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Abstract

An acetylenic alcohol **1** was isolated from a lipophilic extract of the stony coral *Alveopora verrilliana* collected at Komesu, Okinawa. The structure of compound **1** was elucidated to be a new member of polyacetylenes by analyzing spectroscopic data and by comparing the data with those of metabolites having similar structural moieties.

Introduction

The phylum Cnidaria consists of organisms from aquatic environments such as stony and soft corals, sea anemones, jellyfishes, sea wasps, and hydrozoas. As many species can be accessed easily, soft corals or octocorals have been important targets for new secondary metabolites from the early stages of marine natural products research.[1] Consequently, these organisms have been found to be rich sources of diterpenoids or sesquiterpenoids in addition to some other classes such as prostanoids.[2] Far fewer new secondary metabolites have been isolated from stony corals than from soft corals. Among them, representative ones include tubastrine from the coral *Tubastrea aurea*[3] and a series of polyacetylenes from corals of the genus *Montipora*.[4-7] When we carried out chemical investigation on stony corals in the late 1980s,[8] most of the lipophilic extracts were found to consist of simple fats or glycerides as major constituents except for those from two genera: *Montipora*[4] and *Alveopora*. Chromatographic separation of the extract prepared from the latter coral gave a new acetylenic molecule **1** (Figure 1), the structure of which is the subject of this note. The contents are mainly based on the 1988 undergraduate thesis of the first author (TT).

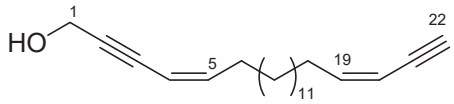

Figure 1. Structure of compound **1**

Results and Discussion

In our past collaboration with PharmaMar, a Spanish company, we conducted screening on Okinawan marine organisms for cytotoxic, antiviral, antimicrobial, and immunomodulatory activity. As a lipophilic extract of the title coral was found to show cytotoxicity to the cell line P388 (IC_{50} 1.7 μg/mL) and weak antimicrobial activity against *Bacillus subtilis*, it was chosen for chemical characterization of the major constituent. Compound **1** gave a molecular ion at *m/z* 314 in EIMS and its exact mass indicated the molecular formula as $C_{22}H_{34}O$ with 6 degrees of unsaturation. In the ^{13}C NMR spectrum, it contained four signals

δ 80.5 s, 81.1 d, 82.2 s, 91.4 s suggesting the presence of two acetylenes, as with the acetylenic molecules we found from *Montipora* and sponges.[4,9] Additional functional groups including two double bonds (δ 108.0, 108.3, 144.3, 145.8; δ 5.40, 5.98), a primary alcohol (δ 51.2; δ 4.41; 3645 cm^{-1}) and allylic methylenes (δ 29.1, 30.1; δ 2.29) were observed in the spectroscopic data. Therefore, the molecular structure was suggested to be a linear skeleton with two double bonds and two triple bonds. Enyne moiety is one of common structural features in marine natural products such as petrosynol and related molecules,[9] so the above multiple bonds were elucidated to two sets of enyne moieties inferred by the presence of a terminal acetylenic proton at δ 3.07 (d, J = 2.2 Hz) coupled to a *cis* olefin at δ 5.44 (brd, J = 10.8 Hz) and 5.92 (dt J = 10.8 Hz) and by an oxymethylene signal at δ 4.41 coupled to another *cis* olefin at δ 5.44 (brd, J = 10.8 Hz) and 6.00 (dt, J = 7.2, 10.8 Hz). A large methylene signal at δ 1.33 indicates the presence of a long aliphatic chain and can be placed between the two terminal groups.

After checking a recent review of acetylenic compounds from marine sources,[10] callyspongenol B was selected as a reference molecule.[11] In addition to ^{1}H NMR signals, Δδ values of ^{13}C NMR signals between the terminal portions of two compounds were small (Figure 2), so the whole structure of compound **1** was elucidated.

Although the structures of compound **1** and callyspongenol B are similar, their sources are quite different: a stony coral and a sponge. However, this is not the first case of isolating a similar or the same molecule from totally different organisms, for example curcuphenols from sponges and a plant[12] and verrucosanols from a sponge and a liverwort.[13]

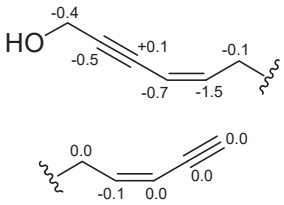

Figure 2. Δδ values (**1**-callyspongenol B) of ^{13}C NMR data for two terminal structures

Experimental

General experimental conditions. NMR data were obtained on a Jeol FX-90Q or PMX-60 instrument. Multiplicities of ^{13}C NMR signals were determined by INEPT data and expressed as follows: s for C, d for CH, t for CH_2, and q for CH_3. EIMS spectra were obtained on a Jeol D-300 instrument. IR spectrum was obtained on a Hitachi 260-10 spectrophotometer. Solvents used were reagent grade without distillation.

Extraction and Isolation. A specimen (8.8 kg, wet) of the coral *A. verrilliana* was collected off the coast of Komesu, Okinawa, April 1987. The specimen was identified by Dr. J. E. N. Veron, Australian Institute of Marine Science, during a visit to Okinawa.

After extraction with acetone (10 L) three times, the hexane soluble portion (108 g) was taken. Half of the extract (54 g) was subjected to silica gel chromatography to give four fractions. The second fraction (15 g) was further separated successively on Sephadex LH20, silica gel, Lobar column, and reversed phase HPLC to give 87.0 mg of compound **1**.

Compound 1. Colorless oil; $[\alpha]_D$ 0; IR (CCl_4) 3645,

3325, 2930, 2850, 2100 (weak), 1470, 1380, 1010 cm^{-1}; UV (MeOH) 226 nm (log ε 4.4); ^1H NMR ($CDCl_3$) δ 1.33 (22H, s, H-7~17), 2.29 (4H, m, H-6, 18), 3.07 (1H, d, *J* = 2.2 Hz, H-22), 4.41 (2H, d, *J* = 2.0 Hz, H-1), 5.44 (2H, brd, *J* = 10.8 Hz, H-4, 20), 5.92 (1H, td, *J* = 7.2, 10.8 Hz, H-5), 6.00 (1H, td, *J* = 7.2, 10.8 Hz, H-19); ^{13}C NMR ($CDCl_3$) δ 28.6-28.7 t (C-7~17), 29.0 t (C-6), 30.1 t (C-18), 51.2 t (C-1), 80.5 s (C-21), 81.1 d (C-22), 82.2 s (C-3), 91.4 s (C-2), 108.0 d (C-20), 108.3 d (C-4), 144.3 d (C-5), 145.8 d (C-19); EIMS *m/z* 314 (M^+), 299, 285, 283, 271, 257, 155; HREIMS obsd. 314.2601 (calcd. for $C_{22}H_{34}O$ 314.2607).

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