Triterpenoid Oligoglycosides from the Sea Cucumber *Stichopus parvimensis*

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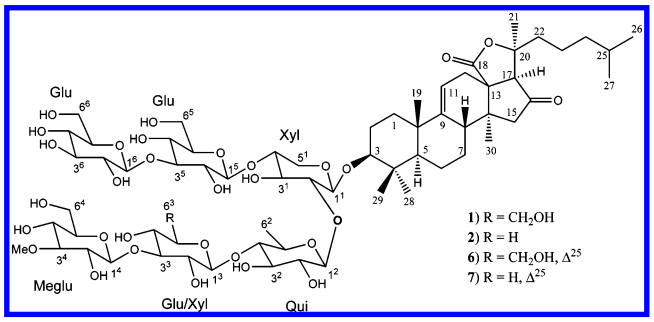
Two new holostan-type triterpenoid oligoglycosides, named parvimosides A (**1**) and B (**2**), were isolated from the warty sea cucumber *Stichopus parvimensis* (syn. *Parastichopus parvimensis*). Their structures and total assignments of the proton and carbon signals were established on the basis of spectral evidence, mainly ^{1}H and ^{13}C 1D and 2D NMR spectroscopy including DEPT, COSY, TOCSY, NOESY/ROESY, HMQC/HSQC, and HMBC experiments, as well as FABMS.

Sea cucumbers are soft-bodied wormlike echinoderms that belong to the class Holothurioidae. They have economic importance in southern Asia, where several species are used in folk medicine or eaten as delicacies.[1,2] Sea cucumbers produce characteristic toxic and antifungal triterpenoid glycosides of the holostane-type. Their complex structures can be distinguished by the composition and number of monosaccharide units in the carbohydrate chain, which are mainly composed by D-xylose, D-glucose, D-quinovose, and 3-*O*-methyl-D-glucose. The more commonly studied sea cucumbers belong to the Holothuriidae, Cucumariidae, and Stichopodidae families. The structures of 16 triterpene glycosides (biosides, tetraosides, and hexosides) have been elucidated from members of the Stichopodidae family (six *Stichopus*, two *Thelenota*, and one *Astichopus* species). Most of them have been shown to produce hexosides as major components of the glycosidic fraction.[3]

In this paper we describe the isolation and structure elucidation of parvimosides A (**1**) and B (**2**), the major triterpene oligoglycosides of the aspidichirotid holoturian *Stichopus parvimensis* (syn. *Parastichopus parvimensis*), a species with a wide distribution from Monterey, CA (United States) to Cedros Island, B.C. (México). The structures of the new compounds were established by homo- and heteronuclear 1D and 2D NMR techniques (^{1}H and ^{13}C, COSY, TOCSY, NOESY/ROESY, HMQC/HSQC, and HMBC), FABMS, and comparison with data reported in the literature.



Compound **1** was obtained as an amorphous solid, mp 270−275 °C. The FABMS showed a molecular ion at *m/z* 1410, consistent with the molecular formula $C_{66}H_{106}O_{32}$.

The glycosidic nature of **1** was suggested by the strong hydroxyl IR absorption band at 3332 cm^{-1}. The IR spectrum also showed characteristic absorptions at 1749 and 1645 cm^{-1}, indicating the presence of the characteristic γ-lactone of the holostane skeleton, and a double bond.

The ^{1}H and ^{13}C NMR spectra of **1** suggested the presence of a triterpene glycoside bearing a cyclopentanone carbonyl group and an olefinic group. The ^{13}C NMR spectrum indicated the presence of 66 carbon atoms, of which 30 were assigned to the triterpene moiety, while the remaining 36 were attributed to the oligosaccharide chain. DEPT experiments showed the presence of 9 methyl groups, 14 methylenes, 35 methines, and 8 quaternary carbons. The ^{1}H NMR spectrum displayed five three-proton singlet signals at δ_H 0.93, 1.13, 1.30, 1.42, and 1.44, indicating the presence of five tertiary methyl groups (δ_C 20.66, 16.66, 28.05, 26.80, 22.11), as well as two three-proton doublets at δ_H 0.85 and 0.86 (J = 6.8 Hz) due to two secondary methyl groups (δ_C 22.57). The olefinic proton H-11 (δ_H 5.35 br s) showed an HMQC correlation to its corresponding carbon (δ_C 111.91). The signal at δ 151.38 in the downfield region of the ^{13}C NMR spectrum indicated the presence of a double bond at position 9(11) of the aglycone moiety. Two further low-field resonances at δ 176.05 and 213.08 were assigned to the γ-lactone and the cyclopentanone carbonyl carbons, respectively.

Comparison between the ^{13}C NMR data of the aglycon moiety of **1** with those published for DS-penaustroside (**3**), a 25-dihydroholotoxigenol pentaoside isolated from *Pentacta australis* (Cucumariidae),[4] revealed that the carbon signals of the aglycone of the two compounds were almost identical, suggesting that the aglycone in **1** must be the same 25-dihydroholotoxigenol.

As for the oligosaccharide chain, the sugar sequence and the interglycosidic linkages were determined mainly by 2D NMR experiments (COSY, NOESY, HMQC, and HMBC) and comparison with reported data. The chemical shift assignments for the proton and carbon signals are summarized in Tables 1 and 2. The NMR data confirmed the presence of six sugar residues clearly indicated by six anomeric carbon signals at δ_C 102.87, 104.99, 105.29, 105.67, 105.67, and 105.85, which showed correlations in the HMQC experiment with six anomeric proton signals at δ_H 5.01 (d, J = 8 Hz), 4.98 (d, J = 8 Hz), 4.75 (d, J = 7.5 Hz), 5.16 (d, J = 7.5 Hz), 5.30 (d, J = 7.5 Hz), and 5.31 (d, J = 8.0 Hz), respectively. The coupling constant values around 8.0 Hz indicated an axial orientation of all six

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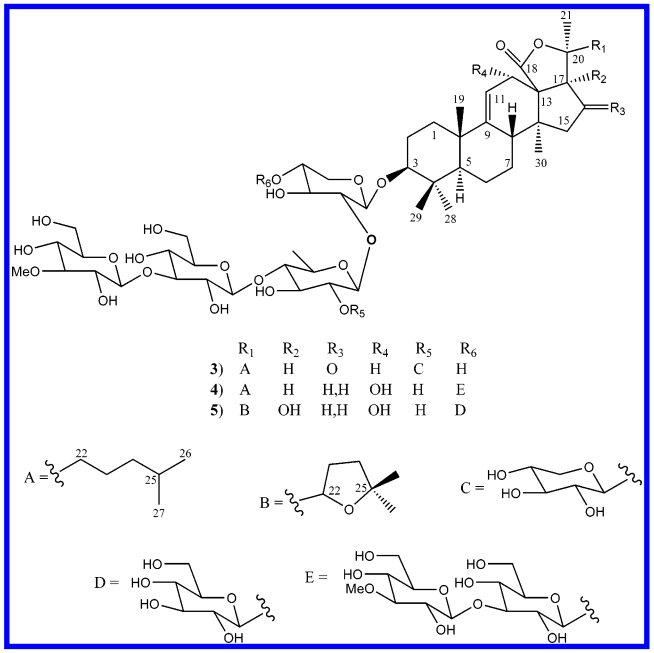
Table 1. ^{13}C and ^{1}H NMR Spectral Data for the Aglycon Moieties of Parvimoside A (**1**) and Parvimoside B (**2**) (in pyridine-d_5, 500/125 MHz)[a]

	1			**2**		
position	δ_C	δ_H	HMBC	δ_C	δ_H	HMBC
1α	36.29	1.47 m[b]		36.32	1.44 m[b]	
1β		1.88 dbr (13.0)			1.84 dbr (13.0)	
2β	27.09	2.01 m[b]		27.13	1.98 dt (12.0, 10.0)	
2α		2.24 dbr (11.5)			2.20 dbr (12.0)	
3	88.66	3.26 dbr (~12.0)		88.71	3.22 dd (12, 4)	C-1[1], C-4, C-28, C-29
4	39.96			40.00		
5	52.90	0.95 dbr (~12.0)		52.92	0.92 d (~12.0)	
6β	21.09	1.52 m[b]		21.14	1.50 d (~12.0)	
6α		1.72 m[b]			1.69 m[b]	
7β	28.50	1.26,		28.54	1.22 m[b]	
7α		1.63 m[b]			1.58 m[b]	
8	38.72	3.29 dbr (~12.0)		38.76	3.25 dbr (~12.0)	
9	151.38			151.38		
10	39.74			39.77		
11	111.91	5.35 sbr		111.11	5.31 sbr	
12	32.13	2.52 sbr		32.17	2.48 sbr	
13	55.71			55.75		
14	42.06			42.10		
15β	52.01	2.27 d (15.0),	C-14, C-16	52.04	2.24 d (16.0)	C-8, C-14, C-16, C-30
15α		2.41 d (15.0)	C-13, C-16		2.38 d (16.0)	C-13, C-16, C-17, C-30
16	213.08			213.10		
17	61.41	2.83 s	C-12, C-13, C-16, C-18, C-20, C-21	61.44	2.79 s	C-12, C-13, C16, C-18, C-20, C-21
18	176.05			176.08		
19	22.11	1.44 s	C-1, C-5, C-10	22.15	1.40 s	C-1, C-5, C-9, C-10
20	83.18			83.22		
21	26.80	1.42 s	C-9, C-17, C-20, C-22	26.83	1.38 s	C-17, C-20, C-22a
22a	39.08	1.62 m[b]		39.12	1.60 m[b]	
22b		1.80 m[b]			1.78 m[b]	
23a	22.17	1.36 m[b]		22.21	1.32 m[b]	
23b		1.64 m*			1.60 m[b]	
24a	39.31	1.12 m[b]		39.34	1.06 m[b]	
24b					1.10 m[b]	
25	27.98	1.48 m[b]		28.09	1.44 m[b]	C-26, C-27
26	22.57	0.85 d (6.8)	C-24, C-25	22.61	0.81 d (6.5)	C-24a, C-25, C-27
27	22.57	0.86 d (6.8)	C-24, C-25	22.64	0.82 d (6.5)	C-24a, C-25, C-26
28	28.05	1.30 s	C-3, C-4, C-5, C-29	28.09	1.27 s	C-3, C-4, C-5, C-29
29	16.66	1.13 s	C-3, C-4, C-5, C-28	16.71	1.10 s	C-3, C-4, C-5, C-28
30	20.66	0.93 s	C-8, C-13, C-14, C-15	20.70	0.89 s	C-8, C-12, C-14, C-15

[a] Assignments and chemical shifts of ^{1}H multiplets are based on 2D COSY, NOESY and HMQC for **1**, and COSY, TOCSY, ROESY, and HSQC for **2**. [b]Overlapping signals.



anomeric protons, and therefore all beta glycosidic linkages. Diagnostic signals at δ_H 3.88 (δ_C 60.77), due to a methoxy group, and at δ 1.77 (δ_C 18.21), due to a secondary methyl group on an oxygenated carbon, confirmed the presence of the 3-*O*-methylglucose and the quinovose units.

Comparison of the ^{13}C NMR data of the oligosaccharide moiety in **1** with those reported for the hexoside **4**, isolated from *Thelenota ananas*,[5] and those for holothurinoside A (**5**), isolated from *Holothuria forskalii*,[6] revealed close similarities. Compared with compound **5**, the spectrum of **1** showed six extra signals with resonances suggesting the presence of an extra glucose unit in the molecule. This assumption was in good agreement with a molecular ion at *m/z* 1410 and other significant fragment peaks in the mass spectrum, which were indicative of the sugar sequence in **1**. Thus, the loss of sugar units from the molecular ion led to ions at *m/z* 1248 and 1085, corresponding with a stepwise elimination of two glucose units. Peaks at *m/z* 1234, 1072, and 926 corresponding with a step by step elimination of 3-*O*-methylglucose, glucose, and quinovose, respectively, and a peak at *m/z* 748 corresponded to the loss of three glucose and one methylglucose units. The NMR spectra confirmed the glycosidic linkage between xylose and the hydroxyl group at C-3 of the aglycone, since the xylose anomeric proton signal at δ 4.75 (δ_C 105.29) correlated in the NOESY spectrum with the C-3 methine signal at δ 3.26 (δ_C 88.66) and the 28-CH_3 signal at δ_H 1.30 (δ_C 28.05).

The above data suggested that the structure of parvimoside A (**1**) must be related with holotoxin B (**6**), a holotoxigenol hexaoside isolated from *S. japonicus*,[7] with the difference being the absence of a double bond at position 25 in the aglycon of **1**, that is, the 25-dihydroholotoxin B.

Table 2. ^{13}C and ^{1}H NMR Spectral Data for the Oligosaccharide Moieties of Parvimoside A (**1**) and Parvimoside B (**2**) (in pyridine-d_5, 500/125 MHz)[a]

	1			**2**		
position	δ_C	δ_H	HMBC	δ_C	δ_H	HMBC
Xyl-1^1	105.29	4.75 d (7.5)		105.32	4.72 d (7.0)	C-3
2^1	83.59	4.05 m[b]		83.48	4.03 m[b]	C-3^1, C-1^2
3^1	75.78	4.25 m[b]		75.84	4.22 m[b]	C-2^1
4^1	77.97	4.28 m[b]		77.52	4.26 m[b]	C-1^5
$5^1\alpha$	64.08	3.64 t (10.5)		64.10	3.61 t (11),	C-1^1
$5^1\beta$		4.40 m[b]			4.38 dd (11.5, 4.5)	C-1^1, C-3^1, C-4^1
Qui-1^2	105.67	5.16 d (7.5)		105.63	5.15 d (7.5)	C-2^1
2^2	76.39	4.05 m[b]		76.58	4.03 m[b]	C-3^2
3^2	75.93	4.09 m[b]	C-2^2	75.59[c]	4.08[c] m[b]	C-2^2, C-4^2, C-6^2
4^2	87.53	3.68 t (8.5)		86.00	3.66 t (9)	C-3^2, C-5^2
5^2	71.66	3.82 m[b]		71.84	3.77 dq (9, 6)	C-4^2
6^2	18.21	1.77 d (5.5)	C-5^2, C-4^2	18.10	1.74 d (6)	H-4^2, C-5^2
Glu/Xyl-1^3	104.99	4.98 d (8)		105.22	4.84 d (8)	C-2^3, C-3^3, C-4^2
2^3	73.74	4.04 m[b]	C-3^3	73.53	3.98 m[b]	C-3^3
3^3	88.29	4.24 m[b]		87.51	4.13 t (9)	C-2^3, C-4^3
4^3	69.75	4.10 m[b]		69.14	4.02 m[b]	C-3^3, C-5^3
$5^3\alpha$	77.45	4.04 m[b]	C-3^3	66.57	3.61 t (11),	C-1^3, C-3^3, C-4^3
$5^3\beta$					4.19 m[b]	
6^3a	62.20	4.20 m[b]				
6^3b		4.50 m[b]				
Meglu-1^4	105.67	5.30 d (7.5)		105.49[d]	5.28[c]d (8)	C-3^4
2^4	75.05	4.00 m[b]		75.14	3.98 m[b]	
3^4	88.02	3.73 t (9)	C-2^4, C-4^4, OMe	88.08	3.70 t (9)	C-2^4, C-4^4, OMe
4^4	70.58	4.14 t (9)		70.67	4.13 t (9)	C-6^4
5^4	78.35	4.24 m[b]		78.68	4.00 m[b]	
6^4a	62.49	4.32 m[b]		62.52	4.30 dd (11.5, 6),	C-5^4
6^4b		4.55 dbr (12.5)			4.52 dd (12, 2.5)	
OMe	60.77	3.88 s	C-3^4	60.85	3.85 s	C-3^4
Glu-1^5	102.87	5.01 d (8)		102.86	4.98 d (8)	C-4^1
2^5	73.16	4.06 m[b]		73.23	4.02 m[b]	C-1^5
3^5	88.11	4.24 m[b]	C-4^5	88.30	4.20 m[b]	C-1^6, C-2^5, C-4^5
4^5	69.91	4.02 m[b]		69.77	4.08 m[b]	
5^5	78.19	3.93 m[b]		78.35[e]	3.94 m[b]	
6^5a	62.17	4.24 m[b]		62.17	4.20 m[b]	H-4^5
6^5b		4.46 m[b]			4.43 dbr (10)	
Glu-1^6	105.85	5.31 d (8)		105.87[d]	5.29[d] d (7.5)[b]	C-3^5,C-3^6
2^6	75.54	4.08 m[b]		75.55[c]	4.06[c] m[b]	
3^6	78.63	4.14 m[b]		78.22	4.22 m[b]	C-2^6, C-4^6
4^6	71.58	4.22 m[b]		71.60	4.18 m[b]	C-6^6
5^6	78.35	3.96 m[b]		78.38[e]	3.88 m[b]	
6^6a	62.26	4.28 m[b]		62.26	4.24 m[b]	
6^6b		4.48 m[b]			4.45 dd (11.5, 2.5)	

[a] Assignments and chemical shifts of ^{1}H multiplets are based on 2D COSY, NOESY, and HMQC for **1** and COSY, TOCSY, ROESY, and HSQC for **2**. [b] Overlapping signals. [c,d,e] Assignments may be interchanged.

On the basis of the above data, if xylose, quinovose, glucose, and 3-*O*-methylglucose are assumed to be the commonly found D-series, parvimoside A was established to be 3β-*O*-{2-*O*-[3-*O*-methyl-β-D-glucopyranosyl(1→3)-β-D-glucopyranosyl(1→4)-β-D-quinovopyranosyl]-4-*O*-[β-D-glucopyranosyl(1→3)-β-D-glucopyranosyl]-β-D-xylopyranosyl}-holost-9(11)-en-16-one (**1**).

Parvimoside B (**2**) was an amorphous solid, mp 215−218 °C. The FABMS displayed a molecular ion at *m/z* 1380, lower by 30 Da (CH_2O) than that of **1**, and in agreement with the molecular formula $C_{65}H_{104}O_{31}$, which was supported by the ^{13}C NMR and DEPT spectroscopic data. The ^{1}H and ^{13}C NMR profiles of compound **2** were very similar to those of **1**. The ^{13}C NMR spectrum indicated the presence of 65 carbon atoms, one carbon atom less than compound **1**, a methine carbon, according to DEPT experiments. The ^{1}H and ^{13}C NMR spectra also showed the presence of six sugar residues, indicated by six anomeric proton signals (δ 4.72, 4.84, 4.98, 5.15, 5.28, and 5.29) coupled with six anomeric carbon signals (δ 105.32, 105.22, 102.86, 105.63, 105.49, and 105.87, respectively) in the HSQC spectrum. The presence of a methoxy group (δ_H 3.85, δ_C 60.85) and a secondary methyl group at δ 1.74 (δ_C 18.10) indicated the presence of the 3-*O*-methylglucose and the quinovose units. Detailed analysis of the ^{13}C NMR data of **2** and comparison with those of **1** indicated that these compounds are different in the saccharide portions. The difference between them is in the third sugar of the main chain, which is a xylose unit instead of glucose, as in holotoxin B_1 (**7**).[8] Moreover, comparison of the ^{13}C NMR chemical shifts of the carbohydrate side chain in **2** with those published for holotoxin B_1 (**7**) and holotoxin A_1 with a similar side chain, indicated close similarities.[8] Therefore, compound **2** must be the 25-dihydroderivative of holotoxin B_1 (**7**).

Sequential assignments of the signals from H-1 to H-6 or H-5 of the monosaccharide residues were established by careful analysis of the 2D $^{1}H-^{1}H$ COSY, TOCSY, and NOESY spectra, starting from the characteristic anomeric proton signals. The sugar sequence and the interglycosidic linkages were confirmed using the combination of ROESY and HMBC experiments (Table 3) and supported by FABMS. Cross-peaks between signals at δ_H 4.72/3.22, 1.27 (H-1^1/H-3, H-28) and 4.22, 3.61 (H-1^1/H-3^1, H-$5^1\alpha$), 5.15/4.03, 4.08, 3.77 (H-1^2/H2^1, H-3^2, H-5^2), 4.84/3.66, 4.13, 3.61 (H-1^3/H-4^2, H-3^3, H-$5^3\alpha$), 5.28/4.13, 3.70, 4.00 (H-1^4/ H-3^3, H-3^4, H-5^4), 4.98/4.26, 4.20, 3.94 (H-1^5/H-4^1, H-3^5, H-5^5), and 5.29/4.20, 4.22, 3.88 (H-1^6/H-3,[5] H-3,[6] H-5^6) in the ROESY experiment, and the cross-peaks between δ_H/δ_C

Table 3. Selected COSY and NOESY/ROESY Data of the Oligosaccharide Moieties of Parvimoside A (**1**) and Parvimoside B (**2**) (in pyridine-d_5, 500 MHz)

	1			**2**		
proton	δ_H	COSY	NOESY	δ_H	COSY	ROESY
Xyl-1[1]	4.75	H-2[1]	H-3, 28, 3[1], 5[1]	4.72	H-2[1]	H-3, 28, 3[1], 5[1]
5[1]α	3.64	H-5[1]*β*, H-4[1]		3.61	H-5[1]*β*, H-4[1]	
5[1]*β*	4.40	H-5[1]α		4.38	H-5[1]α	
Qui-1[2]	5.16	H-2[2]	H-2[1], 3[2], 5[2]	5.15	H-2[2]	H-2[1], 3[2], 5[2]
4[2]	3.68	H-3[2], H-5[2]		3.66	H-3[2], H-5[2]	
5[2]	3.82	H-6[2]		3.77		
6[2]	1.77	H-5[2]	H-1[3], 4[2], 5[2]	1.74		H-1[3], 4[2], 5[2]
Glu/Xyl-1[3]	4.98	H-2[3]	H-4[2], 5[2], 3[3], 5[3]	4.84	H-2[3]	H-4[2], 6[2], 3[3], 5[3]
4[3]	4.10			4.02		
5[3]α	4.04	H-6[3]		3.61,	H-5[3]*β*, H-4[3]	
5[3]*β*				4.19	H-5[3]α	
Meglu-1[4]	5.30	H-2[4]	H-3[3], 3[4], 5[4]	5.28	H-2[4]	H-3[3], 3[4], 5[4], OMe
3[4]	3.73	H-2[4], H-4[4]		3.70	H-2[4], H-4[4]	
6[4]a	4.32	H-6[4]b		4.30,		
6[4]b	4.55	H-6[4]a		4.52		
OMe	3.88			3.85		
Glu-1[5]	5.01	H-2[5]	H-4[1], 5[1],3[5], 5[5]	4.98	H-2[5]	H-4[1], 3[5], 5[5]
5[5]	3.93	H-6[5]		3.94	H-4[5], H-6[5]	
6[5]a	4.24	H-6[5]b		4.20,	H-6[5]b,	
6[5]b	4.46	H-6[5]a		4.43	H-6[5]a	
Glu-1[6]	5.31	H-2[6]	H-3[5], 3[6], 5[6]	5.29	H-2[6]	H-3[5], 3[6], 5[6]
6[6]a	4.28	H-6[6]b		4.24,	H-6[6]b	
6[6]b	4.48	H-6[6]a		4.45	H-6[6]a	

4.72/88.71 (H-1[1]/C-3), 5.15/83.48 (H-1[2]/C-2[1], 4.84/86.0 (H-1[3]/C-4[2]), 5.28/87.51 (H-1[4]/C-3[3]), 4.98/77.52 (H-1[5]/C-4[1]), and 5.29/88.30 (H-1[6]/C-3[5]) in the HMBC experiment, confirmed the sugar sequence indicated in structure **2**.

On the basis of the above data, parvimoside B was established to be 3*β*-*O*-{2-*O*-[3-*O*-methyl-*β*-glucopyranosyl-(1→3)-*β*-xylopyranosyl(1→4)-*β*-quinovopyranosyl]-4-*O*-[*β*-glucopyranosyl(1→3)-*β*-glucopyranosyl]-*β*-xylopyranosyl}-holost-9(11)-en-16-one (**2**).

From a taxonomic point of view, *S. parvimensis* and *S. californicus* are considered problematic representatives of the family. Diechmann in 1937 placed these two species from the Pacific coast of México and United States into the genus *Parastichopus*, which was established by Clark in 1922.[9] On the basis of the main components of the glycosidic fractions, holotoxins A_1 and B_1, and morphological similarities, Levin[9] pointed out the close relationship between *S. japonicus* and *S. californicus* and their distinct difference from the type species *S. chloronotus*. This suggested the separation of these two species from the genus *Stichopus* and placing them in the genus *Apostichopus*, in which Liao[9] had included *S. japonicus*. The isolation of dihydroholotoxins B (**1**) and B_1 (**2**) from *S. parvimensis* supported the close taxonomic relationship among the three species *S. parvimensis* (syn. *P. parvimensis*), *S. californicus* (syn. *P. californicus, A. californicus*), and *S. japonicus* (syn. *P. japonicus, A. japonicus*).

Experimental Section

General Experimental Procedures. Melting points were determined on a Fisher-Jones type apparatus and are uncorrected. IR spectra were recorded as a Nujol suspension on a Nicolet Magna 750 Fourier transform IR spectrometer. NMR spectra were recorded on Varian Unity 300 and Varian Unity Plus 500 spectrometers in pyridine-d_5 solutions with TMS as internal standard; chemical shifts are recorded in δ values. FABMS were recorded with a nba-glycerol-tioglycerol matrix in the negative-ion mode, on a JEOL JMS.SX 102A.

Animal Material. Fifty specimens (14.5 kg) of *Stichopus parvimensis* were collected in June 1989 by scuba at the area known as "Arbolitos", southeast of Bahia de Todos los Santos, Baja California (México), 31°43′−31°45′ N; 116°45′−116°40′ W, depth 5−8 m, and authenticated by Dr. Bruce Halstead.

Extraction and Isolation. The collected specimens were rinsed with distilled water, weighed, and immediately deposited in distilled water (about 1 kg per L). After 4 h the animals were removed before evisceration. The water extract was filtered, the pH was adjusted to 4, and the extract was saturated with NaCl and extracted with butanol. The butanol extract was concentrated under vacuum, dialyzed, and separated by TLC using silica gel Merck G-60 and $CHCl_3$−MeOH−H_2O (65:35:10) as eluent. Parvimoside A (**1**) (13 mg) was obtained from the less polar band, and parvimoside B (**2**) (21 mg) was obtained from the more polar band. Compounds **1** and **2** were precipitated from ethanol.

Parvimoside A (1): amorphous solid, mp 270−275 °C; IR (Nujol suspension) ν_{max} 3332 broad, 1749, 1645 cm^{-1}; ^{1}H and ^{13}C NMR (see Tables 1 and 2); FABMS *m/z* 1410 [M]$^-$ (32), 1248 [M − $C_6H_{10}O_5$ (G)]$^-$ (7), 1234 [M − $C_7H_{12}O_5$ (MG)]$^-$ (7), 1085 [M−$C_{12}H_{21}O_{10}$(2G)]$^-$ (5), 1072 [M − $C_{13}H_{22}O_{10}$ (MG + G)]$^-$ (10), 926 [M − $C_{19}H_{32}O_{14}$ (MG + G + Q)]$^-$ (82), 910 [M − $C_{13}H_{22}O_{10}$ (MG + G) − $C_6H_{10}O_5$ (G)]$^-$ (35), 764 [M − $C_{13}H_{22}O_{10}$ (MG + G) − $C_6H_{10}O_5$ (G)]$^-$ (13), 748 [M − $C_{13}H_{22}O_{10}$ (MG + G) − $C_{12}H_{20}O_{10}$ (2G)]$^-$ (18), 602 (5), 339 (25), 325 (39).

Parvimoside B (2): amorphous solid, mp 215−218 °C; ^{1}H and ^{13}C NMR (see Tables 1 and 2); FABMS *m/z* 1380 [M]$^-$ (57), 1218 [M − $C_6H_{10}O_5$ (G)]$^-$ (10), 1204 [M − $C_7H_{12}O_5$ (MG)]$^-$ (10), 1072 [M−$C_{12}H_{20}O_9$ (MG + X)]$^-$ (11), 1056 [M − $C_{12}H_{21}O_{10}$(2G)]$^-$ (7), 926 [M − $C_{18}H_{30}O_{13}$ (MG + X + Q)]$^-$ (10), 910 [M − $C_{12}H_{20}O_9$ (MG + X) − $C_6H_{10}O_5$ (G)]$^-$ (4), 764 [M − $C_{18}H_{30}O_{13}$ (MG + X + Q) − $C_6H_{10}O_5$ (G)]$^-$ (2), 748 [M − $C_{12}H_{20}O_9$ (MG + X) − $C_{12}H_{20}O_{10}$ (2G)]$^-$ (1), 602 (1).

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References and Notes

(1) Fredalina, B. D.; Ridzwan, B. H.; Zainal Abidin, A. A.; Kaswandi, M. A.; Zaiton, H.; Zali, I.; Kittakoop, P. *Gen. Pharmacol.* **1999**, *33*, 337−340.
(2) Clarke, S. *Fish Fisheries* **2004**, *5*, 53−74.
(3) Moraes, G.; Norhcote, P. C.; Kalinin, V. I.; Avilov, S. A.; Silchenko, A. S.; Dmitrenok, P. S.; Stonik, V: A.; Levin, V. S. *Biochem. Syst. Ecol.* **2004**, *32*, 637−650.
(4) Miyamoto, T.; Togawa, K.; Higuchi, R.; Komori, T. *J. Nat. Prod.* **1992**, *55*, 950−946.

(5) Hegde, V. R.; Chan, T. M.; Pu, H.; Gullo, V. P.; Patel, M. G.; Das, P.; Wagner, N.; Parameswaran, P. S.; Naik, C. G. *Bioorg. Med. Chem, Lett*. **2002**, *12*, 3203−3205.
(6) Rodriguez, J.; Castro, R.; Riguera, R. *Tetrahedron* **1991**, *47*, 4753−4762.
(7) Maltsev, I. I.; Stonik, V. A.; Kalinovsky, A. I.; Elyakov, G. B. *Comp. Biochem. Physiol.* **1984**, *78B*, 421−426.
(8) Kitagawa, I.; Yamanaka, H.; Kobayashi, M.; Nishino, T.; Yosioka, I.; Sugawara, T. *Chem. Pharm.* Bull. **1978**, *26*, 3722−3731.
(9) Levin, V. S. *Mar. Biol.* (Vladivostok) **1998**, *24*, 65−66 (English translation).

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