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Intercedenol A and B, Two New Triterpenoids from the Sea Cucumber *Mensamaria intercedens*

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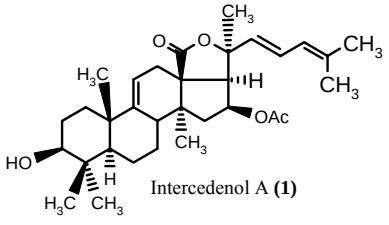
Abstract: Two new triterpenoids named intercedenol A and B were isolated from the acid hydrolysate of the crude glycoside fraction. The structures were elucidated by ESI-MS and NMR spectrum.

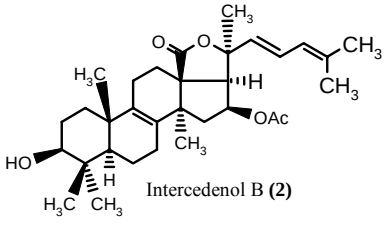
Keywords: *Mensamaria intercedens* Lampert, intercedenol A, intercedenol B, triterpenoids**.**

Mensamaria intercedens Lampert, a kind of sea cucumber, is widely distributed in Southern China Sea, especially in the Dongshan Gulf[1]. We report here the isolation, purification, and structural elucidation of two new triterpenoids named intercedenol A **(1)** and B **(2)** from the acid hydrolysate of the crude glycoside fraction.

The whole sea cucumbers were extracted with 85% EtOH. The extract was then partitioned between water and dichloromethane and the water layer was extracted with *n*-butanol. The *n*-butanol extracts mainly contain the triterpene glycosides. Complete acid hydrolysis of this glycosides mixture with 15% H_2SO_4 afforded the aglycone products, which were extracted with chloroform and separated by reverse-phase HPLC on a Zobax SB C-18 column using 85% MeOH as the mobile phase and in the flow rate of 1.5 mL/min to give intercedenol A (**1**) (Rt=15.5 min) and intercedenol B (**2**) (Rt=14.6 min).



Intercedenol A **(1)**



Intercedenol B **(2)**

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Intercedenol A, $C_{32}H_{46}O_5$, a white powder, mp 212.5-213.4 ℃, exhibited pseudomolecular ion peaks at *m/z* 533 [M+Na] and 549 [M+K] in the positive-ion mode ESI-MS. It was given the molecular formula $C_{32}H_{46}O_5Na$ and $C_{32}H_{46}O_5K$ by HRESI-MS at *m/z* 533.3235 [M+Na] and 549.3026 [M+K]. The IR spectrum showed absorptions due to hydroxyl (3440 cm^{-1}), γ-lactone (1763 cm^{-1}) and carbonyl (1742 cm^{-1}) groups. The ^{13}C NMR and DEPT spectrum exhibited 32 carbon signals ($8\times CH_3$, $6\times CH_2$, $9\times CH$, $9\times C$). The ^1H and ^{13}C NMR spectra (**Table1**) indicated that compound **1** is a triterpenoid compound with three olefinic bonds, one ester, and one lactone carbonyl group. These features resemble those of the triterpenoid lactone aglycone cucumechinol A except for the side chain moiety and the acetoxy group[2]. This acetoxy group was located at C-16 based on a cross peak at δ 5.56/171.1 (H-16/CH_3CO) in HMBC spectrum and its β configuration was confirmed by cross peaks at δ 2.19/5.56 (H-15α/ H-16α) and at δ 2.71/5.56 (H-17α/ H-16α) in the NOESY spectrum (**Figure 1**) and the coupling constants of H-16α and H-17α (9.2Hz). Cross peaks at δ 5.63/6.73 (H-22/H-23) and 5.73/6.73 (H-24/H-23) in ^1H-^1H COSY spectrum suggested that these three olefinic protons δ 5.63 (d, 1H, J=15.6Hz, H-22); 6.73 (dd, 1H, J=11.2, 15.6Hz, H-23); 5.73 (d, 1H, J=11.2Hz, H-24) comprised a three-spin system; Correspondingly, a conjugate double bond (22E, 24-diene) must be present in the side chain of **1**. The E stereochemistry of the Δ^{22} double bond was deduced from the large coupling constant for H-22 with H-23 (15.6Hz). This conclusion was also confirmed by the correlations of 5.63/83.0 (H-22/C-20), 5.63/124.8 (H-22/C-24), 1.48/132.4 (H-21/C-22), 1.76/18.3 (H-26/C-27), 1.76/135.4 (H-26/C-25) and 1.76/124.8 (H-26/C-24) in the HMBC spectrum (**Figure 2**). Therefore, the structure of intercedenol A was determined as 16β-acetoxy-9 (11), 22 (23) E, 24 (25) -triene -3β-hydroxyholost.

Intercedenol B, $C_{32}H_{46}O_5$, a white powder, mp 203.5-205.4 ℃, exhibited pseudomolecular ion peaks at *m/z* 511 [M+H], 533 [M+Na] and 549 [M+K] in the positive-ion mode ESI-MS. It was given the molecular formula $C_{32}H_{46}O_5Na$ and $C_{32}H_{46}O_5K$ by HRESI-MS at *m/z* 533.3207 [M+Na] and 549.3022 [M+K]. The IR spectrum showed absorptions of hydroxyl (3443 cm^{-1}), γ-lactone (1761 cm^{-1}) and carbonyl (1746 cm^{-1})groups. The ^1H and ^{13}C NMR spectra (**Table1**) of **2** showed the features similar to those of intercedenol A except for the signals of carbon atoms at the B/C-ring junction.

Figure 1 The key NOESY correlations of **1**

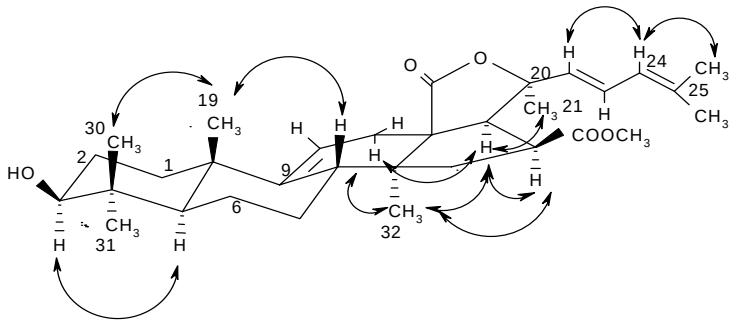
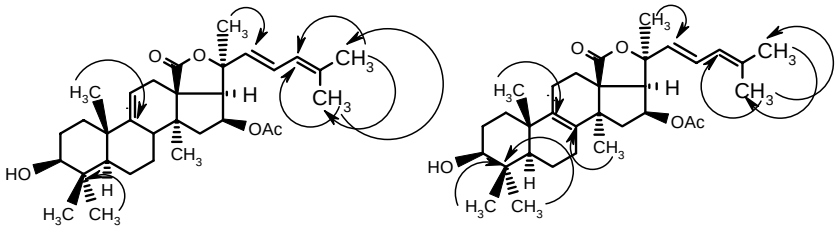


Table 1 ^{1}H and ^{13}C NMR data for compounds **1** and **2** (in $CDCl_3$, 400/100MHz δ ppm)

	1			**2**	
Carbon	δ_C m[a]	(J in Hz)	Carbon	δ_C m[a]	(J in Hz)
1	36.1t	1.42(1H,m), 1.84(1H,m)	1	35.7t	
2	27.8t		2	28.4t	
3	78.9d	3.22 (1H, dd, 5.2, 11.6)	3	79.0d	3.23 (1H, dd, 5.2, 11.2)
4	39.2s		4	39.0s	
5	52.5d	0.88(1H, m)	5	50.6d	1.04 (1H,m)
6	21.1t		6	18.2t	
7	27.7t		7	21.0t	
8	39.4d	3.09(1H,m)	8	130.1s	
9	151.1s		9	135.9s	
10	39.6s		10	37.3s	
11	110.3d	5.21(1H,m)	11	27.0t	
12	33.7t	2.49 (2H, m)	12	27.8t	
13	58.6s		13	59.4s	
14	43.1s		14	44.9s	
15	43.3t	1.44(1H,m), 2.19(1H,m)	15	40.7t	
16	73.4d	5.56 (1H, m)	16	73.6d	5.55 (1H, m)
17	54.2d	2.71(1H, d, 9.2)	17	53.5d	2.63 (1H, d, 9.2)
18	176.6s		18	176.6s	
19	21.8q	1.19(3H, s)	19	18.7q	1.10(3H, s)
20	83.0s		20	82.6s	
21	30.6q	1.48(3H, s)	21	30.6q	1.50(3H, s)
22	132.4d	5.63(1H, d, 15.6)	22	132.8d	5.63(1H, d, 15.6)
23	122.7d	6.73 (1H, dd, 11.2,15.6)	23	122.5d	6.73 (1H, dd, 10.4,15.6)
24	124.8d	5.73(1H, d, 11.2)	24	124.8d	5.73(1H, d, 10.4)
25	135.4s		25	135.3s	
26	25.9q	1.76 (3H, s)	26	25.9q	1.76 (3H, s)
27	18.3q	1.75 (3H, s)	27	18.3q	1.75 (3H, s)
30	15.6q	0.84 (3H, s)	30	15.4q	0.84 (3H, s)
31	28.2q	1.0 (3H, s)	31	28.1q	1.0 1(3H, s)
32	21.2q	0.92 (3H, s)	32	26.9q	1.06 (3H, s)
CH_3COO	171.1s		CH_3COO	171.1s	
CH_3COO	21.3q	1.90 (3H, s)	CH_3COO	21.3q	1.90 (3H, s)

[a]multiplicity by DEPT

Figure 2 The key HMBC correlations of **1** and **2**



Cross peaks at 0.92/130.1 (H-32/C-8) and 1.10/135.9 (H-19/C-9) in the HMBC spectrum (**Figure 2**) indicated that intercedenol B (**2**) is the $\Delta^{8\,(9)}$ isomer of intercedenol A (**1**).

Thus, Intercedenol B **(2)** was determined as 16β-acetoxy-8(9), 22(23) E, 24(25)-triene-3β-hydroxyholost.

Acknowledgments

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