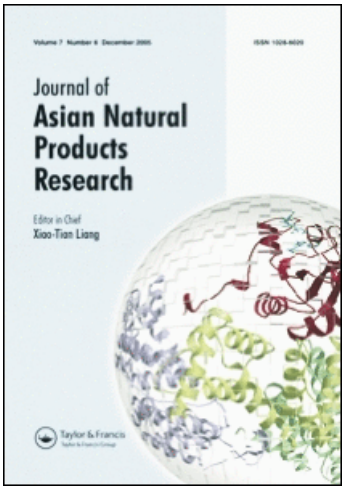

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SULFOGLYCOLIPID FROM THE MARINE BROWN ALGA *SARGASSUM HEMIPHYLLUM*

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One kinds of glycolipid (**SBI**) have been isolated from the marine brown alga *Sargassum hemiphyllum* (Turn.) Ag. The structures of SBI have been determined as the sodium salt of 1-0-acyl-3-0-(6′-sulfo-α-D-quinovopyrannosyl) glycerol (acyl: tetradecanoyl, pentadecanoyl, 11-hexadecenoyl, hexadecanoyl, 10,13-octadecadienoyl, 9-octade cenoyl, 15-metylheptadecanoyl and 11-eicosenoyl 17 : 1.5 : 19 : 153 : 1 : 19 : 1 : 2) on the basis of chemical and spectral evidence and GC-MS analysis, respectively. Four constituents of the SBI were new compounds [the sodium salt of 1-0-(11″-hexadecenoyl)-3-0-(6′-sulfo-α-D-quinovopyrannosyl) glycerol, the sodium salt of 1-0-(10″,13″-octadecadienoyl)-3-0-(6′-sulfo-α-D-quinovopyrannosyl) glycerol, and the sodium salt of 1-0-(15″-metylhexadecenoyl)-3-0-(6′-sulfo-α-D-quinovopyrannosyl) glycerol, and the sodium salt of 1-0-(11″-eicosenoyl)-3-0-(6′-sulfo-α-D-quinovopyrannosyl) glycerol]. All compounds were isolated from marine brown alga for the first time.

Keywords: Marine; Brown alga; *Sargassum hemiphyllum*; Sulfonoglycolipid

INTRODUCTION

Sargassum hemiphyllum (Turn.) Ag. is native to Eastsea and Southsea of China. The alga is used in Chinese folk medicine for the treatment of goiter, tumor, scrofula painful, swollen testis and edema due to the retention of phlegm [1]. In a preliminary investigation the *n*-butanolic extract of the alga exhibited anti-cancer activities in mouse S_{180} tumor model (0.19 g/kg) [2]. During the course of our investigation on marine natural products, we have

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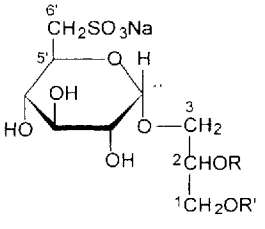
reported the isolation and identification of nine compounds from *S. hemiphyllum* [3, 4]. In the continuing study on the butanolic extract of the same alga, we have isolated one glycolipid: a sulfonoglycolipid designated as SBI (**1**). This paper deals with the structure elucidation of **1**.

RESULTS AND DISCUSSION

The butanol extract was fractionated by vacuum liquid chromatography over silica gel, and the fractions were further purified by repeated column chromatography over silica gel and Sephadex LH-20 resulting in the isolation of **1**.

The IR spectrum of **1** showed absorption bands at 3428(br. hydroxyl), 1733 (ester), 1172 and 1033 (sulfonate) cm^{-1}, while the ^{1}H-NMR spectrum showed a characteristic signal pattern due to a glyceroglycolipid [5]: *e.g.*, a triplet (3H) at δ 0.87 (terminal methyl), a broad signal centered at δ 1.25(methylene in the fatty acid chain), a mass of signals between δ 3.0–4.5(11H, sugar and glycerol moiety), and a doublet signal (1H, $J = 3.7$ Hz) at δ 4.83 (anomeric proton). The ^{13}C-NMR spectrum of **1** revealed one anomeric carbon atom at δ 100.1. Comparison of the ^{1}H and ^{13}C-NMR spectra with those of 2 obtained from marine red alga *Gracila verrucosa* [6] and 3 from a marine sponge *Phyllospongia foliascens* [7] suggested that **1** was a sulphonoglycolipid (Fig. 1; Tab. I). The FDMS of **1** exhibited a series of peaks at *m/z* 601,627 and 655 *etc.*, which corresponded to $(M+Na)^+$, indicating that **1** was the sodium salt of 1-0-acyl-3-0-(6′-sulfo-α-D-guinovopyrannosyl) glycerol with different acyl groups [5–7].

On treatment with sodium methoxide in methanol, **1** furnished a glycerol–sulfonoglycoside and a mixture of fatty acid methyl esters [6].



1: R = H, R' = (a:b:c:d:e:f:g:h = 17:1.5:19:153:1:19:1:2)
2: R , R' = (a:d:f = 4:15:1)
3: R , R' = H
a = $-OC(CH_2)_{12}CH_3$ b = $-OC(CH_2)_{13}CH_3$
c = $-OC(CH_2)_9CH{=}CH(CH_2)_3CH_3$ d = $-OC(CH_2)_{14}CH_3$
e = $-OC(CH_2)_8CH{=}CHCH_2CH{=}CH(CH_2)_3CH_3$
f = $-OC(CH_2)_7CH{=}CH(CH_2)_7CH_3$
g = $-OC(CH_2)_{13}CHCH_2CH_3$ (CH$_3$ branch)
h = $-OC(CH_2)_9CH{=}CH(CH_2)_7CH_3$

FIGURE 1

TABLE I ^{13}C NMR Data for SBI(1), 2_and 3 (in CD_3OD)

Carbon	1	2	3
1′	100.1 (d)	100.2 (d)	99.2 (d)
2′	73.4 (d)	73.5 (d)	72.2 (d)
3′	75.0 (d)	75.0 (d)	73.9 (d)
4′	74.7 (d)	75.0 (d)	73.4 (d)
5′	69.7 (d)	69.8 (d)	69.1 (d)
6′	54.1 (t)	54.4 (t)	53.1 (t)
1	66.5 (t)	64.4 (t)	63.7 (t)
2	70.4 (d)	71.8 (d)	71.7 (d)
3	69.7 (t)	67.3 (t)	69.8 (t)

The sulfonoglycoside was determined as 6′-sulfo-0-α-quinovopyranosyl-(1′→ 3)-glycerol by comparison of the ^{13}C-NMR data of 3 from a marine sponge [7]. The mixture of fatty acid methyl esters was subjected to GC-MS for identification (Fig. 2). The fatty acid compositions in 1 were shown to be methyl tetradecanoate [242(M^+), 211, 74]; methyl pentadecanoate [256(M^+), 225, 74]; methyl 11-hexadecenoate [268 (M^+), 236, 208 $(C_{15}H_{28})^+$, 194 $(C_{14}H_{26})^+$, 152 $(C_{11}H_{20})^+$, 83 $(C_6H_{11})^+$, 74, 69 $(C_5H_9)^+$]; methyl hexadecanoate [270 (M^+), 239, 185, 74]; methyl 10,13-octadecadienoate [294(M^+), 263, 124 $(C_9H_{16})^+$, 81 $(C_6H_9)^+$, 67 $(C_5H_7)^+$]; methyl 9-octadecenoate [296(M^+), 264 $(C_{18}H_{32}O)^+$, 222 $(C_{16}H_{30})^+$, 166 $(C_{12}H_{22})^+$, 152 $(C_{11}H_{20})^+$, 74]; methyl 15-methylheptadecanoate [298 $(M)^+$, 267 $(C_{18}H_{35}O)^+$, 255, 199 $(C_{12}H_{23}O_2)^+$, 143 $(C_8H_{15}O)^+$, 129 $(C_7H_{13}O)^+$, 74]

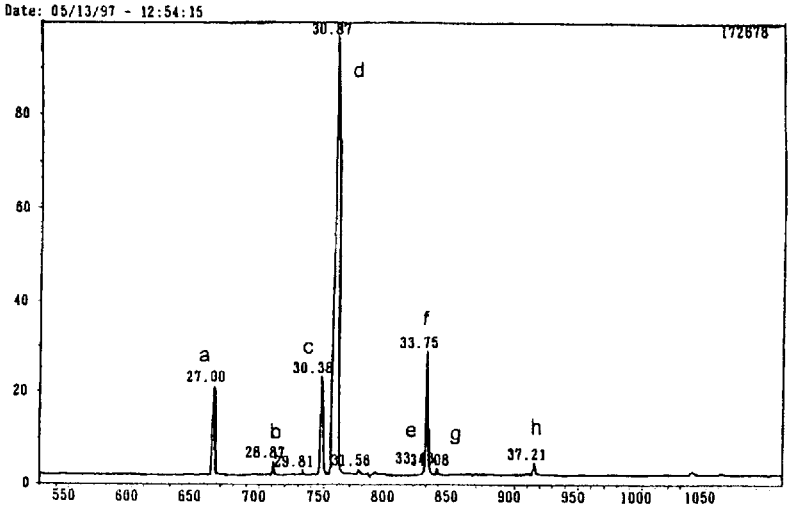


FIGURE 2 The GC-MS analysis of SBI (1).

and methyl 11-eicosenoate [324 $(M)^+$, 292, 250 $(C_{18}H_{34})^+$, 208 $(C_{15}H_{28})^+$, 152 $(C_{11}H_{20})^-$, 137 $(C_{10}H_{18})^+$, 123 $(C_9H_{15})^+$, 74] (17 : 1.5 : 19 : 153 : 1 : 19 : 1 : 2). Consequently, the chemical structure of **1** was determined as the sodium salt of 1-0-acyl-3-0-(6′-sulfo-α-D-quinovopyrannosyl) glycerol (acyl: tetradecanoyl, pentadecanoyl, 11-hexadecenoyl, hexadecanoyl, 10, 13-octadecadienoyl, 9-octadecenoyl, 15-methyl heptadecanoyl, 11-eicosenoyl).

It is interesting to note that a 6′-sulfoquinovosyl glyceride, a substance closely related to SBI from the blue alga, could restrains the copy of HIV. It was a new kind of substance having anti-HIV activity [8].

EXPERIMENTAL SECTION

General Experimental Procedures

The IR spectra were recorded on a Bruker IFS-55 spectrometer. The ^{1}H-NMR and ^{13}C-NMR spectra were run on a Bruker AC-250 and a Bruker AC (X)-300 spectrometer. The FABMS were taken on a JNS-D 300 mass spectrometer, EIMS on a DX-300 mass spectrometer. The GC-MS was taken on a VG700 mass spectrometer. Separation and purification were performed by column chromatography on silica gel (300–400 and 180–200 mesh) and Sephadex LH-20.

Plant Material

The *Sargassum hemiphyllum* (Turn.) Ag. were collected in July, 1992 from Naozhou, Guangdong Province, China. The sample was provided and identified by Prof. LU, Qingdao Institute of Marine, Chinese Academy of Sciences, China. The sample has been deposited in Traditional Chinese Medicine Department of Shenyang Pharmaceutical University.

Extraction and Isolation

Air-dried finely cut alga (1.8 kg) was successively extracted with petroleum ether, EtOAc and MeOH at room temperature. The methanol extract was then partitioned into *n*-BuOH-H_2O to give the *n*-BuOH extract (8 g). This extract was fractionated by vacuum liquid chromatography over silica gel developing with EtOAc–MeOH (20 : 1→1 : 1) to furnish two fractions FrII and FrV. The FrV was subjected to column chromatography over silica gel ($CHCl_3$–MeOH–H_2O 10 : 3 : 1) and Sephadex LH-20 ($CHCl_3$–MeOH 1 : 1) to afford SBI (30 mg).

SBI (1)

White amorphous powder; IR(KBr) ν_{max} 3428, 1733, 1462, 1172, 1033 cm^{-1}; FDMS *m/z*: 601 $(M+Na)^+$, 627 $(M+Na)^+$, 655 $(M+Na)^+$. EIMS *m/z*: 550 (M^+), 576 (M^+). ^{1}H-NMR (^{1}H-^{1}H COSY) (250MHz, CD_3OD, δ): 0.87 (3H,t), 1.25 (br. s), 1.65 (2H, m), 2.06 (*m*, =C—CH_2), 2.42 (2H, t, $J=7.4$ Hz), 2.96 (1H, dd, $J=9.4$ Hz, 1-H), 3.13 (1H, d, $J=9.6$ Hz, 4′-H), 3.43 (1H, m, 1-H), 3.47 (1H, dd, $J=9.6$, 3.1 Hz, 2′-H), 3.74 (1H, t, $J=$ 9.6 Hz, 3′-H), 4.08 (1H, m, 2-H), 4.12 (1H, m, 5′-H), 4.15 (2H, m, 3-H), 4.23 (2H, d, $J=7.3$ Hz, 6′-H), 4.83 (1H, d, $J=3.7$ Hz, 1′-H), 5.38 (t-like, $J=9.2$, 4.4 Hz, =C—H). ^{13}C-NMR (62.5 MHz, CD_3OD, δ c):175.7 (s, 1″-C), 130.8 (d), 34.9, 33.0, 30.7, 30.4, 30.2, 28.1, 25.9, 23.7, 14.5 and for sulfonoquinovosyl glyceride moiety of **1** see Table I.

Alkaline Treatment of SBI

A solution of 0.17N NaOMe–MeOH(1ml) was added to SBI(1 mg) and the solution was left standing at 20°C for 1 hr. The reaction mixture was neutralized with 2N HCl–MeOH and evaporated, it was partitioned into *n*-hexane–MeOH (3 : 2) mixture. The *n*-hexane phase containing a mixture of the fatty acid methyl esters was concentrated to 1 ml under reduced pressure and subjected to GC-MS analysis for identification [column PB × 5, 30M × 0.022 mm; programmed temperature gas chromatography(33°C,0.6 min; 6°C/min;250°C,20 min); carrier gas, N_2 at a flow rate of 12 ml/min]. The t_R (min) = a 27.00, b 28.87, c 30.38, d 30.87, e 33.63, f 33.75, g 34.08, h 37.21; a: b: c: d: e: f: g: h = 17 : 1.5 : 19 : 153 : 1 : 19 : 1 : 2 (see Fig. 1).

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