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Isolation of Epidioxysteroids from a Sponge of the Genus Tethya

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Four steroids including two novel compounds have been isolated from a sponge of the genus *Tethya*. All of the compounds possess a 5α,8α-epidioxy functionality as a common structural feature. Two new steroids, **1** and **2**, possess a cyclopropyl ring at C-24(26) of the side chain. The structures of these compounds have been determined by combined spectroscopic methods.

Introduction

Sponges (phylum Porifera) are widely recognized as the most prolific sources of both structurally unique and biologically active marine natural products.[1] In a recent literature survey conducted by this group, more than 40% of marine-originated metabolites have been isolated from these animals.[2] Metabolites of sponges are consisting of compounds originated from various biogenetic origins; steroids, terpenoids, peptides, polyketides, purines and pyrimidines, and mixed biosynthetic products.[1,3] In addition, numerous compounds have been reported to exhibit potent and diverse

bioactivities. Consequently, several leading compounds on the development of new drugs from marine sources have been derived from these animals.[4-6] In Korean water, sponges are also among the most abundant benthic colonial animals. However, chemistry of these organisms have attracted very little attention.

Steroids are among the major groups of sponge metabolites. As in the cases of metabolites of other structural classes, numerous steroids possessing unprecedented carbon skeletons and functionalities have been isolated from these animals.[1,7,8] In addition, several sponge-derived steroids have been reported to exhibit cytotoxic, antiviral, antimicrobial, and enzyme-inhibitory activities. As a part of our search for novel substances from benthic organisms of the Korean water, we collected a sponge of the genus *Tethya* off the shore of Keomun Island.[9] Silica vacuum flash chromatography of the crude extract followed by silica and reversed-phase HPLC has yielded several steroids possessing the 5α,8α-epidioxy functionality as a common structural feature. Herein we report the structures of four compounds (**1-4**) including two novel ones bearing an unusual cyclopropyl ring at the side chain. All of protons and carbons of these compounds were also assigned on the basis of 2-D NMR experiments.

Results and Discussion

Compound **1** was isolated as a white amorphous solid. The molecular formula of $C_{27}H_{40}O_3$ was deduced by a combination of high-resolution mass and ^{13}C NMR spectrometry. A strong absorption band at 3400 cm^{-1} in the IR spectrum indicated the presence of a hydroxyl group(s). Characteristic signals of a 3-hydroxysterol were observed at δ 4.01 (1H, m, H-3) and 0.72 (3H, s, H-18) in the 1H spectrum. Since 27 carbon signals were observed in the ^{13}C NMR spectrum, **1** was thought to be a sterol of the cholestane class.

Careful examination of the NMR data revealed several structural features. The ^{13}C NMR spectrum showed carbon signals of a di- and a tri-substituted double bond at δ 142.38 (C), 135.39 (CH), 130.76 (CH), and 119.80 (CH). Downfield signals at δ 6.60 (1H, d, *J*=8.8 Hz), and 6.29 (1H, d, *J* =8.8 Hz) in the ^1H NMR spectrum revealed that the disubstituted double bond was indeed an isolated one. Although there are several positions, *e.g.* C-4, C-5, and C-22, possible for a double bond in the framework of steroids, the chemical shifts and coupling modes of these protons were indicative of the presence of C-6 double bond with a 5,8-epidioxy functionality. The location of a trisubstituted double bond was assigned to C-9(11) since the C-9 carbon, frequently observed in the region of δ 60-50 in common steroids, was not found in the ^{13}C NMR spectrum of **1**. In addition, carbon signals at δ 20.17 (CH), 12.98 (CH), and 12.68 (CH_2) and corresponding proton signals at δ 0.40 (1H, m), 0.30 (1H, m), and 0.03 (2H, m) in the NMR data revealed the presence of a disubstituted cyclopropyl ring. Observation of four methyl carbons, instead of five or more methyls of common steroids, in the ^{13}C NMR spectrum revealed that one of the methyls of cholestane skeleton must be converted to a methylene forming a cyclopropane moiety.

Based on these interpretations, the structure of **1** was determined by a combination of 2-D NMR methods. All of the proton-bearing carbons and their protons were precisely matched by a HMQC experiment (Table 1). Tracing of the proton spin-couplings by the ^1H COSY data, initiated from the H-3 proton, readily determined that **1** possessed the same A ring as cholesterol. Since the H-4 protons at δ 2.12 (1H, ddd, *J*=13.7, 5.2, 1.7 Hz) and 1.92 (1H, dd, *J*=13.7, 11. 7 Hz) were not coupled with any of the olefinic protons, the adjacent C-5 carbon must be oxidized. In the same manner, a combination of the ^1H COSY and HMQC experiments allowed the assignment of a spin system including the H-21 methyl protons at δ 0.88 (3H, d, *J*=5.9 Hz) and the cyclopropyl protons suggesting the C-26 methyl group to be converted to a methylene. Thus, the structure of **1** was defined as a 5,8-epidioxysteroid possessing two double bonds at C-6 and C-9(11) and a cyclopropyl ring at C-24(26).

The structure of **1** was confirmed by a HMBC experiment (Table 1). Several long-range couplings were observed between the key protons and their adjacent carbons. In particular, the presence of a 5,8-epidioxy group was confirmed by couplings between the H-2, H-6, and H-7 protons and the C-5 and C-8 carbons. Couplings between the H-11 proton and C-8 and C-10 carbons assigned the C-9(11) double bond. Similarly the presence of a cyclopropane ring at C-24(26) was confirmed by long-range correlations between the H-27 methyl protons and C-24, C-25, and C-26 carbons.

Compound **1** possessed asymmetric carbon centers at C-5, C-8, C-24, and C-25 which are uncommon among steroids. Stereochemistry of the cyclopropyl centers at C-24 and C-25 was determined by a combination of proton-decoupling and NOEDS experiments. Signals of the H-24 and H-25 protons were changed from multiplets to double-double-doublets (*J*= 8.3, 4.4, 4.4 Hz for both) by irradiations of the H-23 and H-27 protons, respectively. The small coupling between the adjacent protons ($J_{24,25}$=4.4 Hz) assigned trans orientation for the C-24(26) cyclopropane ring. This interpretation was supported by a NOEDS experiment in which irradiation of the H-27 protons at δ 1.00 significantly enhanced the signal of the H-24 proton at δ 0.30. Thus, the relative configurations of the cyclopropyl centers were determined as 24*R**,25*R**. Due to the spatial distance between the cyclopropane and D ring of steroidal nucleus, however, the absolute configurations of these centers were unable to be assigned.[10]

The stereochemistry of the epidioxy centers at C-5 and C-8 could be either 5α,8α- or 5β,8β-. Since the C-5 and C-8 carbons did not contain any protons, the stereochemistries of these centers were assigned by the chemical shifts of the adjacent protons. Chemical shifts of the H-6, H-7, H-18, and H-19 protons which would be influenced by the orientation of the epidioxy group were found at δ 6.29, 6.60, 0.72, and 1.09, respectively. A literature survey revealed that these values were very similar to those of the same protons reported as δ 6.30, 6.61, 0.74, and 1.01, respectively, of a structurally related 5α,8α-epidioxysteroid recently isolated from the plant *Typha latifolia*.[11] Therefore, the configurations of these centers were inferred as 5α,8α-, as further discussed later. Thus, the structure of compound **1** was determined as 5α,8α-epidioxy-24(26)-cyclopropylcholesta-6, 9(11)-dien-3β-ol.

A closely related compound **2** was isolated as a white solid which was analyzed for $C_{27}H_{42}O_3$ by a combination of

Table 1. NMR assignments for compounds **1** and **2**

no	1			2		
	H[a]	C[b]	HMBC[c]	H[a]	C[b]	HMBC[c]
1	2.09 (m)	32.54		1.95 (m)	34.70	
	1.67 (ddd, 13.7, 3.4, 3.4)			1.69 (ddd, 13.7, 3.4, 3.4)		
2	1.94 (m)	30.59		1.84 (br dd, 12.7, 2.5)	30.13	
	1.56 (m)			1.55 (m)		
3	4.01 (m)	66.33		3.97 (m)	66.46	
4	2.12 (ddd, 13.7, 5.2, 1.7)	36.05	2, 3, 5, 10	2.11 (br dd, 13.7, 3.4)	36.95	2, 3, 5, 10
	1.92 (dd, 13.7, 11.7)			1.91 (dd, 13.7, 13.7)		
5		82.70			82.13	
6	6.29 (d, 8.8)	135.39	5, 8	6.24 (br d, 8.3)	135.32	5, 8, 10
7	6.60 (d, 8.8)	130.76	5, 8	6.51 (d, 8.8)	130.71	5, 8
8		78.36			79.43	
9		142.38		1.49 (m)	51.04	
10		37.91			36.93	
11	5.42 (dd, 6.3, 2.0)	119.80	8, 10, 13	1.49 (m)	23.43	
				1.20 (m)		
12	2.27 (dd, 17.1, 5.9)	41.26	9, 11, 13, 14, 18	1.98 (m)	39.42	
	2.05 (br d, 17.1)			1.20 (m)		
13		43.77			44.73	
14	1.82 (dd, 12.2, 7.8)	48.01	7, 8, 13, 18	1.58 (m)	51.57	7, 8, 13, 18
15	1.71 (m)	20.88		1.63 (m)	20.65	13, 14
	1.60 (m)			1.43 (m)		
16	1.97 (m)	28.10		1.93 (m)	28.26	
	1.43 (m)			1.39 (m)		
17	1.31 (m)	55.99		1.17 (m)	56.35	
18	0.72 (s)	12.75	12, 13, 14, 17	0.80 (s)	12.72	12, 13, 14,
17						
19	1.09 (s)	25.53	1, 5, 9, 10	0.88 (s)	18.59	1, 5, 9, 10
20	1.43 (m)	34.92		1.39 (m)	34.83	
21	0.88 (d, 5.9)	18.39	17, 22	0.87 (d, 6.1)	18.20	17, 22
22	1.51 (m)	35.52		1.49 (m)	35.55	
	1.15 (m)			1.11 (m)		
23	1.17 (m)	30.59		1.15 (m)	30.64	
24	0.30 (m)	20.17		0.29 (m)	20.22	
25	0.40 (m)	12.93		0.39 (m)	12.97	
26	0.03 (m)	12.68		0.11 (m)	12.65	23, 24, 27

[a,b] measured in $CDCl_3$ solutions at 125 and 500 MHz, respectively. Assignments were aided by ^1H COSY, TOCSY, HMQC, and DEPT experiments. [c] Positions of correlated carbons. Parameters were optimized for 8 Hz of coupling constants.

high-resolution mass and ^{13}C NMR spectrometry. The NMR data of this compound were very similar to those obtained for **1**. The only significant difference in the ^{13}C NMR spectrum was the replacement of the C-9 and C-11 olefinic carbons of **1** by upfield signals. Corresponding difference was also observed in the ^1H NMR spectrum in which the signal of the H-9 olefinic proton of **1** disappeared. Therefore, compound **2** was defined as the 9,11-dihydro derivative of **1** that was confirmed by a combination of the ^1H and ^{13}C NMR, ^1H COSY, HMQC, and HMBC experiments (Table 1).

Compound **2** possessed all of the asymmetric carbon centers (C-5, C-8, C-24, and C-25) of **1**. By utilizing the same proton-decoupling and NOEDS experiments as **1**, the configurations of the cycloproyl centers were assigned as 24*R**, 25*R**. Stereochemistry of the epidioxy centers at C-5 and C-8 was approached by the chemical shifts of the adjacent protons. A literature survey revealed that the chemical shifts of the H-6, H-7, H-18, and H-19 protons were significantly influenced by the stereochemistry at C-5 and C-8.[11] That is, the orientations of oxygens attached to the epidioxy centers influence the chemical shifts of the H-18 and H-19 methyl protons which in turn would change those of the H-6 and H-7 olefinic protons. In the case of a 5β,8β-epidioxide, due to the spatial proximity with oxygens, the H-18 and H-19 methyl protons would be shifted downfield. In contrast, the H-6 and H-7 protons would be shifted upfield because the interactions with the H-18 and H-19 methyls disappeared. This phenomenon would be reversed in a 5α,8α-epidioxide in that the olefinic protons would be shifted downfield by the spatial proximity with the methyl protons which were shifted upfield by the disappearance of the interaction with the oxygens. As a result, the chemical shifts of the H-6, H-7, H-18, and H-19 protons in a 5α,8α-epidioxide were observed at δ 6.25, 6.51, 0.82, and 0.89, respectively, while signals of the same protons were found at δ 5.57, 5.89, 1.18,

and 0.93, respectively, in the corresponding 5β,8β-epidioxide.[11] Since the chemical shifts of the same protons of **2** were found at δ 6.24, 6.51, 0.80, and 0.88, respectively, which were very similar to those observed for the 5α,8α-epidioxide, stereochemistry of **2** was assigned as 5α,8α. Thus, the structure of compound **2** was defined as 5α,8α-epidioxy-24(26)-cyclopropylcholesta-6-en-3β-ol.

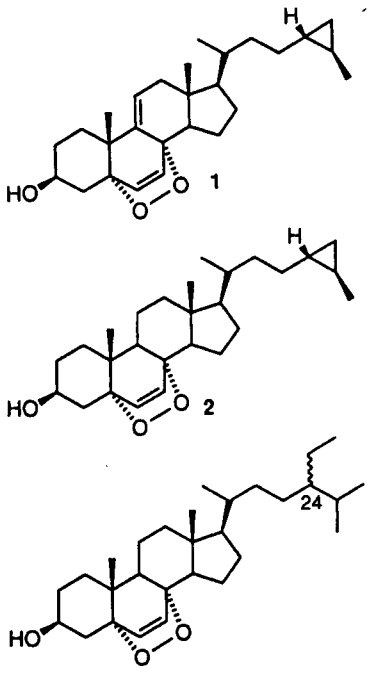
In addition to these compounds, two epimeric steroids (**3** and **4**) were isolated as a mixture. The molecular formula of a white solid isolated by silica and reversed-phase HPLC was defined as $C_{29}H_{48}O_3$ by high-resolution mass data. However, ^{13}C NMR spectrum of this material showed 41 instead of the expected 29 carbon signals suggesting that this material was indeed a mixture of two compounds. Since all of the efforts to separate these compounds by chromatographic techniques did not succeed, however, the structural elucidation was made to the mixture. Comparison of the ^{13}C NMR data revealed that most of carbon signals corresponding to the A-C rings of **2** were also present in the mixture. Moreover, the intensities of these signals were much stronger than those of other carbons. Therefore, the mixture was thought to be composed of two compounds whose structural differences must exist only at the side chain.

A combination of ^1H COSY and HMQC experiments of the mixture revealed that the cyclopropyl moiety of **2** was converted to an isopropyl group. In addition, a new ethyl group was attached to the C-24 carbon. Therefore, these compounds were defined as 5α,8α-epidioxysteroids of the stigmasterol class of which structural difference was present in the stereochemistry of C-24, the only asymmetric carbon center at the side chain. This interpretation was supported by the ^{13}C NMR data. Differences between chemical shifts of pairing carbons were generally larger for those located at C-24 and vicinity (for carbons at C-23~C-29, Δδ 0.06~0.35 ppm) than other carbons (for carbons at C17 and C-20~C-22, Δδ 0-0.12 ppm). Thus, the structures of these compounds (**3** and **4**) were defined as 24*R* and 24*S* isomers of 5α,8α-epidioxystigmasta-5-en-3β-ol. A literature survey revealed that these steroids have been isolated as metabolites of several marine animals such as the coelenterates *Dendrogyra cylindrus* and *Metridium senile*, the mollusc *Aplysia dactylomela*, the sponges *Suberites carnosus* and *Thalysias juniperina*, and the tunicate *Ascidia nigra*.[12-14] However, signals of the methyl protons at the side chain were not separated enough to assign the stereochemistry of the C-24 asymmetric center. Based on the intensity of the H-21 methyl protons at δ 0.90 and 0.89, the relative intensities between the epimers, **3** and **4** were estimated as 3 : 2.

Epidioxysteroids have been isolated from various natural sources. In marine environment, these compounds have been frequently isolated from invertebrates.[12-16] To the best of our knowledge, however, the C-24(26) cyclopropyl-containing side chain of **1** and **2** is an unprecedented one among the natural epidioxysteroids.

Experimental

General. NMR spectra were recorded in $CDCl_3$ solutions on a Varian Unity-500 spectrometer. Proton and carbon NMR spectra were measured at 500 and 125 MHz, respectively. All chemical shifts were recorded with respect to internal Me_4Si. IR spectra were recorded on a Mattson GALAXY spectrophotometer. Mass measurements were provided by the Mass Spectrometry Facility, Department of Chemistry, University of California, Riverside. Melting points were measured on a Fisher-Jones Apparatus and are reported uncorrected. All solvents used were spectral grade or were distilled from glass prior to use.



3 and **4**
(epimers at C-24)

Collection, extraction, and isolation. *Tethya* sp. (sample number 94K-31) was collected by hand using SCUBA at 20-25 m depth in Nobember, 1994, along the shore of Keomun Island.[9] The collected specimens were immediately frozen by dry ice and sent to the laboratory. The lyophilized animals (0.28 kg) were repeatedly extracted with CH_2Cl_2 (1 L×2) and MeOH (1 L×2) and dried under vacuum to yield dark brown syrup (11.23 g). The crude extract was partitioned between hexane (500 mL) and 10% aqueous methanol (500 mL). The hexane layer was dried (2.87 g) and separated by silica vacuum flash chromatography (10 cm×7 cm, $60PF_{254}$) by using sequential mixtures of *n*-hexane and EtOAc as eluents. The fractions eluted with moderately polar solvents (20-40 % EtOAc in hexane) were combined and dried under vacuum to yield a pale yellow solid (0.87 g). This material was redissolved in 30% EtOAc in hexane and filtered through a silica Sepak column. The filterate was subjected to semi-preparative HPLC (YMC silica column, 1 cm×25 cm, 30% EtOAc in hexane) to yield epidioxysteroids. Final purification was made by reversed-phase HPLC (Shiseido Capcell ODS column, 20% MeOH in CH_3CN) to give pure compounds; 12.7, 49.2, and 16.5 mg for **1-3**, respectively.

Compound 1. a white amorphous solid, mp 89-90 °C; IR (KBr) ν_{max} 3400, 2950, 2920, 2860, 1460, 1380, 1080, 1030, 970 cm^{-1}; HREIMS $[M]^+$ obsd 412.2971; calculated for $C_{27}H_{40}O_3$, 412.2977; LRMS m/z (relative intensity) 412 (17), 396 (22), 380 (70), 362 (59), 285 (23), 251 (23), 209

(16), 152 (25), 55 (100).

Compound 2. a white amorphous solid, mp 114-115 °C; IR (KBr) ν_{max} 3400-3300 (broad), 2950, 2860, 1470, 1450, 1380, 1080, 1040 cm^{-1}; HREIMS $[M]^+$ obsd 414. 3133; calculated for $C_{27}H_{42}O_3$, 414.3134; LRMS m/z (relative intensity) 414 (22), 398 (29), 382 (22), 362 (13), 267 (12), 219 (13), 152 (67), 135 (23), 44 (100).

Compound 3 and 4. a white amorphous solid; HRCIMS $[M+H]^+$ obsd 445.3610; calculated for $C_{29}H_{49}O_3$, 445.3681; ^1H NMR ($CDCl_3$, key protons of the major diastereomer) δ 6.48 (1H, d, *J*=8.7 Hz, H-7), 6.22 (1H, d, *J*= 8.7 Hz, H-6), 3.95 (1H, m, H-3), 2.09 (1H, br dd, *J*=13.8, 3.9 Hz, H-4), 0.89 (3H, d, *J*=6.3 Hz, H-21), 0.86 (3H, s, H-19), 0.82 (3H, t, *J*=7.3 Hz, H-29), 0.80 (3H, d, *J*=6.3 Hz, H-26), 0.79 (3H, d, *J*=6.8 Hz, H-27), 0.78 (3H, s, H-18); ^{13}C NMR ($CDCl_3$, numbers in parenthesis are chemical shifts of the minor diastereomer) δ 135.34 (CH, C-6), 130.72 (CH, C-7), 82.13 (C, C-5), 79.44 (C, C-8), 66.47 (CH, C-3), 56.31 (56.33, CH, C-17), 51.59 (CH, C-14), 51.07 (CH, C-9), 45.81 (46.03, CH, C-24), 44.75 (C, C-13), 39.44 (CH_2, C-12), 36.97 (C, C-10), 36.95 (CH_2, C-4), 35.62 (35.74, CH, C-20), 34.72 (CH_2, C-1), 33.75 (33.72, CH_2, C-22), 30.15 (CH_2, C-2), 29.17 (28.96, CH, C-25), 28.29 (CH_2, C-16), 26.10 (26.39, CH_2, C-28), 23.44 (CH_2, C-11), 23.08 (23.02, CH_2, C-23), 20.67 (CH_2, C-15), 19.85 (19.62, CH_3, C-26), 19.06 (18.99, CH_3, C-27), 18.67 (18.72, CH_3, C-19), 18.20 (CH_3, C-21), 12.66 (CH_3, C-18), 12.00 (12.35, CH_3, C-29).

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