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Secondary metabolites from *Senecio burtonii* (Compositae)

J.C. Ndom [a,*], J.T. Mbafor [b,*], A.G.B. Azebaze [a], J.C. Vardamides [a], Z. Kakam [b], A.F.W. Kamdem [a], A. Deville [c], T.M. Ngando [a], Z.T. Fomum [b]

[a] *Department of Chemistry, Faculty of Science, University of Douala, P.O. Box 24157, Douala, Cameroon*
[b] *Department of Chemistry, Faculty of Science, University of Yaounde I, P.O. Box 812, Yaounde, Cameroon*
[c] *Laboratoire de Chimie des Substances Naturelles, USM 0502 MNHN, UMR 5154 CNRS, 63 rue Buffon, 75005 Paris, France*

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Abstract

A cacalolide derivative named 4α-[2′-hydroxymethylacryloxy]-1β-hydroxy-14-(5 → 6) abeo eremophilan-12,8-olide and a shikimic acid derivative named (3′*E*)-(1α)-3-hydroxymethyl-4β,5α-dimethoxycyclohex-2-enyloctadec-3′-enoate along with three known compounds, octacosan-1-ol, 3β-hydroxyolean-12-en-28-oic acid and 3β-acetoxyolean-12-en-28-oic acid were isolated from *Senecio burtonii*. Their structures and relative configurations were established on the basis of spectroscopic analysis.

Keywords: *Senecio burtonii*; Compositae; Cacalolide; Shikimic

1. Introduction

A large variety of sesquiterpenoids (Bohlmann et al., 1985; Dupré et al., 1991), triterpenoids (Torres et al., 1998), diterpenoids, (Dong-Liang et al., 1992), pyrrolizidines (Bohlmann et al., 1986) and shikimic acid (Cardoso et al., 1987) have been characterized from *Senecio* species. This group of plants is of interest since several species belonging to it are used in traditional medicine (Steenkamp et al., 2001) while others are highly toxic (Rotshild et al., 1970). Here we report the isolation and elucidation of the structure of two new compounds among which a cacalolide derivative (Wayne et al., 1999) designated 4α-[2′-hydroxymethylacryloxy]-1β-hydroxy-14-(5 → 6) abeo eremophilan-12,8-olide **1** and a shikimic acid derivative named (3′*E*)-(1α)-3-hydroxymethyl-4β,5α-dimethoxycyclohex-2-enyloctadec-3′-enoate **2** together with two known compounds, octacosan-1-ol **3**, 3β-hydroxyolean-12-en-28-oic acid **4** and 3β-acetoxyolean-12-en-28-oic acid **5**.

* Corresponding authors. Tel.: +2377128376 (J.C. Ndom).
E-mail addresses: ndomjefr@yahoo.fr (J.C. Ndom), Jtmbafor@yahoo.fr (J.T. Mbafor).

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2. Results and discussion

The MeOH extract of the finely powdered *Senecio burtonii* on chromatography separation afforded compounds **1**–**5**. Analysis by ^{1}H, ^{13}C NMR and 2D NMR spectroscopy led to the determination of their structures.

Compound ***1*** was obtained as white crystals. Its molecular formula $C_{19}H_{26}O_6$ was deduced from the negative high-resolution electrospray-TOF mass spectrum running on an API QSTAR pulsar mass spectrometer (HRESI-TOF-MS), which shows the pseudomolecular ion peak $[M-H]^-$ at *m*/*z* 349.1652 (calc. for $C_{19}H_{26}O_6$, 350.1651). The IR spectrum of **1** showed characteristic bands at 3450 (free OH), 1750, 1760 (COOR) and 1650, 1692, 872 cm^{-1} (olefinic C=C) suggesting that its skeleton contained a free hydroxyl, γlactone, carbonyl of ester and double bond groups. Analysis of UV spectrum showed an intense absorption band at 263.5 nm λ_{max} (MeOH) suggesting the presence of a conjugated chromophore.

The broad band decoupled ^{13}C NMR Jmod spectrum displayed 19 carbon signals. This spectrum indicated the presence of five quaternary carbons with two carbonyl, two sp^2 and one sp^3 carbons; six sp^3 methine carbons, six

methylene carbons with four sp^3 and two sp^2 carbons, two primary sp^3 methyl carbons.

The ^1H NMR spectra of **1** revealed the presence of two methyls, one at δ_H 1.10 (*d*, $J = 6.2$ Hz, CH_3-13) and the other at δ_H 1.05 ppm (*s*, CH_3-15); two oxymethine at δ_H 4.35 (*ddd*, $J = 10.8$, 6.2, 3.3 Hz, H-8α) and at δ_H 4.44 ppm (*dt*, $J = 5.3$, 4.9 Hz, H-1α); three methine at δ_H 3.10 (*dd*, $J = 6.2$, 7.0 Hz, H-7), δ_H 2.50 (*dq*, $J = 6.2$, 7.0 Hz, H-11), δ_H 2.25 (*dd*, $J = 2.5$, 4.9 Hz, H-5), δ_H 1.45 ppm (*m*, H-4); an exocyclic methylene at δ_H 4.90 (*brs*, H14a) and 5.00 ppm (*brs*, H14b); three methylene at δ_H 2.15 (*dt*, $J = 12.5$, 3.0 Hz, H-3β) and δ_H 2.00 (*dt*, $J = 12.5$, 3.0 Hz, H-3α); at δ_H 1.95 (*ddd*, $J = 12.0$, 4.9, 3.0 Hz, H-2); δ_H 1,85 (*ddd*, $J = 13.5$, 10.8, 10.3 Hz, H-9α) and δ_H 1.65 ($J = 13.5$, 4.5, 4.3 Hz, H-9β) (see Table 1). This hypothesis was confirmed by the ^{13}C NMR Jmod spectrum of **1** which showed two oxygenated sp^3 methine at δ_C 81.4 and 81.0 ppm attributed, respectively, to (C-8) and (C-1); four methine at δ_C 49.9 (C-7), 41.2(C-11), 57.7 (C-5), 46.5 (C-10); three methylene at δ_C 26.5 (C-9), 28.9(C-3), 29.8 (C-2); one quaternary carbon bearing an oxygen at δ_C 78.7(C-4), one methylene sp^2 at δ_C 110.4 (C-14), one quaternary sp^2 carbon at δ_C 147.9 (C-6) and a carbonyl at δ_C 178.1 ppm attributed to γlactone (C-12) (see Table 1).

HMBC correlations between C-5 (δ_C 57.7)/H14b, C-5 (δ_C 57.7)/H14a, C-5 (δ_C 57.7)/H-1, C-5 (δ_C 57.7)/H-7, C-5 (δ_C 57.7)/CH_3-15, C-6 (δ_C147.9)/H-8, C-6 (δ_C147.9)/H-10, C-6 (δ_C147.9)/H-11, C-7 (δ_C 49.9)/H14a, C-7 (δ_C 49.9)/H14b, C-7 (δ_C 49.9)/H-5, C-7 (δ_C 49.9)/CH_3-13, C-8 {δ_C 81.4}/H-10, C-8 {δ_C 81.4}/H-11, C-10 (δ_C 46.5)/H-8, C-12 (δ_C 178.1)/H-11, C-12 (δ_C 178.1)/H-7 and C-12 (δ_C 178.1)/CH_3-13, C-14 (δ_C110.4)/H-7, C-14 (δ_C110.4)/H-5 permit us to locate one double bond at C-6 and others carbons.

From this evidence, the structure of **1** resembled that of cacalolide derivatives (Torres et al., 1997; Bohlmann et al., 1985) in the coupling pattern and most of the chemical shifts.

Furthermore, the 2′-hydroxymethylacryloxyl moiety was required in the ^1H NMR and ^{13}C NMR spectrum. It showed a typical exocyclic methylene at δ_H 6.10 (*dd*, $J = 1.1$, 3.0 Hz) and at δ_H 5.65 ppm (*dd*, $J = 1.0$, 3.0 Hz); at δ_H 4.00 (*dd*, $J = 1.1$, 11.0 Hz) and δ_H 3.99 ppm (*dd*, $J = 1.0$, 11.0 Hz); two oxymethylene. This was corroborated in ^{13}C NMR spectra by signals at δ_C 62.6 an oxymethylene carbon (C-4′), a methylene sp^2 at δ_C 119.7 (C-3′), a quaternary sp^2 at δ_C 147.7 (C-2′) and another signal at δ_C 172.8 attributed to a carbonyl of α,β unsaturated ester (C-1′). The loss of 2′-hydroxymethylacryloxyl chain from the molecular ion peak at *m/z* 350 in the mass spectrum of **1** confirmed the presence of this moiety. The coupling (COSY) relationship established completely different patterns in compound **1**.

The linkage of the 2′- hydroxymethylacryloxyl moiety at C-4 position was established by HMBC correlations between C-4/H-10, C-4/H-2, C-4/CH_3-15, C-5/H-1, C-5/H-3.

Table 1
^1H and ^{13}C spectral data of 1 (DMSO, δ values)

Attribution	δ_H (J = Hz)	δ_C	HMBC
1			
Hα	4.44 (*dt*, 5.3, 4.9)	81.0	H-5α, H-9α, H-9β, H-3α, H-3β
2			
Hα	1.95 (*ddd*, 12.0, 4.9, 3.0)	29.8	H-10α
Hβ	1.95 (*ddd*, 12.0, 4.9, 3.0)		
3			
Hα	2.00 (*dt*, 12.5, 3.0)	28.9	H-5, H-1α, CH_3-15
Hβ	2.15 (*dt*, 12.5, 3.0)		
4		78.7	H-10α, CH_3-15, H-2α, H-2β
5			
Hα	2.25 (*dd*, 1.5, 4.9)	57.7	H-1α, H14a, H14b, CH_3-15, H-9α, H-9β, H-7α
6			
Hα		147.9	H-8α, H-10α, H-11α
7			
Hα	3.10 (*dd*, 6.2, 7.0)	49.9	H14a, H14b, H-5α, CH_3-13, H-9α, H-9β
8			
Hα	4.35 (*ddd*, 10.8, 6.2, 3.3)	81.4	H-11, H-10α
9			
Hα	1.85 (*dd*, 13.5, 10.8, 10.3)	26.5	H-5α, H-7α, H-1α
Hβ	1.65 (*dd*, 13.5, 4.5, 3.3)		
10			
Hα	1.45 (*m*)	46.5	H-8α, H-2α, H-2β
11			
Hα	2.50 (*dq*, 6.2, 7.0)	41.2	H-8α, H-7α
12		178.1	H-11α, CH_3-13, H-7α
13	1.10 (*d*, 6.2)	12.6	
14			
	4.90 *br*(*s*)	110.4	H-7α, H-5α
	5.00 *br*(*s*)		
15			
	1.05 (*s*)	23.8	
1′		172.8	H-3′, H-4′
2′		147.7	H-4′
3′			
Ha	6.10 (*dd*, 1.1, 3.0)	119.7	
Hb	5.65 (*dd*, 1.0, 3.0)		
4′			
Ha	4.00 (*dd*, 1.1, 11.0)	62.6	H-3′
Hb	3.99 (*dd*, 1.0, 11.0)		

NOESY correlations between H-11 (δ_H 2.50)/H-8 (δ_H 4.35), H-8 (δ_H 4.35)/H-10 (δ_H 1.45), H-5 (δ_H 2.20)/H-7 (δ_H 3.10), H-5 (δ_H 2.20)/H-1 (δ_H 4.44) (Fig. 1) and the various observed coupling constants (see Table 1) indicated the close spatial proximity of particular protons and their relative configurations. All these data confirmed that compound **1** is an eremophila-12,8-olide in which the CH_3-14 has probably transferred from C-5 to C-6. In agreement with all these data, compound **1** was determined as 4α-

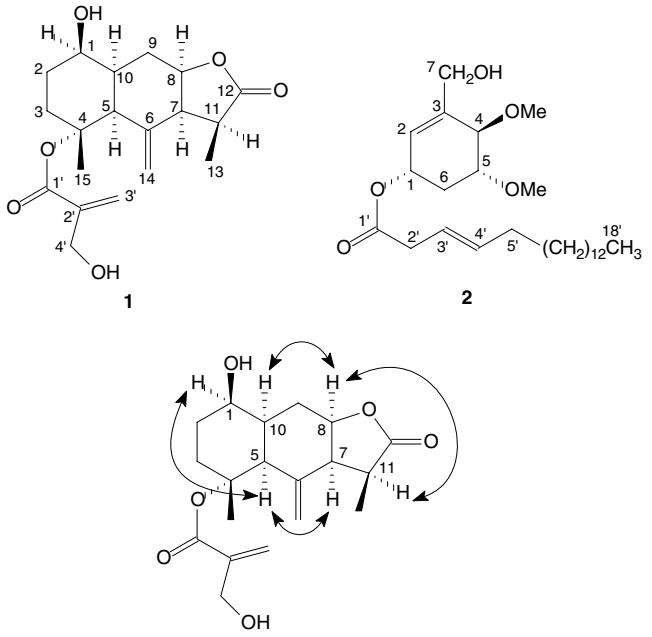

Fig. 1. Selected NOESY correlations.

[2′-hydroxymethylacryloxy]-1β-hydroxy-14-(5 → 6) abeo eremophilan-12,8-olide.

Compound **2** was obtained as a white powder. Its molecular formula $C_{27}H_{48}O_5$ was deduced from the positive high-resolution electrospray-TOF mass spectrum running on a API QSTAR pulsar mass spectrometer (HRESI-TOF-MS) which showed the pseudomolecular ion peak $[M+H]^+$ m/z = 453.3580 $[M+H]^+$ (calc. for $C_{27}H_{48}O_5$452.3579).

IR spectrum of compound **2** showed absorption bands at 3450 (free OH); 1750 (COOR) and 1600 (C=C) suggesting that its skeleton contained a free hydroxyl group and an ester function. The ^{1}H NMR spectra of **2** showed signals of three oxmethine at δ_H 4.63 (*ddd*, J = 11.2, 4.3, 6.5 Hz), δ_H 4.35 (*d*, J = 10.8 Hz), δ_H 4.28 (*ddd*, J = 10.8, 11.0, 4.3 Hz) assigned, respectively, to H-1β, H-4α, H-5β and also the hydroxymethylene at δ_H 4.50 (*dd*, J = 4.6, 8.0 Hz, H-7a) and δ_H 4.45 (*dd*, J = 4.6, 8.0 Hz, H-7 b), a vinylic proton at δ_H 5.46 (*d*, J = 6.5 Hz, H-2), two methylene at δ_H 2.25 (*ddd*, J = 14.2, 11.2, 11.0 Hz, H-6α) and δ_H 2.18 (*ddd*, J = 14.2, 4.3, 6.5 Hz, H-6β), two methoxyl groups at δ_H 3.50 ppm. (see Table 2). This hypothesis was confirmed by the ^{13}C NMR Jmod spectrum of **2** which showed three oxymethine at δ_C 77.2 (C-4), 73.5(C-1) and 73.0 (C-5), a methylene at δ_C 36.1 (C-6), a quaternary sp^2 carbon at δ_C 136.4 (C-3), a sp^2 methine at δ_C 123.5 (C-2), a hydroxymethylene at δ_C 62.4 (C-7) and two methoxyl at δ_C 53.4 (OMe-4) and 50.1 ppm (OMe-5). The position of methoxyl groups were determined by HMBC correlations between OMe-4 (δ_C 53.4)/H-4α and OMe-5 (δ_C 50.1)/H-5β. These data suggested that structure **2** was resembled to the shikimic acid derivatives (Bohlman and Zdero, 1982; Bohlman et al., 1984, 1985; Torres et al., 2000).

Table 2
^{1}H and ^{13}C spectral data of **2** (pyridine, δ values)

Attribution	δ_H (J = Hz)	δ_C	HMBC
1			
H-1β	4.63 (*ddd*, 11.2, 4.3, 6.5)	73.5	H-5β, H-2
2			
H-2	5.46 (*d*, 6.5)	123.5	H-4α, H-7a, H-7b, H-6α,
3		136.4	H-1β, H-5β
4			
H-4α	4.35 (*d*, 10.8)	77.2	H-2, H-6α, H-6β, H-7a, H-7b
5			
H-5β	4.28 (*ddd*, 10.8, 11.0, 4.3)	73.0	H-1β
6			
H-6α	2.25 (*ddd*, 14.2, 11.2, 11.0)	36.1	H-4α, H-2
H-6β	2.18 (*ddd*, 14.2, 4.3, 6.5)		
7			
7a	4.50 (*dd*, 4.6, 8.0)	62.4	H-4α, H-2
7b	4.45 (*dd*, 4.6, 8.0)		
CH_3O-4	3.5 (*s*)	53.4	H-4α
CH_3O-5	3.5 (*s*)	50.1	H-5β
OCOR			
1′		175.9	H-3′, H-1β
2′	2.3 (*dd*, 14.2, 3.6)	34.3	
	1.98 (*dd*, 14.2, 3.6)		
3′	5.50 (*dt*, 11.4, 3.6)	131.3	H-5′
4′	5.50 (*dt*, 11.4, 3.6)	131.2	H-2′a, H-2′b
5′	1.75 (*dt*, 3.6, 6.6)	26.3	
	1.75 (*dt*, 3.6, 6.6)		
6′–17′	1.30	30.3	
18′	0.91 (*t*, 6.8)	14.8	

Furthermore, the ^{1}H NMR spectra showed signals corresponding to two methylenes at δ_H 2.30 and 1.98 ppm (2H, *dd*, J = 14.2, 3.6 Hz, H-2′), at δ_H 1.75 (*dt*, J = 3.6, 6.6 Hz, H-5′), two vinylic protons at δ_H 5.50 (*dt*, J = 11.4, 3.6, 3.3 Hz, H-3′ and H-4′), one methyl at δ_H 0.91 (*t*, J = 6.8 Hz) and a long methylene aliphatic chain at δ_H1.30 ($(CH_2)_{14}$).

This hypothesis was confirmed by the ^{13}C NMR Jmod which showed a carbonyl at δ_C 175.9 (C-1′), two sp^2 methine at δ_C 131.3 and 131.2, a methyl at δ_C 14.8 (C-18), three methylene at δ_C 34.3, 26.3 and 30.3 ppm.

At this stage, the presence of a strong peak due to the loss of the long fatty acid chain at m/z 282 ($C_{18}H_{34}O_2$) was observed. This was confirmed by the elimination of ester side chain during the reaction of saponification. Consequently, the 3-position for the C-18 acid was favoured and this was strongly supported by the result of saponification since the allylic position is preferred. Examination of the COSY spectrum helped us to assign the different pattern in compound **2**. All protons and the ester side chain were located using HMBC correlations between C-1/H-2, C-1/H-5β, C-2/H-4α, C-2/H-7a, C-2/H-7b, C-2/H-6α,

C-2/H-6β, C-3 /H-1β, C-3/H-5β, C-4/H-7a, C-4/H-7b, C-4/H-2, C-4/H-6α, C-4/H-6β, C-5/H-1β, C-1′/H-1β, C-1′/H-3′.

NOESY correlations between H-1 (δ 4.63)/H-5 (δ 4.28), lack of correlation between H-1 (δ_H 4.63)/H-4 (δ 4.35) and observed coupling constant between H-4 and H-5 (see Table 2) indicated the close spatial proximity of proton H-1/H-5. Thus compound **2** was determined as (3′*E*)-(1α)-3-hydroxymethyl-4β,5α-dimethoxycyclohex-2-enyloctadec-3′-enoate.

Compound ***3*** was found to be octacosan-1-ol (Piatak and Reimann, 1970).

Compounds ***4*** *and* ***5*** were identified, respectively, as olean-12 derivatives, namely 3β-hydroxyolean-12-en-28-oic acids, and 3β-acetoxyolean-12-en-28-oic acids, all in agreement with the results reported by (Maillard et al., 1992).

3. Experimental

3.1. General experimental procedures

Melting points were determined on a Buchi apparatus and were uncorrected. UV spectra were obtained on a Shimadzu-265 Spectrometer. IR spectrum was recorded on a Perkin–Elmer 727B spectrometer in KBr disks. The HRESI-TOF-MS and ESI-TOF-MS/MS were obtained in the positive and negative ion mode on an API QSTAR pulsar mass spectrometer. NMR spectra were run on a Bruker instrument equipped with a 5 mm ^{1}H and ^{13}C probe operating at 300 and 75 MHz, respectively, with TMS as internal standard. ^{1}H assignments were made using 2D-COSY and NOESY (mixing time 500 ms experiments) while ^{13}C assignments were made using 2D-HSQC and HMBC (time 70 ms) experiments. Silica gel, 230–400 Mesh (Merk) and silica gel 70–230 Mesh (Merk) were used for flash and column chromatography, respectively, while precoated aluminium sheets silica gel 60 F_{254} were used for TLC with a mixture of hexane–ethyl acetate as eluents; spot were visualised by UV lamp (254 nm) and (365 nm) or by MeOH–H_2SO_4 reagent.

3.2. Plant material

Senecio burtonii Hook is a perennial medicinal herb native to mount Cameroon (2300 m) in the South-West of Cameroon. A voucher specimen (ICN 13468) is deposited in the botanical garden Limbe. Aerial parts of *Senecio burtonii* (*Compositae*) were collected from mount Cameroon in the South west province of Cameroon.

3.3. Extraction and isolation

Air-dried and ground aerial plants of *Senecio burtonii* were successively extracted with water and methanol. The methanol extract (100 g) after concentration under reduced pressure was subjected to column chromatography over Si gel 60 (70–230 mesh) using hexane–EtOAc mixture in increasing polarity as eluent. A total of 200 frs of ca. 250 ml each were collected and combined on the basis of TLC analyses leading to six series (A–F).

Series A (2.5 g) eluted with hexane–EtOAc (97.5:2.5) was column chromatographed over Si gel using hexane–EtOAc mixtures of increasing polarity. A total of 40 frs of ca. 100 ml each were collected. Fr 26–28 (1 g), eluted with hexane–EtOAc (97.5:2.5) were subjected to column chromatography over Si gel using hexane–EtOAc (95:5) to afford compound **3** (100 mg) and compound **2** (75 mg).

Series E (3 g) eluted with hexane–EtOAc (4:1) was chromatographed over Si gel using hexane–EtOAc mixtures of increasing polarity to give 45 frs of ca. 50 ml. Eluted with hexane–EtOAc (85:15) were combined on the basis of TLC and was further purified by column chromatography to yield compound **4** (30 mg) and 5 (25 mg).

Series D (1 g) eluted with hexane–EtOAc (75: 25) was chromatographed over Si gel using hexane–EtOAc mixtures of increasing polarity to give 25 frs of ca. 50 ml eluted with hexane–EtOAc (75:25) were combined on the basis of TLC and a compound linked with oil was obtained. The mixture was subjected to prep TLC with hexane–EtOAc (75:25) to yield compound **1** (10 mg).

3.3.1. 4α-[2′-hydroxymethylacryloxy]-1β-hydroxy-14-(5 → 6) abeo eremophilan-12,8-olide 1

White crystals m.p. 185–187 °C; (HRESI-TOF-MS) $[M-H]^-$ at *m*/*z* 349.1652 (calc. for $C_{19}H_{26}O_6$, 350.1651); UV λ_{max} (MeOH) 263.5 nm; IR ν_{max} (KBr) 3450, 1750, 1760, 1650, 1692 and 872 cm^{-1}; ^{1}H NMR and ^{13}C NMR Jmod (DMSO) (see Table 1); ESI-TOF-MS/MS *m*/*z* 102 ($C_4H_6O_3$).

3.3.2. (3′E)- (1α)-3-hydroxymethyl-4β, 5α-dimethoxycyclohex-2-enyloctadec-3′-enoate

White crystals m.p. 162–164 °C; (HRESI-TOF-MS) $[M+H]^+$ *m*/*z* 453.3580 $[M+H]^+$ (calc. for $C_{27}H_{48}O_{5452.3579}$); IR ν_{max} (KBr) 3450, 1750, 1600 cm^{-1}; ^{1}H NMR and ^{13}C NMR Jmod (Pyridine) (see Table 2); ESI-TOF-MS/MS *m*/*z* 284 ($C_{18}H_{36}O_2$).

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