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New septanoside and 20-hydroxyecdysone septanoside derivative from *Atriplex portulacoides* roots with preliminary biological activities

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ABSTRACT

The phytochemical investigation of a Tunisian plant *Atriplex portulacoides* (Chenopodiaceae) led to the isolation of two new compounds designated as portulasoid (**2**) and septanoecdysone (**3**) along with the known 20-hydroxyecdysone (20HE) (**1**). Their chemical structures were elucidated on the basis of extensive spectroscopic methods including ES-HRMS, 1D and 2D-NMR. The isolated compounds were finally tested for their antioxidant activity by using DPPH$^{\cdot}$, ABTS$^{\cdot+}$, Fe^{3+} and catalase assays and also for their antibacterial and anticholinesterase activities.

Atriplex portulacoides L. [Syn. *Obione portulacoides* (L.) Moq., *Halimione portulacoides* Aellen] is a perennial, shrubby halophytic plant. Widespreaded in salt marshes along the coasts of Europe, North Africa and South-West Asia, its belongs to Chenopodiaceae family (goosefoot family), that is largely distributed throughout the world especially in arid and saline regions.[1] This family is consisted of 104 genus and more than 1400 species, the majority growing naturally in saline soils.[2] Different species of *Atriplex* (*A. hortensis*, *A. fruticosa*, *A. inflata*, *A. parvifolia*, *A. semibaccata*, *A. undulata*, *A. vestita*) including *A. portulacoides* were reported as sources of interesting biological effects (antifungal, antiviral, antioxidant, cytotoxic, antimicrobial, etc.) through their extracts or their chemical constituents.[3–8] In a phytochemical point of view, previous investigations of some *Atriplex* species revealed the presence of many classes of secondary metabolites such as tannins, flavonoids, alkaloids, proteins and amino acids as well as terpenoids, saponins and long chain alcohols.[7–11] Surprisingly and according to literature, only a few phytochemical study of *Atriplex portulacoides* was reported.[11] The present research work describes the isolation and the structural elucidation of the known 20-hydroxyecdysone (20HE) (**1**) from *n*-BuOH aerial parts extract of *A. portulacoides*, along with two new compounds: an *O*-butylated septanoside **2** and an *O*-ecdysone septanoside **3** from *n*-BuOH roots extract.[12]

Compound **1** (m = 15 mg) (Fig. 1) was isolated as a white solid from the *n*-BuOH extract. Its UV spectrum exhibited a band at λ_{max} (MeOH): 243 nm. The ^{1}H NMR (300 MHz) spectrum recorded in CD_3OD showed five methyl groups: δ_H 0.90 (H_{18}); δ_H 0.98 (H_{19}); δ_H 1.18 (H_{21} and H_{26}) and δ_H 1.19 (H_{27}), a set of methylene group signals between δ_H 1.00 to δ_H 2.00, the ethylenic CH (δ_H 5.81; H_7), along with 3 × CH-OH (δ_H 3.32; 3.83; 3.95) and 3 × quaternary *O*-bonded carbons, that constitute a fingerprint of 20HE skeleton. This was corroborated by ^{13}C NMR spectrum which revealed, beside the three *O*-bonded quaternary carbons (δ_C 71.3; 77.9; 85.2), the presence of α,β-unsaturated ketone (δ_C 122.1; 168.0; 206.5). The spectral data using ^{1}H and ^{13}C NMR spectra were consolidated through the 2D NMR spectroscopy examination such as: COSY, HMQC and HMBC (Table 1). Finally, the acquisition of the mass spectrum by using the ES-HRMS in a positive mode showed a peak at m/z 503.2986 that corresponds to a $[M+Na]^+$ pseudo-molecular ion. From the latter, a molecular formula of $C_{27}H_{44}O_7$

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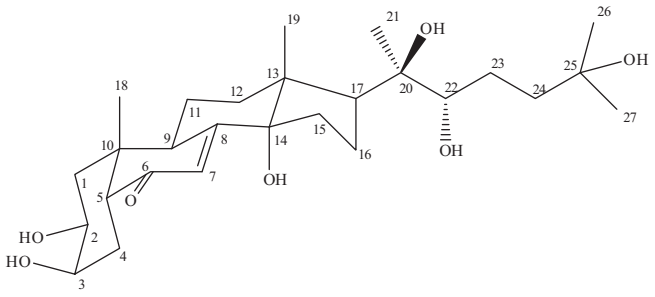

Figure 1. The structure of compound **1**.

related to 20-hydroxyecdysone (20HE), already known in *Atriplex* genus[11a,13] was confirmed according to literature spectral data.[14]

Compound **2** (20 mg) (Fig. 2) was obtained as a white solid from the *n*-BuOH roots extract of *A. portulacoides*. Its molecular formula $C_{10}H_{20}O_6$ was deduced from ES-HRMS analysis through $[M+Na]^+$ pseudo-molecular ion peak at *m*/*z* 259.0847. The ^1H and ^{13}C NMR spectra showed two different moieties: alkyl chain and polyol chain.

Alkyl chain moiety: Analysis of the high field or low-frequency region of 1D NMR and HMQC experience pointed out three signals [H_{12} (δ_H 0.93, 3H, t, J = 7.3 Hz)/δ_C 14.3; H_{11} (δ_H 1.39, 2H, sex, J = 7.3 Hz)/δ_C 20.4 and H_{10} (δ_H 1.50, 2H, quit, J = 7.3 Hz)/δ_C 33.5] suggesting the presence of an alkyl chain. Moreover, the ^1H–^1H COSY spectrum revealed three correlations between H_{12}–H_{11}; H_{11}–H_{10} and another one between H_{10} at δ_H 1.50/δ_C 33.5 and deshielding H_9 (2H) at δ_{Ha} 3.45; δ_{Hb} 3.71/δ_C 62.2. The above chemical shift values of protons and carbons, suggest the presence of a butyloxy group.

Polyol chain moiety: The set of signals between δ_H 3.45 and δ_H 4.11 in ^1H NMR and δ_C 62.2 and δ_C 78.4 in ^{13}C NMR revealed the presence of a polyol chain consisted of five *O*-bonded carbons (two methylenes and three methines groups) in the structure of compound **2**. Moreover, the quaternary di-oxygenated carbon observed at δ_C 105.2 (C_1), suggest the presence of 'sugar like' anomeric carbon (acetal group). Beside the six carbons observed in ^{13}C*jmod* and attributed according to HMQC experiment, the

Table 1
^1H (300 MHz) and ^{13}C (75 MHz) NMR and HMBC spectral data for compounds **1** and **3** in CD_3OD (δ in ppm; J Hz).

Compound **1**				Compound **3**					
Pos	δ ^{13}C	δ ^1H	HMBC	Pos	δ ^{13}C	δ ^1H	COSY	HMBC	NOESY
20-Hydroxyecdysone (C_{27} moiety)				*20-Hydroxyecdysone (C_{27} moiety)*					
1α	37.3	1.80 m	C_3; C_2; C_5; C_{10}; C_9; C_{18}	1α	37.3	1.80 m	H_2; H_1	C_2; C_3; C_5; C_9; C_{10}; C_{18}	–
1β		1.42 m		1β		1.42 m			
2	68.7	3.83 m	C_3	2	68.7	3.83 m	H_3; H_1	C_3	H_1; H_9; H_3
3	68.5	3.95 m	C_1; C_5; C_2	3	68.5	3.95 m	H_2; H_1	C_1; C_2; C_5	H_2
4α	32.9	1.75 m	C_3; C_2; C_5; C_{10}; C_9	4α	32.8	1.66 m	H_3; H_5	C_2; C_3; C_5; C_9; C_{10}	H_2
4β		1.66 m		4β		1.75 m			
5	51.8	2.38 m	C_7; C_3; C_2; C_{13}; C_{10}; C_1; C_9; C_4; C_{18}	5	51.7	2.38 m	H_1	C_1; C_3; C_4; C_7; C_9; C_{10}; C_{18}	H_1; H_4
6	206.5	–	–	6	206.5	–	–	–	
7	122.1	5.81 s	C_9; C_5; C_{14}	7	122.1	5.81 s	H_9; H_5	C_5; C_9; C_{14}	H_{12}
8	168.0	–	–	8	168.0	–	–	–	
9	35.1	3.14 m	C_8; C_7; C_{10}; C_{18}; C_{11}	9	35.1	3.14 m	H_7; H_{11}	C_7; C_8; C_{10}; C_{11}; C_{18}	H_4; H_2
10	39.3	–	–	10	39.3	–	–	–	–
11α	21.4	1.78 m		11α	21.5	1.78 m	H_{12}		–
11β		1.65 m		11β		1.65 m			
12α	32.5	2.13 m	C_{14}; C_{13}; C_9; C_{11}	12 α	32.5	2.15 m	H_{11}	C_9; C_{11}; C_{13}; C_{14}	H_{19}; H_{21}; H_{15}; H_{11}
12β		1.85 m		12β		1.86 m			H_{21}; H_{17}
13	48.6	–	–	13	48.6	–	–	–	–
14	85.2	–	–	14	85.2	–	–	–	–
15α	31.8	2.00 m	C_{14}; C_{17}; C_{13}	15α	31.8	1.99 m	H_{16}	C_{13}; C_{14}; C_{17}	H_{12}
15β		1.56 m		15β		1.56 m			
16α	21.5	1.77 m	C_8; C_{14}; C_{20}; C_{17}; C_{15}; C_{21}	16α	21.5	1.77 m	H_{15}	C_8; C_{14}; C_{15}; C_{17}; C_{20}; C_{21}	–
16β		1.99 m		16β		1.97 m			
17	50.5	2.39 m	C_{13}; C_{12}; C_{11}; C_{19}	17	50.5	2.39 m	H_{16}	C_{11}; C_{12}; C_{13};C_{19}	H_{18}; H_{21}; H_{12}
18	18.1	0.90 s	C_2; C_5; C_{10}; C_9; C_{11}	18	24.4	0.90 s	–	C_2; C_5; C_9; C_{10}; C_{11}	H_{17}
19	24.4	0.98 s	C_{14}; C_{17}; C_{13}; C_{12}	19	18.3	0.98 s	–	C_{12}; C_{13}; C_{14}; C_{17}	H_{12}
20	77.9	–	–	20	77.9	–	–	–	–
21	21.0	1.18 s	C_{17}; C_{24}	21	21.0	1.18 s	–	C_{17}; C_{24}	–
22	78.4	3.32 m	$C_{1'}$; C_{20}; C_{17}; C_{24}; C_{23}; C_{21}	22	78.4	3.32 m	H_{23}	C_{17}; C_{20}; C_{21}; C_{23}; C_{24}; $C_{1'}$	–
23a	27.3	1.67 m	C_{25}; C_{24}	23a	27.3	1.66 m	H_{22}; H_{24}	C_{24}; C_{25}	–
23b		1.30 m		23b		1.30 m			
24a	42.4	1.80 m	C_{22}; C_{25}; C_{27}; C_{26}; C_{23}	24a	42.4	1.80 m	H_{23}	C_{22}; C_{23}; C_{25}; C_{26}; C_{27}	–
24b		1.43 m		24b		1.44 m			
25	71.3	–	–	25	71.5	–	–	–	–
26	28.9	1.18 s	C_{20}; C_{25}; C_{24}; C_{27}	26	29.0	1.18 s	–	C_{20}; C_{24}; C_{25}; C_{27}	–
27	29.7	1.19 s	C_{20}; C_{25}; C_{24}; C_{26}	27	29.7	1.19 s	–	C_{20}; C_{24}; C_{25}; C_{26}	–
				Septanose moiety					
				1′	105.2	–	–	–	–
				2′	78.4	4.13 d (8.0)	$H_{3'}$	$C_{3'}$	$H_{3'}$; $H_{8'}$
				3′	77.3	3.95 dd (7.8; 7.5)	$H_{2'}$; $H_{4'}$	$C_{2'}$; $C_{4'}$; $C_{5'}$	H'_2; $H_{4'}$
				4′	83.4	3.76 m	$H_{3'}$; $H_{5'}$	$C_{5'}$	$H_{3'}$; $H_{5'b}$
				5′a	64.7	3.75 m	$H_{4'}$; $H_{7'}$	$C_{4'}$; $C_{7'}$	$H_{7'a}$
				5′b		3.57 m	$H_{4'}$; $H_{7'}$		$H_{4'}$
				7′a	61.4	3.66 m	$H_{5'}$	$C_{1'}$; $C_{2'}$; $C_{8'}$	$H_{5'a}$
				7′b		3.50 m	$H_{5'}$		–
				8′	49.5	3.34 s	–	$C_{1'}$	$H_{2'}$