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COMMUNICATION

Cytotoxic Petrosiacetylenes from the Marine Sponge *Petrosia* sp.

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Abstract A novel petrosiacetylene analog (petrosiacetylene E) has been isolated from the Korean marine sponge *Petrosia* sp., along with petrosiacetylene A, B and C. Their structures were elucidated on the basis of spectroscopic methods and the stereochemistry of the new compound was determined by using the modified Mosher's method. Petrosiacetylene E showed higher cytotoxicity against five human cancer cell lines than petrosiacetylene A and B, presumably due to the additional hydroxy group located at C-16.

Keywords Sponge · *Petrosia* · Polyacetylenic alcohol · Petrosiacetylene · Cytotoxicity

Abbreviations

NMR	Nuclear magnetic resonance
COSY	Correlation spectroscopy
HMBC	Heteronuclear multiple-bond correlation
HSQC	Heteronuclear single-quantum coherence
MTPA	α-Methoxy-α-(trifluoromethyl)phenylacetic
HPLC	High performance liquid column chromatography
FABMS	Fast-atom bombardment mass spectrometry

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Introduction

Sessile marine organisms such as seaweeds, sponges, ascidians, and soft corals are known to produce a diverse array of secondary metabolites which are often toxic, to protect themselves from predators [1, 2]. Polyacetylenic alcohols represent a class of these metabolites, which has been shown to exhibit potent cytotoxicity [3–8]. Various linear polyacetylenic alcohols which usually bear more than one terminal alkyne, internal alkene and allylic or propargylic hydroxy group, differing in the position of double bonds and triple bonds, number of hydroxy groups and chain lengths, have been reported up to now [9].

In our search for toxic metabolites from Korean marine sponges, we have examined a crude extract of *Petrosia* sp. collected off the coast of Dokdo, which showed high (considering that it is a crude extract) cytotoxicity against the human lung cancer cell line NCI-H23 (IC_{50} of 6.83 μg/mL). Investigation of the organic constituents of this extract resulted in the isolation of petrosiacetylenes [10, 11], including a novel analog, which showed higher cytotoxic activity against several cancer cell lines. In this paper, bioassay-guided isolation, structure elucidation, and cytotoxicity of petrosiacetylenes against a panel of human cancer cell lines with consideration of the mode of cytotoxic actions of these compounds are presented.

Materials and Methods

General Experimental Procedure

^{1}H-NMR spectra were recorded on a Varian Unity 500 (500 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance

Detailed Bathymetry and Submarine Terraces in the Coastal Area of the Dokdo Volcano in the Ulleung Basin, the East Sea (Sea of Japan)

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ABSTRACT

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In the northeastern part of the Ulleung Back-Arc Basin, the East Sea, the Dokdo volcano anomalously emerges, rising abruptly from the sea floor (~2,100 m below sea level). It is lying as a cluster of emerged small islets surmounting a larger submerged volcanic edifice. In order to investigate the detailed bathymetry and morphologic characteristics around the volcano's underwater guyot type summit, we carried out multi-beam surveys from 2006 to 2011 and analyzed the data. From the near islets to ~30 m depth, the flank slopes are very steep and irregular, overlain by sunken rocks, indicating partial erosion and talus formation due to waves, currents and weathering. The area from ~30 m to ~80 m depth shows gentle rises and falls, with a modest slope. Below ~80 m, the bathymetry gradually transitions to a relatively flat undulation with a smooth slope, extending to offshore areas. The bathymetry and the seafloor image from backscattering data show that there are small islets of the Dokdo volcano and a rocky sea bottom elongated from the islets, probably originating from residual parts of the eroded and collapsed main crater of the volcano. The seafloor images identify typical rocky bottoms, like rocky protrusions, and less sediment around the survey area, except for some areas with shallow sand sedimentary deposits. The stepped slopes of the study area are interpreted to be wave-cut submarine terraces rather than terraces from other origins, based on their relatively flat morphology and lack of sediments. The submarine terraces suggest a repetition of sea level changes (transgressions and regressions) in the Quaternary.

ADDITIONAL INDEX WORDS: *Dokdo volcano, detailed bathymetry, multi-beam survey, seafloor image, crater, submarine terraces, sea level changes.*

INTRODUCTION

The East Sea is located in a complex junction between the Eurasian, Pacific, and Philippine plates (Uyeda and Miyashiro 1974). While the Japan islands drifted apart from the Eurasian margin, the East Sea might have been formed in response to the subduction of the Pacific and Philippine plates (Hilde and Wageman, 1973; Uyeda and Miyashiro, 1974). Tectonically, the East Sea (Sea of Japan) is a back-arc basin, comprised of the Ulleung, Japan, and Yamato deep basins, and it is geographically surrounded by Korea, Russia, and Japan (Jolivet *et al.*, 1991). The Ulleung Basin is situated in the southwestern part of the East Sea and separated on the north from the Japan Basin by the Korean Plateau, and distinguished from the Yamato Basin northeastward by the Oki Bank. The basin has an uneven seabed morphology above 2,200 m b.s.l. (below sea level), but its floor is quite smooth and gently deepens northeastward from about 1,000 m b.s.l. at the basin margin, to about 2,500 m b.s.l. near the Korea Gap (Figure 1).

In the northeastern part of the Ulleung Basin, there are five pronounced volcanoes; Dokdo (Dok Island), Ulleungdo (Ulleung Island) and other three submerged seamounts (Figure 1) (KORDI, 2000). These linear volcanic chain is composed of Ulleungdo, Dokdo, the Anyongbok Seamount, the Simheungtaek and the Isabu Tablemounts (Figure 1). The NE–SW trending Korea Gap lies between the Anyongbok Seamount and Dokdo up to 2500 m b.s.l. Dokdo and the two tablemounts have submerged guyot summits, occurring at about 200 m b.s.l., which are gently sloping and flat but steep on their flanks (Figure 1).

Dokdo, our study area, is a volcanic island, which is located in the northeastern part of the Ulleung Basin and approximately 216.8 km away from the eastern part of the Korean peninsula. It is situated about 87.4km from Ulleungdo, the biggest volcanic island in the Ulleung Basin of the East Sea. Dokdo consists of two main islets and the associated submerged volcanic edifice. The height of the Dokdo volcano is about 2,100 m from the seafloor and the diameter of the submerged summit is more than 10 km. The subaerial part of the Dokdo volcano is composed of volcanic rocks such as alkali basalts, trachytes, and trachyandesites (Sohn and Park, 1994). Rock samples from its subaerial portion have been

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ORIGINAL ARTICLE

Occurrence of the newly described kinorhynch genus *Meristoderes* (Cyclorhagida: Echinoderidae) in Korea, with the description of four new species

Martin V. Sørensen · Hyun Soo Rho · Won-Gi Min · Dongsung Kim · Cheon Young Chang

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Abstract *Meristoderes* is the most recently described kinorhynch genus and has until now only accommodated its type species *M. macracanthus* from the Mediterranean and *M. galatheae* from the Solomon Islands in Southeast Asia. The present contribution is an account on the genus based on samples from the ongoing exploration of the kinorhynch fauna in coastal and subtidal waters around in the Korean Peninsula. The samples yielded no less than five new species of *Meristoderes*, of which four are formally described herein, whereas only diagnostic notes are provided for the fifth. The descriptions are supplemented with a key to species of the genus, and morphological notes on the organization of cephalic structures and cuticular trunk structures. New morphological findings include intrageneric variation in the composition of the terminal segment, which may have either one unpaired or two paired tergal plates. The data also show that the differentiation of a tergal and sternal plate in segment 2 varies greatly between the species. Results of the present study indicate that the genus probably holds a significant, unrecovered biodiversity, but the data also shed light on potential future taxonomic problems among genera of Echinoderidae and stress the importance of identifying additional diagnostic traits to define *Meristoderes*.

Keywords Biodiversity · Kinorhyncha · East Asia · Morphology · Taxonomy

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Introduction

Very recently, two new kinorhynch species were described and assigned to the new genus *Meristoderes* Herranz et al. 2012. One of them, *Meristoderes macracanthus* Herranz et al. 2012, is Mediterranean with type locality near Blanes, north of Barcelona in Spain. The species has furthermore been recorded from Sardinia, also in the Mediterranean (M. V. Sørensen personal observations). The second species, *M. galatheae* Herranz et al. 2012, was described almost from the opposite side of the globe, from localities around Ghizo Island, in the Solomon Island archipelago. The new genus could beyond any doubt be assigned to the family Echinoderidae, but species of the genus differs from other echinoderids in having segment 2 partially differentiated into a tergal and sternal plate (Herranz et al. 2012). This partial differentiation is in some species marked by distinct fissures, in others only by superficial subcuticular lines, in the lateroventral/ventrolateral parts of the segment. Since only two species have been known until now, and they were discovered so recently, our knowledge about morphology or geographical distribution of the genus is rather limited.

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독도 인근 해저퇴적물과 유기 퇴적물 분포 특성

Characterization of Clastic and Organic Sediments Near Dokdo, Korea

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요약 : 독도로부터의 거리 및 수심에 따라 채취된 표층 퇴적물에 대하여 입도분석, 광물분석, 유기물 분석 및 미화석 분석 결과를 이용하여 독도 인근 해저의 퇴적 기작 및 유기 퇴적물의 분포를 규명하였다. 독도 인근 해저 퇴적물은 자갈 및 사질이 우세하며, 끌림에 의한 퇴적 작용이 주를 이루는 반면에 독도와 거리가 멀어짐에 따라 실트와 머드의 비율이 증가하며 점토광물과 장석 등의 광물 성분의 변화를 보이고 뜬짐에 의한 퇴적이 우세해지는 경향을 보인다. 퇴적물에 포함된 유기 퇴적물의 군집 조성 또한 큰 변화를 보이는데, 연안 퇴적물에서는 해양 기원의 유기 퇴적물이, 심해 퇴적물에서는 육상 기원의 유기 퇴적물이 우점한다. 이러한 유기 퇴적물의 군집 변화는 퇴적물의 입도에 큰 영향을 받는 것으로 밝혀졌으며 유기 퇴적물중 높은 화분 농집도는 심해 퇴적물의 유기탄소 함량을 증가시키는데 중요한 역할을 하는 것으로 판단된다.

주요어 : 독도, 퇴적 기작, 유기 탄소, 유기 퇴적물, 화분

ABSTRACT : Sediment transport mechanism and distribution of organic sediments are elucidated by the study of particle size, mineralogy, organic matters and microfossils of the surface samples collected from seafloor adjacent Dokdo island. Shallow marine sediments are dominated by coarse- grained sediments including gravel and sand, and their sedimentation has mainly been controlled by traction. While the samples collected from oceanic zone are characterized by high contents of fine- grained sediments such as silt and mud in bulk sediments, and the changes of mineral compositions including clay minerals and feldspar, and the fine sediments have been deposited mainly by suspension. The change of organic sedimentary communities is detected between neritic and oceanic zone. Although marine organic matter is predominant in neritic zone, terrestrial organic matter is monopolized according to increasing water depth. This trend is associated with grain size of sediments. The results also suggest that high pollen concentrations in whole organic matters may played an important role in excessive organic carbon in sediment.

Key words : Dokdo, sediment transport mechanism, organic carbon, palynomorph, pollen

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Late Quaternary Paleoceanographic Changes in the Northeastern Ulleung Basin, East Sea, Inferred from Variations in Biogenic Components

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Abstract – Two piston cores (DD09-ST21, DD09-ST39B) from the northeastern Ulleung Basin in the East Sea were obtained to investigate variations in the biogenic components (calcium carbonate, organic carbon) and biogeochemical processes ($\delta^{13}C$ and $\delta^{15}N$). The two cores had distinctive characteristics in terms of surface production, preservation and dissolution capacity of carbonate, and redox conditions of bottom-water. Core DD09-ST21 was characterized by an oxygen-depleted condition from 15 ka (MIS 2) to 60 ka (MIS 3). Core DD09-ST39B, on the other hand, showed oxic bottom-water conditions, possibly due to shallow water depth. These two cores with different redox condition showed opposite trends in terms of $CaCO_3$, TOC, and C_{37} alkenone concentrations. $CaCO_3$ and C_{37} concentrations were higher during the LGM in DD09-ST21 while lower contents were observed in DD09-ST39B in the same period. Moreover, consistently low TOC in DD09-ST39B and higher fluctuation of organic matters in DD09-ST21 may suggest difference in primary productivity, preservation capacity, or a potential dissolution effect. During the Holocene, the surface productivity of both cores increased, probably due to renewed ventilation and vertical mixing in the East Sea. Therefore, this study suggests spatial variation in production and preservation of biogenic components in the two cores since last 50 ka for DD09-ST39B and 80 ka for DD09-ST21 due to difference in environmental conditions such as water depth, bottom-water conditions, surface productivity and preservation.

Key words – East Sea, biogenic components, productivity, paleoceanography

1. Introduction

The East Sea is a semi-isolated back-arc basin connected by four shallow straits, the Soya, Tsugaru, Tartar, and Korea straits (Fig. 1a). Glacioeustatic sea level variation is the most critical factor affecting glacial-interglacial environmental changes in the East Sea because of the sea's shallow straits. A lowering of global sea level by approximately 120-130 m during the Last Glacial Maximum (LGM) (Fairbanks, 1989) led to isolation of the East Sea from neighboring open oceans and subsequent restriction of water exchange with adjacent seas during the glacial period (Oba et al. 1991; Keigwin and Gorbarenko 1992; Gorbarenko and Southon 2000; Kim et al. 2000; Khim et al. 2007). A limited supply of cold deep water, consequent stratification of the water column, and restricted vertical ventilation within the East Sea during LGM led to bottom-water anoxia, as indicated by the formation of laminated sediments and high concentrations of certain redox-sensitive elements such as Re and Mo (Piper and Isaacs 1996; Crusius et al. 1999; Bahk et al. 2000).

These paleoceanographic changes were accompanied by changes in sea surface temperatures in East Sea on a glacial-interglacial time scale. The past sea surface temperatures (SSTs) in East Sea have been estimated using alkenone unsaturation index and anomalously higher temperatures during LGM have been reported. Ishiwatari et al. (2001), Lee and Kim (2002) and Seki et al. (2004) interpreted these atypical temperatures as a shift in the season of maximum alkenone production. Gorbarenko and Southon (2002) have found isotopically lighter $\delta^{18}O$ records of planktonic foraminifera in East Sea during the last glaciations suggesting glacial warming and/or low salinity water. Study on surface production changes and planktonic ecological structure over glacial-interglacial time scales would be helpful to understand the

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Seasonal changes in picocyanobacterial diversity as revealed by pyrosequencing in temperate waters of the East China Sea and the East Sea

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ABSTRACT: To elucidate the seasonal and spatial changes in picocyanobacterial diversity in temperate waters, the abundance and genetic diversity of picocyanobacteria and environmental variables were investigated at 3 stations located in the East China Sea and the East Sea. Barcoded amplicon pyrosequencing of 16S-23S internal transcribed spacer sequences was applied to study picocyanobacterial diversity using 36 samples. Through pyrosequencing, sequences belonging to 27 distinct Synechococcus and Prochlorococcus clades were retrieved, which showed high picocyanobacterial diversity and obvious seasonal variation in marginal waters. The coastal and cold water-adapted Synechococcus Clades I and IV were dominant during winter and spring, whereas the warm water-adapted Synechococcus Clade II and Prochlorococcus HLII ecotype were dominant during the summer and autumn. urther, Synechococcus Clades III, V, VII and 5.3-I as well as Prochlorococcus LLI opportunistically occupied distinct niches in the summer and early winter. In these temperate marginal seas, the seasonal distribution of picocyanobacterial diversity was mainly controlled by temperature and nutrient level. In addition, the seasonal circulation pattern of ad acent water masses was a ey determinant of the physicochemical properties of water and consequently of picocyanobacterial diversity.

KEY ORDS: Synechococcus Prochlorococcus Diversity East China Sea East Sea Pyroseqencing

INTRODUCTION

In marine environments, Synechococcus and Prochlorococcus are the dominant cyanobacteria, and they are nown to be important primary producers Li 1994, Liu et al. 1997, Jardillier et al. 2010 . Prochlorococcus is more abundant in oligotrophic and tropical open oceans, whereas Synechococcus dominates in mesotrophic coastal waters and in upwelling regions Partens y et al. 1999 .

Picocyanobacterial diversity has been studied using various genetic mar ers, such as 16S rRNA uller et al. 2003 , the 16S-23S internal transcribed spacer ITS Rocap et al. 2002, Ahlgren Rocap 2006, Choi Noh 2009, Mella- lores et al. 2011, Huang et al. 2012 , nitrogen regulatory gene ntcA Penno et al. 2006, Post et al. 2011 , nitrate reductase narB Jen ins et al. 2006, Paerl et al. 200 , RNA polymerase rpoC1 Toledo Paleni 1997, M hling et al. 2005 and cytochrome b6 subunit petB Ma ard et al. 2012 . These studies have revealed the existence of diverse Synechococcus and Prochlorococcus clades or ecotypes. Most studies of picocyanobacterial distribution in marine environments have been conducted using dot-blot hybridi ation and real-time quantitative polymerase chain reaction qPCR methods using clade-specific probes uller et al. 2003, wirglmaier et al. 200 , Tai Paleni 2009, Post et al. 2011, Ahlgren

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