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HOPANE-TYPE SAPONINS FROM *POLYCARPON SUCCULENTUM* GROWING IN EGYPT

MESELHY R. MESELHY* and EL-SAYED A. ABOUTABL

Department of Pharmacognosy, College of Pharmacy, Cairo University, Cairo 11562, Egypt

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Key Word Index—*Polycarpon succulentum*; Caryophyllaceae; hopane-type saponins; succulentosides A and B.

Abstract—Two new hopane-type saponins, succulentosides A and B, were isolated from *Polycarpon succulentum* (whole plant). Based on spectral analyses (including 2D NMR, and FAB-mass spectroscopy), the structures of succulentosides A and B were characterized as 6α-*O*-[α-L-arabinopyranosyl-(1-3)-α-L-arabinopyranosyl]-β-*O*-β-D-xylopyranosyl-16β-*O*-β-D-xylopyranosyl-22-hydroxyhopane, and 6α-*O*-α-L-arabinopyranosyl-3β-*O*-β-D-xylopyranosyl-16β-*O*-β-D-xylopyranosyl-22-hydroxyhopane, respectively.

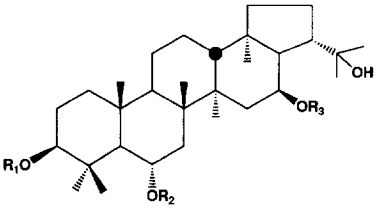
INTRODUCTION

Polycarpon succulentum (Del.) G. Gay is a small annual herb spread throughout the Sainai Desert near El-Arish. The butanol-soluble fraction of the ethanolic extract of *P. succulentum* exhibited considerable anti-inflammatory and antispasmodic activities [1]. This observation prompted us to perform detailed chemical investigations of this plant. This paper is concerned with the isolation and structure elucidation of two new hopane-type saponins, succulentosides A (**1**) and B (**2**).

RESULTS AND DISCUSSION

The 70% alcoholic extract of *P. succulentum* (whole plant) was extracted successively with carbon tetrachloride, ethyl acetate and butanol. Repeated DCCC of the saponin mixture prepared from the butanol extract yielded succulentosides A (**1**) and B (**2**).

Succulentoside A (**1**) was crystallized from methanol–diethylether as needles, mp 258–260° and reacted positively to the Liebermann–Burchard and Molisch tests. The IR spectrum showed the presence of a hydroxyl group (3420 cm^{-1}). The FAB-mass spectrum (positive ion mode) spectrum showed a quasi-molecular ion peak at *m/z* 1027 $[M+Na]^+$, revealing its M_r to be 1004 consistent with the molecular formula $C_{50}H_{84}O_{20}$ and indicating the presence of 9 double bond equivalents in the molecule. Microhydrolysis of **1** on TLC, afforded xylose and arabinose.



	R_1	R_2	R_3
1:	Xylose	Arabinose (3"—1"') arabinose	Xylose
1a:	Xylose (x 3 Ac)	Arabinose (3"—1"') arabinose (x 5 Ac)	Xylose (x 3 Ac)
2:	Xylose	Arabinose	Xylose
3:	H	H	H

The ^1H NMR spectrum (pyridine-d_5, 400 MHz) showed signals characteristic for eight tertiary methyls as singlets at δ0.80, 0.94, 1.05, 1.09, 1.30, 1.44, 1.52 and 1.85, and four anomeric protons at δ4.84, 4.89, 4.90 and 5.16 (each *d*, $J = 7.5$ Hz) (Table 1). By inspection of the ^1H–^1H COSY spectrum the following spin systems were identified: H-17–H-21–H-$20_{A/B}$–H-$19_{A/B}$; H-3–H-$2_{A/B}$–H-$1_{A/B}$; H-5–H-6–H-$7_{A/B}$ and H-17–H-16–H-$15_{A/B}$ (Table 1).

The ^{13}C NMR spectrum of **1** (pyridine-d_5, 100 MHz) analysed by the aid of APT, DEPT and ^1H–^{13}C COSY, revealed the presence of 50 carbon atoms in the molecule (Table 2). Thirty carbon signals were indicated

* To whom correspondence should be addressed.

Present address: Department of Cell-resources Engineering, Research Institute for Wakan-Yaku, Toyama Medical and Pharmaceutical University, 2630 Sugitani, Toyama 930-01, Japan.

Table 1. ^{1}H NMR spectral data of compounds **1** and **2** in pyridine-d_5

H	1	2	H	1	2
Aglycon			Xylose		
1_A	1.69 *brdt* (12.5, 20)	1.70 *m*	1′	4.90 *d* (7.5)	4.92 *d* (7.5)
1_B	0.99 *brdd* (12.5, 2.5)	1.04*	2′	4.06 *t* (7.5)	4.05 *t* (7.5)
2_A	2.26 *m*	2.26 *dd* (10.0, 4.0)	3′	4.14*	4.17 *m*
2_B	1.96 *m*	1.98 *m*	4′	4.20*	4.17 *m*
3	3.42 *dd* (12.0, 4.5)	3.43 *dd* (11.5, 5.0)	$5'_A$	4.39 *m*	4.44 *dd* (10.0, 4.0)
5	1.35 *d* (9.5)	1.36 *d* (10.5)	$5'_B$	3.76 *m*	3.77 *m*
6	4.25 *m*	4.31 *ddd* (10.5, 10.5, 4.0)	Arabinose		
7_A	2.33 *m*	2.39 *dd* (12.0, 4.0)	1″	4.84 *d* (7.5)	4.91 *d* (7.5)
7_B	1.89 *m*	1.93 *m*	2″	3.93 *t* (7.5)	3.95 *t* (7.5)
9	1.41*	1.40*	3″	4.11*	4.13*
11_A	1.55 *m*	1.54 *m*	4″	4.30 *m*	4.26 *m*
11_B	1.46 *m*	1.46 *m*	$5''_A$	4.32 *m*	4.38 *dd* (11.0, 5.0)
12_A	1.43*	1.48 *m*	$5''_B$	3.78 *dd* (11.5, 6.5)	3.78 *m*
12_B	1.33 *m*	1.28*			
13	1.29*	1.24*	Arabinose		
15_A	2.29 *m*	2.29 *dd* (10.0, 5.0)	1‴	5.16 *d* (7.5)	
15_B	1.76 *m*	1.74 *m*	2‴	4.57 *t* (7.5)	
16	4.48 *td* (10.5, 4.0)	4.49 *ddd* (10.0, 10.0, 4.0)	3‴	4.18 *m*	
17	1.83 *t* (10.5)	1.81 *t* (10.0)	4‴	4.04 *m*	
19_A	1.22*	1.18*	$5'''_A$	4.37 *m*	
19_B	0.95*	0.98 *m*	$5'''_B$	3.70 *ddd* (17.0, 11.0, 9.0)	
20_A	1.79 *m*	1.76 *m*	Xylose		
20_B	1.38 *m*	1.38 *m*	1⁗	4.89 *d* (7.5)	4.89 *d* (7.5)
21	2.74 *q* (10.5)	2.73 *q* (10.0)	2⁗	3.95 *t* (7.5)	4.01 *t* (7.5)
23	1.85 *s*	1.86 *s*	3⁗	6.16*	4.14*
24	1.52 *s*	1.62 *s*	4⁗	4.13 *m*	4.28 *m*
25	0.80 *s*	0.80 *s*	$5''''_A$	4.34 *m*	4.41 *dd* (11.0, 5.0)
26	0.94 *s*	0.96 *s*	$5''''_B$	3.80 *dd* (12.0, 7.0)	3.80 *m*
27	1.09 *s*	1.10 *s*			
28	1.05 *s*	1.06 *s*			
29	1.44 *s*	1.43 *s*			
30	1.30 *s*	1.30 *s*			

δ values in ppm and coupling constants (in parentheses) in Hz.
* Signal pattern unclear due to overlapping.

for the aglycone part with signals characteristic for eight tertiary methyls, eight methylenes, eight sp^3 methines and six saturated quaternary carbons (including a carbon signal at δ72.9). Twenty carbon signals were seen for the sugar moieties (including signals for four anomeric carbons at δ107.9, 105.7, 105.6 and 104.7), indicating four monosaccharide moieties.

On the other hand, the FAB-mass spectrum of **1** showed characteristic fragment ions at *m/z* 968 $[(M+Na)-59]^+$ for the loss of a tertiary propanol residue, 459, 441, 423, 207 and 189 suggested that the aglycone part is a 22-hydroxyhopane-type triterpene [2, 3].

Acetylation of **1** with acetic anhydride–pyridine at room temperature afforded **1a**, mp 301–303°, analysed for $C_{72}H_{107}O_{31}$ ($[M+H]^+$ at *m/z* 1467) as indicated by positive ion FAB-mass spectrometry. Its IR spectrum still exhibited the presence of a hydroxyl absorption (3580 cm^{-1}) which presumably is tertiary as it resisted acetylation. The ^{1}H NMR and ^{1}H–^{1}H COSY spectra of **1a** ($CDCl_3$, 400 MHz) displayed signals for eight tertiary methyls (δ0.89–1.83) and eleven acetyl methyls (δ1.98–2.30). Besides, signals for four anomeric protons (δ5.31, 5.41, 5.52 and 5.58) and signals at δ2.60, 3.20, 4.08 and 4.42 assigned for H-21, H-3, H-6 and H-16, respectively, were also observed. The ^{13}C NMR spectrum of **1a** ($CDCl_3$, 100 MHz) showed signals characteristic for eleven ester carbonyl carbons at δ170.79, 170.65, 170.62, 170.49, 170.46, 170.36, 170.31, 170.21, 170.02, 169.79, 169.39.

From the above data, and by comparing ^{13}C NMR shielding data of **1** with the literature reports for triterpenoids [4], the aglycone part was identified as mollugogenol A (**3**), a triterpene isolated from *Mollugo pentaphylla* L. (Syn. *M. stricta* L.) [5].

The assignment of carbon signals due to the common sugar moiety of **1** was carried out by a detailed inspection of 1D and 2D experiments (^{1}H–^{1}H COSY, and HMQC) where information on the respective sugar residues and the anomeric configurations could be obtained. This information together with published chemical shift data for methyl-*O*-glycosides [6] and by considering the glycosidation effect [7], allowed us

Table 2. ^{13}C NMR spectral date of compounds **1** and **2** in pyridine-d_5

^{13}C	1	2	3*	^{13}C	1	2
Aglycon				Xylose		
1	39.1 *t*	39.1 *t*	38.5 *t*	1′	107.9 *d*	107.8 *d*
2	26.5 *t*	26.6 *t*	26.7 *t*	2′	75.5 *d*	75.5 *d*
3	89.1 *d*	89.0 *d*	78.2 *d*	3′	78.2 *d*	78.1 *d*
4	40.4 *s*	40.5 *s*	39.0 *s*	4′	71.2 *d*	71.0 *d*
5	60.5 *d*	60.5 *d*	60.1 *d*	5′	67.3 *t*	67.3 *t*
6	79.8 *d*	80.1 *d*	67.8 *d*	Arabinose		
7	43.0 *t*	43.0 *t*	42.7 *t*	1″	105.6 *d*	106.3 *d*
8	42.9 *s*	42.8 *s*	42.6 *s*	2″	74.0 *d*	71.2 *d*
9	49.7 *d*	49.7 *d*	49.1 *d*	3″	87.0 *d*	74.8 *d*
10	39.0 *s*	39.0 *s*	38.9 *s*	4″	69.3 *d*	70.7 *d*
11	21.1 *t*	21.1 *t*	20.6 *t*	5″	67.0 *t*	67.1 *t*
12	23.7 *t*	23.8 *t*	23.0 *t*	Arabinose		
13	48.9 *d*	49.0 *d*	47.2 *d*	1‴	105.7 *d*	
14	44.0 *s*	44.1*s*	43.4 *s*	2‴	72.4 *d*	
15	43.5 *t*	43.4 *t*	45.4 *t*	3‴	74.4 *d*	
16	79.6 *d*	79.6 *d*	76.3 *d*	4‴	69.1 *d*	
17	59.1 *d*	59.1 *d*	57.3 *d*	5‴	66.5 *t*	
18	46.4 *s*	46.4 *s*	46.5 *s*	Xyloxe		
19	41.7 *t*	41.7 *t*	39.5 *t*	1⁗	104.7 *d*	104.7 *d*
20	28.3 *t*	28.3 *t*	25.9 *t*	2⁗	74.9 *d*	74.9 *d*
21	52.7 *d*	52.6 *d*	51.9 *d*	3⁗	78.4 *d*	78.5 *d*
22	72.9 *s*	73.0 *s*	70.9 *s*	4⁗	70.7 *d*	71.0 *d*
23	30.9 *q*	31.0 *q*	30.0 *q*	5⁗	67.4 *t*	67.0 *t*
24	16.6 *q*	16.7 *q*	16.1 *q*			
25	17.2 *q*	17.2 *q*	15.9 *q*			
26	17.2 *q*	17.2 *q*	16.7 *q*			
27	18.1 *q*	18.1 *q*	17.5 *q*			
28	18.3 *q*	18.4 *q*	17.8 *q*			
29	31.3 *q*	31.3 *q*	30.8 *q*			
30	27.3 *q*	27.3 *q*	22.6 *q*			

Chemical shifts in δ ppm.
* Measured in $CDCl_3$–10% pyridine-d_5. See ref. [5].

to assign the different spin systems to specific sugar residues, where two arabinose and two xylose residues were indicated in the molecule. The downfield shift of four oxygen-bearing methines (C-3, C-6, C-16 and C-3″) indicated the sites of glycosylation (Table 2). One of the arabinose residues is linked at C-6 (δ79.80) and substituted at its C-3″ position (δ87.0) by the second arabinose residue. Two xylose residues were separately linked at C-3 (δ89.1) and C-16 (δ79.6) [8]. The presence of arabinose as the terminal sugar was presumed by the detection of arabinose and xylose, on partial hydrolysis on TLC in a hydrogen chloride atmosphere [9]. Moreover, the FAB-mass spectrum showed a fragment ion peak at *m/z* 895 $[(M+Na)-132]^+$, consistent with the loss of a terminal pentose unit. The fragment ion at *m/z* 879 and subsequent fragment at *m/z* 746 corresponded to the loss of a disaccharide unit from the molecular ion.

The above proposed interglycosidic linkages were further substantiated by measuring HMBC and NOESY spectra of **1**. Cross peaks between H-1′/C-1′ (δ4.90/δ107.9) of the xylose unit and C-3/H-3 (δ89.1/δ3.42) of the aglycone showing that a xylose unit is bound at C-3 of the aglycone. H-1″/C-1″ (δ4.84/δ105.6) correlated with C-6/H-6 (δ79.8/δ4.25). H-1‴/C-1‴ (δ5.16/δ105.7) of an arabinose unit showed cross peaks with C-3″/H-3″ (δ87.0/δ4.11) of another arabinose unit, indicating a disaccharide chain, [arabinose (1-3)-arabinose], linked at C-6 (δ79.8) of the aglycone. Finally, there were cross peaks between H-1⁗/C-1⁗ (δ4.89/δ104.7) of a xylose unit and C-16/H-16 (δ79.6/δ4.48) of the aglycone. Furthermore, the NOESY spectrum showed significant spatial correlation between the proton signals at δ5.16 (H-1‴), 4.90 (H-1′), 4.89 (H-1⁗) and 4.84 (H-1″), and proton signals at δ4.11 (H-3″), 3.42 (H-3), 4.48 (H-16) and 4.25 (H-6), respectively.

The relative stereochemistry of **1** was determined based on the coupling constants of each proton and NOESY experiment. The multiplets and coupling constants (J = 9.5–12.0 Hz) of the axial protons at δ3.42, 4.25 and 4.48 confirmed the equatorial orientation of all the three substitutions in the aglycone part [10] as can be seen in formula **1** and comparable with those

reported for mollugogenol A (**3**) [5], 6α, 16β-dihydroxyhopane-24-oic acid [11] and 6α-acetoxyhopan-16β, 22-diol [12].

On the bases of the above evidence, the structure of succulentoside A is proposed to be 6α-*O*-[α-L-arabinopyranosyl-(1-3)-α-L-arabinopyranosyl]-3β-*O*-β-D-xylopyranosyl-16β-*O*-β-D-xylopyranosyl-22-hydroxyhopane (**1**).

Succulentoside B (**2**), mp 265–266° was analysed for $C_{45}H_{75}O_{16}$. Its ^1H NMR spectrum (Table 1) showed signals for eight methyls, three anomeric protons as doublets ($J = 7.5$ Hz) at δ4.92, 4.91 and 4.89, and characteristic methine protons at δ2.73 (*q*, H-21), 3.43 (*dd*, H-3), 4.31 (*ddd*, H-6) and 4.49 (*ddd*, H-16). The ^{13}C NMR spectrum exhibited signals due to the mollugogenol A moiety (**3**) (Table 2) and three anomeric carbon signals at δ107.8, 106.3 and 104.7. The positive ion FAB-mass spectrum of **2** displayed a quasimolecular ion peak at *m/z* 895 $[M+Na]^+$. Other fragments analogous to those in **1** suggested the same aglycone moiety in the two compounds (**1** and **2**). The only difference was the absence of a pentose substitution to the arabinose moiety. This was further supported by ^1H and ^{13}C NMR values of the sugar moieties of both glycosides (Table 1 and 2) as well as examination of the HMBC and NOESY spectra. The H-3″/C-3″ of the arabinose in **2** were found to be at a higher field (δ4.13/δ74.8) relative to that in **1** due to absence of glycosylation, whereas the remaining ^1H and ^{13}C NMR data closely resembled those of **1**. On microhydrolysis on TLC xylose and arabinose were detected as the sugar part [9].

Thus succulentoside B (**2**) was characterized as 6α-*O*-α-L-arabinopyranosyl-3β-*O*-β-D-xylopyranosyl-16β-*O*-β-D-xylopyranosyl-22-hydroxyhopane.

This is the first report of the isolation and structure elucidation of succulentosides A and B (**1** and **2**) from *P. succulentum* (Del.) G. Gay and from nature.

EXPERIMENTAL

General. Mps: uncorr. IR: KBr. ^1H and ^{13}C NMR (pyridine-d_5 or $CDCl_3$) using JEOL GNM-GX 400 (^1H: 400 MHz, ^{13}C: 100 MHz) spectrometer. FAB-MS (positive ion mode) was made using a JEOL JMS DX-300 spectrometer with glycerol and thioglycerol/or NBA 'in saponin acetate' as a matrix. DCCC: using a Buchi 670 DCC chromatograph with $CHCl_3$–MeOH–*i*-PrOH–H_2O (5:6:1:4, upper layer as stationary phase and lower layer as mobile phase), technique: descending, pump: 20 psi, flow rate: 1 ml $min.^{-1}$. VLC: Silica gel G 60 H TLC (15 μm, Merck) and Sephadex LH-20 (Pharmacia, Sweden). TLC: Silica gel G 60 F_{254} (Merck) using solvent systems (*a*) EtOAc–MeOH–H_2O (100:16:12), (*b*) BuOH–HOAc–H_2O (4:1:1), (*c*) EtOAc–MeOH–H_2O–HOAc (65:20:15:15) and (*e*) $CHCl_3$–MeOH (20:1). The spots were visualized by spraying with anisaldehyde–H_2SO_4 followed by heating.

Extraction and isolation procedure. The plant material was collected from El-Arish region, North Sainai in April 1994 and identified by Dr M. Elgibali, Plant Taxonomy department [National Research Center (N.R.C.), Cairo]. A voucher specimen has been deposited in the Herbarium of the N.R.C. The powdered air-dried whole plant (200 g) was extracted at room temp with 70% EtOH (500 ml × 5) and the solvent was evapd under red. pres. The residue obtained (54.5 g) was suspended in boiling H_2O (200 ml) and successively extracted with CCl_4, EtOAc and BuOH. The BuOH extract was evapd under red. pres. The residue (21 g) was dissolved in MeOH (100 ml) and Et_2O was added portionwise to give a flocculant precipitate. The precipitate was washed with Et_2O and used as the crude saponin mixture (6.2 g, 3.1%). DCCC of the saponin mixture (500 mg, dissolved in 7 ml of the mobile phase) was undertaken and frs (20 ml each) were collected. Frs 31–38 (34 mg) and 39–41 (59 mg) were, separately, chromatographed over a column of Sephadex LH-20 (60 × 1.6 cm i.d, 50% aq. MeOH) to afford succulentoside B (**2**, 23 mg) and A (**1**, 48 mg), respectively.

Succulentoside A (**1**). Needles (MeOH–Et_2O), mp 258–260°, R_f [0.26 in solvent system (*a*), and 0.38 in (*b*)]; $[\alpha]_D$ −34° (MeOH, *c*2.5). IR ν_{max} cm^{-1}: 3420 (OH), 2850 (CH_2). ^1H and ^{13}C NMR (pyridine-d_5): see Tables 1 and 2. FAB-MS (positive ion mode) *m/z* 1027 $[(M+Na]^+$, 968 $[M+Na)-C_3H_7O]^+$, 895 [(M + Na) −pentose]$^+$, 879 $[(M+Na)-C_5H_9O_5]^-$, 746 $[(M+Na)-C_{10}H_{17}O_9]^+$, 613, 574, 459, 441 [574 − pentose]$^+$, 423, 405, 307, 268, 246 and 207.

Microhydrolysis of succulentoside A on TLC. Succulentoside A (**1**) was applied to a silica gel TLC plate and left in an HCl atmosphere in an oven at 100° for 1 hr. HCl vapour was then eliminated under hot ventilation and the authentic sugars were applied to the chromatoplate. The chromatoplate was developed with solvent system (*c*) and the spots were detected by spraying with anisaldehyde–H_2SO_4, followed by heating. The sugar part was identified as arabinose and xylose.

Partial hydrolysis of succulentoside A on TLC. Compound **1** was applied to a silica gel TLC plate and left in an HCl atmosphere at room temp for 1 hr. Arabinose and xylose were identified.

Acetylation of succulentoside A. Succulentoside A (**1**, 20 mg) was dissolved in Ac_2O–pyridine (1:1, 5ml) and left at room temp for 3 days. The solvent and reagent were removed by co-distillation with toluene. The residue was subjected to VLC using $CHCl_3$–MeOH (99:1) as solvent to afford an acetate derivative (**1a**, 31 mg); needles ($CHCl_3$–MeOH), mp 301–303°. IR ν_{max} cm^{-1}: 3580 (OH); FAB-MS: *m/z* 1467 $[M+H]^+$.

Succulentoside B (**2**). Needles (MeOH–Et_2O), mp 265–266°, R_f [0.44 in solvent system (*a*), and 0.50 in (*b*)], $[\alpha]_D$ −27° (MeOH, *c* 2.0). IR ν_{max} cm^{-1}): 3400 (OH), 2840 (CH_2). ^1H and ^{13}C NMR (pyridine-d_5): see

Tables 1 and 2; FAB-MS (positive ion mode) *m/z* 895 $[M+Na]^+$, 459, 441, 423 and 207.

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