

Table 2. Characteristic ¹H NMR data of U-BSPs, **1a-1d** and their precursors, **2, 3 & 4** in the region of 2.5-6.5 ppm (in CDCl₃)

Compound	methylene (=CH ₂)	N-Me (FB)	N-Me (SP) ^a		vinyl (H-3') ^a		ratio ^b
			α	ω	α	ω	
2 (AFB)	3.73	2.96					
3 (BFB)	3.80	2.99					
4a (SP ^H -FB)	3.83	3.01		2.69		5.65	
4b (SP ^{Me} -FB)	3.82	2.98	2.67		5.62		
1a			2.69	2.70	5.67	5.85	1:1
1b			2.63	2.69	5.66	5.71	1:1
1c			2.70	4.05 ^c	5.82	6.54 ^c	1:1
1d			2.61	2.64	5.56	5.76	1:1

^aThe α & ω denote the corresponding peak of α- & ω-ring of U-BSPs. ^bIntegration ratios of the corresponding peak of α- & ω-ring. ^cThe values are of the opened MC form of **1c**.

Table 3. Electron-Spray (ES) mass spectral data* of U-BSPs, **1a-1d**

Compound	Mw	Molecular Ion	
		(m/z)	rel. int. (%)
1a	795.96	796.24	25
1b	1002.76	1003.40	43
1c	840.96	841.21	32
1d	809.96	810.10	12

*ES mass spectra was recorded on a VG Quattro mass spectrometer at Queen's University.

Electron Spray (ES) mass spectral data of the synthesized U-BSPs are summarized in Table 3. Unlikely to the symmetrical bis-spiropyran,⁷ relative intensities of U-BSPs were quiet low.

Investigations on the intra- and intermolecular SP-MC aggregation behaviors are currently underway.

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Selective Reduction of α,β-Unsaturated Aldehydes and Ketones to Allylic Alcohols with Diisobutylchloroalane

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Diisobutylaluminum hydride (DIBAL-H) and triisobutylaluminum (TIBAL) have secured their place as reducing agents in organic synthesis.^{1,2} As may be expected, aldehydes and ketones are easily reduced to the corresponding alcohols on treatment with either of the reducing agents.¹⁻³ Although the reaction of carbonyl compounds with the reagents affords the same reduction products, the modes of reduction are different. Thus, the reduction with DIBAL-H involves hydride shift from the aluminum⁴; the reduction with TIBAL involves hydride shift from the β-carbon atom and thus proves to be very similar to a Meerwein-Ponndorf-Verley reduction process.^{4,5} In general, TIBAL is a mild reducing agent, and hence most organic functional groups, except aldehydes and ketones, are compatible with the reagent^{1,2}; on the other hand, DIBAL-H is a strong one, and hence most organic functional groups are reactive with the reagent even at low temperature.³ These differences led us to extend the use of diisobutylchloroalane (DIBAL-Cl) as a reducing agent, up to now the systematic study on the reagent has been scarcely appeared.⁶ Based on these considerations, we have therefore undertaken an investigation of the reactivity of DIBAL-Cl towards general organic functionalities. In the course of this

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7. DIBAL-Cl can also be prepared by the redistribution of $i\text{-Bu}_3\text{Al}$ with finely crushed anhydrous AlCl_3 in diethyl ether at 0° .
8. In the reaction of α,β -unsaturated ketones with TIBAL, the 1,2-addition of the isobutyl group bound to the aluminum atom is generally competitive with the reduction. See, ref (6).
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19. A solution of DIBAL-Cl in diethyl ether was prepared by the reaction of DIBAL-H with a stoichiometric amount of HCl in diethyl ether at 0° .

New Cytotoxic Anthraquinones from the Crinoid *Ptilometra*: 1'-Deoxyrhodoptilometrin-6-O-sulfate and Rhodoptilometrin-6-O-sulfate

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Anthraquinone pigments have been isolated from the various marine natural sources and extensively studied by the several groups.¹ Crinoids, in contrast with the familiar starfishes and sea urchins, are perhaps the little known and have been described from a restricted geographical area, the Indo-Pacific including the coast of Thailand.² Interests in crinoids chemistry are of the molecular structures and also spectacularly colorful appearance of the pigments. We have studied on the biologically active marine natural products.³ We wish to report two new anthraquinone derivatives along with a known compound. One is the known rhodoptilometrin **1** (3-(1'-hydroxypropyl)-1,6,8-trihydroxy-9,10-anthraquinone). The remaining two had not previously been isolated from a natural source: 1,8-Dihydroxy-3-propyl-9,10-anthraquinone-6-O-sulfate **2** and 1,8-dihydroxy-3-(1'-hydroxypropyl)-9,10-anthraquinone-6-O-sulfate **3**. Specimens of *Ptilometra* were collected subtidally and intertidally in the Eastern coast of the Gulf of Thailand. The pooled *Ptilometra* were homogenized, extracted with methanol, and concentrated to give a sticky syrup (10 g). The residues were partitioned into methylene chloride and water. The methylene chloride extracts were concentrated and chromatographed on silica gel (200-400 μm , Merck, 4 cm \times 50 cm) with a mixture of ethylacetate and n-hexane (2:1). The active fractions were concentrated, and the residue (1.2 g) was further chromatographed on sephadex (LH-20) with methanol to give rhodoptilometrin (**1**, 10 mg, 0.2% from methanol ext.) and a mixture of **2** and **3**, which were separated by a high pressure liquid chromatography (C_{18} , MeOH:H₂O=1:1, **2**:20 mg, 0.2%, **3**:100 mg, 1.0%): **1**; the specific rotation relative to the sodium D line at 20 $^\circ\text{C}$, $[\alpha]_D -8^\circ$ ($c=0.5$, MeOH), values of the wavelength at the maximum molar absorptivity, electron impact mass spectrometry, MS, m/z 314 M^+ ($\text{C}_{17}\text{H}_{14}\text{O}_6$), UV λ_{max} (ϵ), MeOH (nm), 224 (12,000), 258 (8,000), 432 (5,000), IR ν_{max} , KBr (cm^{-1}), 3345 (OH), 1598 (C=O), 1385, 1269 (Me); **2**, $\text{C}_{17}\text{H}_{13}\text{O}_8\text{S}_1\text{Na}_1$, ion spray mass spectrometry (negative), MS, m/z 376.9 M^- , 296.9 $[\text{M}-\text{SO}_3]^-$, UV λ_{max} (ϵ), MeOH (nm), 224 (13,000), 258 (8,000), 432 (6,000), IR ν_{max} , KBr (cm^{-1}), 3402 (OH), 1610 (C=O), 1395 (Me), 1095, 1058 ($-\text{SO}_3^-$), **3**, $[\alpha]_D -14^\circ$ ($c=0.2$, MeOH), $\text{C}_{17}\text{H}_{13}\text{O}_9\text{S}_1\text{Na}_1$, ion spray mass spectrometry (negative), MS, m/z 393.0 M^- , 312.9 $[\text{M}-\text{SO}_3]^-$, UV λ_{max} (ϵ), MeOH (nm), 224 (13,000), 258 (8,000), 432 (6,000), IR ν_{max} , KBr (cm^{-1}), 3350 (OH), 1624 (C=O), 1281 (Me), 1049 ($-\text{SO}_3^-$). The data of ^1H nuclear magnetic resonance