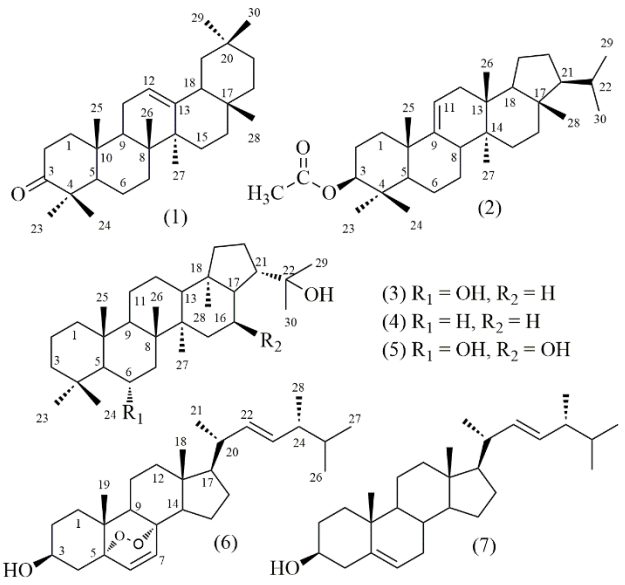

Figure 1: Structures of isolated compounds

3. RESULTS AND DISCUSSION

Compound **1** was isolated as colorless crystals. Mass spectra exhibited a pseudo-molecular ion at 425.3797 (calcd. for $C_{30}H_{49}O^+$, 425.3786), which corresponded with $C_{30}H_{48}O$. The ^1H-NMR indicated that there were 8 methyl groups in the zone of 1.15-0.84 ppm and an olefinic proton at δ_H 5.21 (*t*, 3.5 Hz). The ^{13}C-NMR spectrum of **1** showed 30 carbon signals, including a carbonyl carbon signal (δ_C 217.8), two olefinic carbons (δ_C 121.5 and 145.3) and other carbons in the zone 55.3-15.2 ppm. This suggested that **1** was an unsaturated ketone triterpene. The HMBC correlations of protons H-23 and H-24 with carbonyl carbon supported the position of the carbonyl carbon at C-3 (figure 2). By comparing these data with those in the literature,[3] **1** was suggested to be *β*-amyrone.

Compound **2** was purified as colorless crystals. The 1D NMR data coupled with the 2D NMR data (HSQC and HMBC) of **2** corresponded to a triterpen with the arborane skeleton. The ^{13}C and ^1H-NMR of **2** disclosed an acetyl moiety, comprising a carboxyl carbon at δ_C 171.0 (3-OCOCH$_3$) and a tertiary methyl group at δ_C 21.3/δ_H 2.04 (3H, *s*, 3-OCOCH$_3$), and an oxymethine funtion at δ_C 80.9 (C-3)/δ_H 4.47 (1H, *dd*, J = 4.0 and 11.5 Hz, H-3). The coupling constants of H-3 and H-2 exhibited two coupling values $J_{3a/2a}$ = 11.5 Hz, $J_{3a/2e}$ = 4.0 Hz indicating the *β*-orientation of

3-$OCOCH_3$ group. These NMR spectroscopic data of **2** were in good agreement with those of isoarborinol acetate.[4]

The molecular formula of **3** was determined as $C_{30}H_{52}O_2$ through the sodiated molecular ion peak at *m/z* 467.3888 $[M+Na]^+$ in the HR-ESI-MS spectrum. For the ^{13}C-NMR spectrum of **3**, carbon numbering refers to the hopane skeleton into eight methyl carbons, ten methylene carbons, six methine carbons and six quaternary carbons. On the basic of the HMBC and HSQC spectra, the proton signal at δ_H 2.38 (H-21) showed cross-peaks with the signals at δ_C 54.7 (C-17), 44.3 (C-18), 27.0 (C-20), and 72.5 (C-22) (figure 2). The coupling constants of upfield methine H-5 (δ_H 0.87, *d*, *J* = 11.0 Hz) exhibited 1,2-diaxial ^{1}H-^{1}H coupling to a secondary alcohol methine (δ_H 4.20, *dt*, 10.0, 4.5 Hz, H-6). That means the hydroxyl group at C-6 was at α-orientation. The comparison of these spectroscopic data of compound **3** with those of hopane-6α,22-diol in the literature[5] showed good compatibility. So the structure of compound **3** was suggested to be hopane-6α,22-diol.

The spectral data of compounds **3** and **4** were similar, with a remark that **4** lacked the hydroxyl group at C-6. Analysis of the 1D NMR spectral data and the comparison of these data with the ones in the literature[6] as well as a good candidate of the HR-ESI-MS value suggested that compound **4** was hopane-22-ol.

On the contrary, detailed spectroscopic comparison between **3** and **5** deduced that they were very similar, except for the presence of one additional oxymethine group ($\delta_{H/C}$ 4.09/67.1, C-16) instead of the methylene group at C-16 in **3**. The location of the second oxymethine H-16 was achieved by HMBC cross-peaks. from H-16 to C-15, C-17, and C-21; and H-21 to C-17, C-18, C-20, and C-22 (figure 2). Moreover, this secondary alcohol methine H-16 exhibited two 1,2-diaxial coupling constant values J_{aa} = 9.0 Hz, indicating the β-orientation of 16-OH group. The above data allowed to identify compound **5** as hopan-6α,16β,22-triol or leucotylin.[7]

Compound **6** was obtained as colorless crystals. The HR-ESIMS established the composition of $C_{28}H_{44}O_3$. The ^{1}H-NMR spectrum exhibited signals for six methyl groups at δ_H 0.81 (*s*, H-18), 0.81 (*d*, *J* = 7.0 Hz, H-26), 0.83 (*d*, *J* = 6.5 Hz, H-27), 0.88 (*s*, H-19), 0.91 (*d*, *J* = 7.0 Hz, H-28) and 1.00 (*d*, *J* = 6.5 Hz, H-21), four olefinic protons at δ_H 5.14 (*dd*, *J* = 15.5, 7.5 Hz, H-22), 5.22 (*dd*, *J* = 15.5, 7.5 Hz, H-23), 6.24 (*d*, *J* = 8.5 Hz, H-6) and 6.50 (*d*, *J* = 8.5 Hz, H-7), oxygenated methine at δ_H 3.97 (*m*, H-3), and twenty protons at δ_H 1.23-2.10. The observation of six methyl groups with four doublets of secondary methyls indicates that compound **6** is an ergosterol derivative.

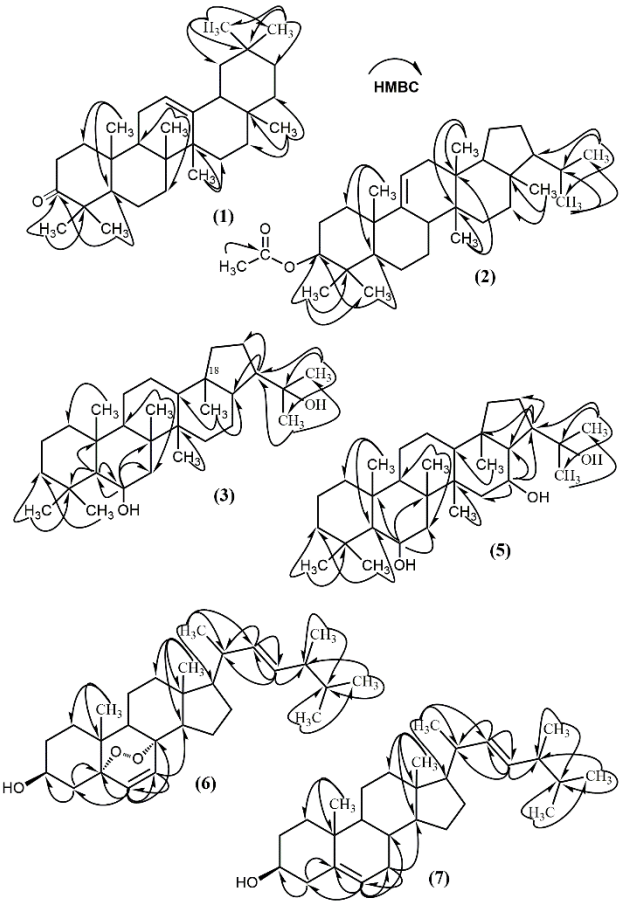

Figure 2: Keys of HMBC correlations for compounds **1**, **2** and **4-7**

In addition, the ^{13}C-NMR spectrum of **6** showed the presence of 28 carbons, including six methyl carbons, seven methylene carbons, eleven methine carbons (one bearing oxygen, four olefinic carbons) and four quaternary carbons (two bearing oxygen) (table 1). The proton and carbon signals of **6** were assigned by analysis of HSQC and HMBC spectra (figure 2). Based on above evidence, compound **6** were in good agreement with ergosterol-5α,8α-peroxide.[5,8]

Compound **7** was also obtained as colorless crystals. The observation of six methyl signals in the ^{1}H-NMR spectrum of compound **7**, δ_H 0.69 (*s*, H-18), 0.82 (*t*, 7.5 Hz, H-26 and H-27), 0.91 (*d*, 6.5 Hz, H-28) and 0.86 (*s*, H-19) and 1.01 (*d*, 6.5 Hz, H-21) indicates that compound **7** is also an ergosterol derivative. However, the ^{1}H-NMR spectrum of **7** only exhibited signals for three olefinic protons at δ_H 5.18 (*m*, H-22 and H-23) and 5.35 (*d*, *J* = 8.5 Hz, H-7). The loss of an olefinic signal, combined with HMBC correlations of H-6 to C-4, C-5, C-7 and C-8 confirmed 5,6-diene olefins in **7** (Figure 2).

Furthermore, the molecular formula for compound **7** was determined to be $C_{28}H_{46}O$ through the sodium adduction at *m/z* 421.3416 $[M+Na]^+$ in the HRESIMS spectrum. Consequently, the structure of **7** was brassicasterol.[5]

4. CONCLUSION

This study detailed the chemical structure of five triterpenes and two sterols from the lichen *Ramalina peruviana* Ach. (Ramalinaceae) using several chromatography methods, intensive spectroscopy analyses and and comparison with those reported in the literature. Except for compound **2** had been known in the lichen *Ramalina hierrensis* Krog & Østh[9], these compounds are reported the first time in *Ramalina* genus.

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Table 1: ^{13}C-NMR data of isolated compounds (125 MHz, δ ppm, $CDCl_3$)

No	1	2	3	4	5	6	7
1	39.3	35.7	40.7	41.4	40.6	34.8	37.4
2	34.2	24.2	19.0	20.1	18.7	30.3	29.9
3	217.8	80.9	44.4	45.4	43.9	66.6	72.0
4	47.5	38.0	34.1	32.7	33.8	37.1	39.8
5	55.3	52.4	61.2	56.3	61.1	82.3	140.9
6	19.7	21.3	67.9	18.9	69.1	135.6	121.9
7	32.2	26.6	45.8	33.4	45.7	130.9	32.1
8	39.8	41.0	43.0	42.1	43.2	79.6	31.8
9	46.9	148.5	50.3	51.6	49.5	51.2	50.3
10	36.6	39.5	39.4	38.0	39.5	37.1	36.7
11	23.7	114.6	21.4	24.3	21.2	20.8	21.2
12	121.5	36.1	24.4	24.6	23.7	39.5	40.3
13	145.3	36.8	49.8	50.5	48.9	44.7	42.5
14	41.9	38.2	42.2	42.1	44.2	51.8	56.2
15	26.2	29.7	34.7	34.6	43.9	23.6	24.4
16	27.0	35.9	22.3	22.1	67.1	28.8	28.7
17	32.5	42.9	54.7	54.1	60.9	56.4	57.0
18	47.3	52.1	44.3	44.3	46.0	12.9	12.2
19	46.8	20.2	41.7	41.5	41.8	18.2	19.6
20	31.1	28.2	27.0	26.7	28.1	39.9	38.1
21	34.7	59.6	51.6	51.3	51.3	21.0	20.1
22	37.1	30.8	72.5	74.1	74.7	135.3	136.0
23	26.5	28.2	37.3	33.6	36.9	132.5	131.9
24	21.5	16.8	22.6	22.1	22.3	42.9	43.0
25	15.2	22.2	17.5	16.4	17.3	33.2	33.3
26	25.9	17.0	18.5	17.1	18.5	19.8	21.2
27	16.7	15.3	17.3	17.1	17.2	20.1	21.1
28	28.4	14.0	16.4	16.4	17.2	17.7	19.8
29	33.3	22.1	29.8	28.9	26.9		
30	23.7	23.0	31.4	31.2	31.2		
31		21.3					
32		171.0					

Table 2: ^{1}H-NMR data of isolated compounds (500 MHz, δ ppm, *J* Hz, $CDCl_3$)

No	1	2	3	4	5	6	7
1	1.88 (*m*); 1.64 (*m*)	1.51 (*m*); 1.76 (*m*)	0.85 (*m*); 1.60 (*m*)	0.89 (*m*); 1.58 (*m*)	0.99 (*m*); 1.67 (*m*)	1.95 (*m*); 1.69 (*dt*, 13.5, 3.5)	1.85 (*m*)
2	2.37 (*m*); 2.55 (*m*)	1.74 (*m*)		1.39 (*m*); 1.45 (*m*)	1.39 (*m*); 1.60 (*m*)	1.57 (*m*); 1.84 (*m*)	
3		4.47 (*dd*, 11.5, 4.0)	1.29 (*m*); 1.39 (*m*)	1.12 (*m*); 1.22 (*m*)	1.12 (*m*); 1.21 (*m*)	3.97 (*m*)	3.52 (*m*)
4						1.93 (*m*); 2.10 (*ddd*, 13.5, 5.0, 2.0)	1.10 (*m*); 1.96 (*m*);
5	1.68 (*m*)	0.96 (*m*)	0.87 (*d*, 11.0)	0.78 (*d*, 14.0)	0.84 (*d*, 10.5)		
6		1.66 (*m*)	4.20 (*dt*, 11.0, 4.5)		4.00 (*dt*, 10.5, 4.0)	6.24 (*d*, 8.5)	5.35 (*d*, 8.5)
7		1.80 (*m*)	1.82 (*m*)		1.60 (*m*); 1.84 (*m*)	6.50 (*d*, 8.5)	1.43 (*m*); 1.93 (*m*)
8		2.02 (*m*)					1.83 (*m*)
9				1.14 (*m*)	1.36 (*m*)	1.51 (*m*)	0.89 (*m*)
10							
11	1.99 (*m*); 1.78 (*m*)	5.22 (d, 6.5)	1.26 (*m*); 1.53 (*m*)	1.36 (*m*); 1.42 (*m*)	1.34 (*m*); 1.51 (*m*)	1.40 (*m*); 1.58 (*m*)	1.43 (*m*)
12	5.21 (*t*, 3.5)	1.41 (*m*); 1.67 (*m*)	1.44 (*m*); 1.46 (*m*)	1.41 (*m*)	1.35 (*m*); 1.60 (*m*)	1.25 (*m*); 1.93 (*m*)	2.02 (*m*)
13				1.39 (*m*)	1.34 (*m*)		
14						1.59 (*m*)	1.10 (*m*)
15	1.38 (*m*)	1.23 (*m*); 1.28 (*m*)	1.19 (*m*); 1.33 (*m*)	1.26 (*m*); 1.38 (*m*)	1.52 (*m*); 1.67 (*m*)	1.24 (*m*); 1.50 (*m*)	1.05 (*m*); 1.49 (*m*)
16	1.32 (*m*)	1.45 (*m*); 1.64 (*m*)	1.72 (*m*); 2.14 (m)	1.52 (*m*); 1.94 (*m*)	4.09 (*dt*, 9.0, 4.0)	1.38 (*m*); 1.86 (*m*)	1.22 (*m*); 1.72 (*m*)
17					1.53 (*m*)	1.23 (*m*)	0,96 (*m*)
18		1.58 (*m*)				0.81 (*s*)	0.69 (*s*)
19	1.42 (*m*); 1.24 (*m*)	1.30 (*m*)	0.87 (*m*); 1.48 (*m*)	0.89 (*m*); 1.58 (*m*)	1.01 (*m*); 1.49 (*m*)	0.88 (*s*)	0.86 (*s*)
20		1.18 (*m*); 1.82 (*m*)	1.69 (*m*); 1.82 (*m*)	1.41 (*m*); 1.65 (*m*)	1.56 (*m*); 1.70 (*m*)	2.20 (*m*)	2.20 (*m*)
21	1.52 (*m*); 1.36 (*m*)	0.98 (*m*)	2.38 (*q*, 11.0)	2.22 (*m*)	2.50 (*q*, 9.5)	1.00 (*d*, 6.5)	1.01 (*d*, 6.5)
22	1.50 (*m*); 1.31 (*m*)	1.42 (*m*)				5.14 (*dd*, 15.5, 7.5)	5.18 (*m*)
23	1.15 (*s*)	0.85 (*s*)	1.56 (*s*)	0.89 (*s*)	1.16 (*s*)	5.22 (*dd*, 15.5, 7.5)	5.18 (*m*)
24	1.07 (*s*)	0.87 (*s*)	1.29 (*s*)	0.96 (*s*)	1.01 (*s*)	1.85 (*m*)	1.81 (*m*)
25	1.02 (*s*)	1.04 (*s*)	0.93 (*s*)	0.87 (*s*)	0.87 (*s*)	1.49 (*m*)	1.42 (*m*)
26	1.06 (*s*)	0.79 (*s*)	1.09 (*s*)	0.96 (*s*)	1.07 (*s*)	0.81 (*d*, 7.0)	0.82 (*t*, 7.5)
27	1.10 (*s*)	0.75 (*s*)	1.00 (*s*)	0.96 (*s*)	1.04 (*s*)	0.83 (*d*, 6.5)	0.82 (*t*, 7.5)
28	0.84 (*s*)	0.74 (*s*)	0.91 (*s*)	0.87 (*s*)	0.77 (*s*)	0.91 (*d*, 7.0)	0.91 (*d*, 6.5)
29	0.87 (*s*)	0.82 (*d*, 5.0)	1.35 (*s*)	1.18 (*s*)	1.27 (*s*)		
30	0.87 (*s*)	0.88 (*d*, 5.0)	1.39 (*s*)	1.21 (*s*)	1.19 (*s*)		
32		2.04 (*s*)					

