Sarcoglycosides A – C, New *O*-Glycosylglycerol Derivatives from the South China Sea Soft Coral *Sarcophyton infundibuliforme*

by **Liang Li**[a]), **Chang-Yun Wang***[a]), **Chang-Lun Shao**[a]), **Yue-Wei Guo**[b]), **Guo-Qiang Li**[a]), **Xue-Ping Sun**[a]), **Lei Han**[a]), **Hui Huang**[c]), and **Hua-Shi Guan**[a])

[a]) School of Medicine and Pharmacy, Ocean University of China, Key Laboratory of Marine Drugs, Ministry of Education, Qingdao 266003, P. R. China (phone: +86-532-82031503; e-mail: changyun@ouc.edu.cn)

[b]) State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, P. R. China

[c]) South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510000, P. R. China

Chemical examination of the soft coral *Sarcophyton infundibuliforme* collected from the South China Sea resulted in the isolation of the three new *O*-glycosylglycerol derivatives sarcoglycosides A – C (**1** – **3**), together with two known compounds, chimyl alcohol (**4**) and hexadecanol (**5**). Their structures were elucidated by combined spectral and chemical methods. All the compounds showed moderate toxicity to brine shrimps *Artemia salina*.

Introduction. – Soft corals are Coelenterates (class Anthozoa, subclass Octocorallia, order Alcyonacea, family Alcyoniidae) [1]. *Sarcophyton*, one of the most widely distributed genus of soft corals, elaborates a rich harvest of secondary metabolites including sesquiterpenes, diterpenes, and polyhydroxylated steroids [2].

O-Glycosylglycerol derivatives are rare in soft corals. Only few glycoglyceryl ethers have been reported from the genus of *Sarcophyton* [3], *Sinularia* [4][5], and *Cladiella* [6], all of them possessing a batyl alcohol (= 3-(octadecyloxy)propane-1,2-diol) moiety. As part of an effort to discover bioactive substances from Chinese marine invertebrates [7], we now found that the 95% EtOH extract of the soft coral *Sarcophyton infundibuliforme* from the South China Sea showed lethal activity toward brine shrimps *Artemia salina*. Bioassay-guided isolation of the extracts led to the identification of three new *O*-glycosylglycerol derivatives, designated as sarcoglycosides A – C (**1** – **3**), together with two known compounds, chimyl alcohol (= 3-(hexadecyloxy)propane-1,2-diol; **4**) and hexadecanol (**5**). The present work deals with the isolation and structure elucidation of the new compounds.

Results and Discussion. – Freshly collected specimens of *S. infundibuliforme* were immediately chilled to $-20°$ and kept frozen until their extraction with 95% EtOH. The EtOH extract was partitioned between AcOEt and H_2O, then between BuOH and H_2O. The BuOH-soluble portion was subjected to column chromatography (CC; silica gel). The fraction showing a strong lethal activity toward brine shrimps *A. salina* was further separated by CC (*Sephadex LH-20*) and reversed-phase CC (silica gel (*ODS*))

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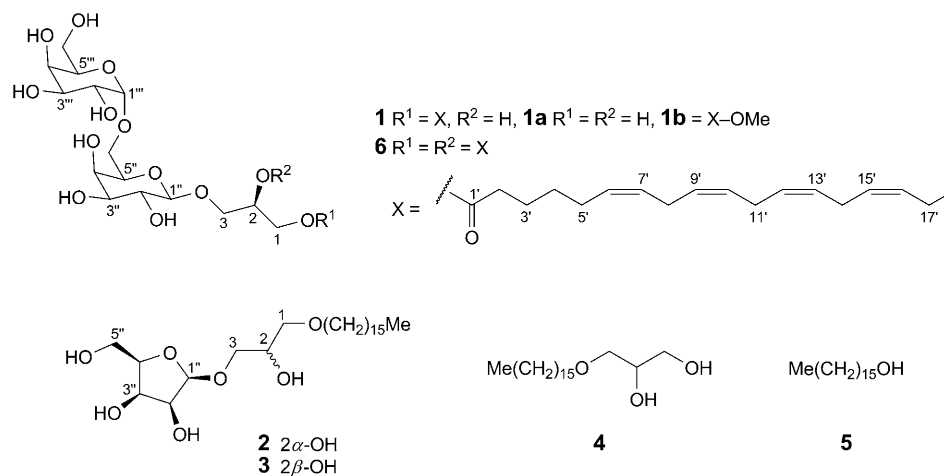

into sarcoglycosides A–C (**1**–**3**). The AcOEt-soluble portion was fractionated by similar procedures into chimyl alcohol (**4**) [8][9] and hexadecanol (**5**) [10].

Sarcoglycoside A (**1**) is a white amorphous powder. The molecular formula, $C_{33}H_{54}O_{14}$, indicating seven degrees of unsaturation, was established by positive-mode HR-ESI-MS (*m/z* 697.3413 ($[M+Na]^+$)). The NMR spectra of **1** revealed two anomeric CH groups (δ(C) 100.0 and δ(H) 4.67 (*d*, $J=4.1$), and δ(C) 104.6 and δ(H) 4.09 (*d*, $J=6.5$)), together with nine CH–O and four CH_2O groups (δ(C) 61.1–73.7 and δ(H) 3.27–4.04), suggesting the presence of two sugar residues and one glycerol unit. Furthermore, the ^{1}H- and ^{13}C-NMR spectra of **1** showed signals attributable to an acyl group (δ(C) 173.4), four disubstituted C=C bonds (δ(C) 127.5–132.1 (*d*, 8 C) and δ(H) 5.30–5.40 (*m*, 8 H)), and a terminal Me group (δ(C) 14.7 and δ(H) 0.92 (*t*, $J=$ 7.2)), which formed a long-chain unsaturated fatty acid ester moiety. Extensive interpretation of 2D-NMR spectra (^{1}H,^{1}H-COSY, HMQC, and HMBC) led to the complete assignments of the ^{1}H- and ^{13}C-NMR data of the sugar and the glycerol moieties (*Table 1*). Furthermore, significant HMBCs (*Fig. 1*) between $CH_2(1)$ and C(1′) indicated that the long-chain unsaturated fatty acyl moiety was linked to C(1).

The above-mentioned structural features of **1** were strongly reminiscent of those of *O*-(galactosylgalactosyl)di-*O*-acylglycerol [11], previously isolated from the cultured marine dinoflagellate *Amphidinium carterae*. In fact, **1** differs from **6** only by the functionality at C(2) which lacks a long-chain unsaturated fatty acyloxy substituent. The loss of the fatty acyl group shifted the signal of H–C(2) significantly upfield from δ(H) 5.30 to 3.49–3.54. Thus, compound **1** was identified as an *O*-(galactosylgalactosyl)-*O*-acylglycerol.

To confirm the absolute configuration, compound **1** was treated with MeONa/MeOH according to a reported method [11][12], yielding an *O*-(galactosylgalactosyl)glycerol **1a** and a fatty acid methyl ester **1b**. Product **1a** ($[\alpha]_D^{25}=+81.0$ ($c=0.36$, H_2O)) was identical with the previously reported (2*R*)-3-*O*-(6-*O*-α-D-galactopyranosyl-β-D-galactopyranosyl)glycerol (=(2*R*)-2,3-dihydroxypropyl 6-*O*-α-D-galactopyranosyl-β-D-galactopyranoside) on the basis of a comparison of the optical rotation

Table 1. *^{1}H- and ^{13}C-NMR Data*[a])[b]) *of the Glycerol and Sugar Moieties of* **1**. δ in ppm, J in Hz.

	δ(H)	δ(C)[c])	HMBC
CH_2(1)	4.04 (*dd*, J = 11.1, 4.0, H_a),	66.1 (*t*)	C(1′), C(3)
	3.97 (*dd*, J = 11.1, 6.2, H_b)		C(1′), C(3)
H−C(2)	3.49–3.54 (*m*)	68.0 (*d*)	
HO−C(2)	4.54 (*d*, J = 5.3)		C(1)
CH_2(3)	3.59–3.64 (*m*, H_a),	71.0 (*t*)	C(1″), C(1)
	3.50–3.56 (*m*, H_b)		C(1″), C(1)
β-D-Gal:			
H−C(1″)	4.09 (*d*, J = 6.5)	104.6 (*d*)	C(3), C(3″)
H−C(2″)	3.58–3.62 (*m*)	71.8 (*d*)	C(4″)
HO−C(2″)	4.50 (*d*, J = 4.1)		C(1″), C(3″)
H−C(3″)	3.27–3.32 (*m*)	73.7 (*d*)	C(1″), C(5″)
HO−C(3″)	4.75 (br. *s*)		
H−C(4″)	3.79–3.83 (*m*)	68.6 (*d*)	C(2″), C(6″)
HO−C(4″)	4.98 (*d*, J = 5.6)		C(5″)
H−C(5″)	3.52–3.57 (*m*)	73.5 (*d*)	C(3″)
CH_2(6″)	3.56–3.61 (*m*, H_a),	67.1 (*t*)	C(4″)
	3.52–3.56 (*m*, H_b)		C(4″)
α-D-Gal:			
H−C(1‴)	4.67 (*d*, J = 4.1)	100.0 (*d*)	C(6″), C(3‴)
H−C(2‴)	3.63–3.67 (*m*)	69.0 (*d*)	C(4‴)
HO−C(2‴)	4.39 (*d*, J = 5.5)		C(1‴)
H−C(3‴)	3.52–3.56 (*m*)	70.1 (*d*)	C(1‴), C(5‴)
HO−C(3‴)	4.90 (br. *s*)		
H−C(4‴)	3.66–3.71 (*m*)	69.4 (*d*)	C(2‴), C(6‴)
HO−C(4‴)	4.38 (br. *s*)		C(5‴)
H−C(5‴)	3.58–3.62 (*m*)	71.1 (*d*)	C(1‴), C(3‴)
CH_2(6‴)	3.48–3.53 (*m*, H_a),	61.1 (*t*)	C(4‴), C(5‴)
	3.40–3.45 (*m*, H_b)		C(4‴)
HO−C(6‴)	4.59 (*d*, J = 6.0)		C(5‴)

[a]) In (D_6)DMSO, referred to the residual DMSO (δ(H) 2.50, δ(C) 39.5); at 600 (^{1}H) and 150 MHz (^{13}C); for the NMR data of the acyl residue, see *Exper. Part.* [b]) Assignments by ^{1}H,^{1}H-COSY, HMQC, and HMBC experiments. [c]) By DEPT sequence.

($[\alpha]^{25}_D = +83.0$ ($c = 0.50$, H_2O)) and NMR data [11–13]. And **1b** was determined as methyl octadeca-6,9,12,15-tetraenoate by GC/MS analysis. Consequently, the whole structure of sarcoglycoside A was identified as shown in formula **1**.

Sarcoglycoside B (**2**) was obtained as a white amorphous powder, and had the molecular formula $C_{24}H_{48}O_7$, as deduced from its HR-ESI-MS exhibiting a *pseudo*-molecular-ion peak at m/z 471.3307 ($[M + Na]^+$). Its ESI-MS exhibited a fragment-ion peak at m/z 317 ($[M + H - 132]^+$) corresponding to the loss of one pentosyl moiety. Analysis of the spectroscopic data of **2** (*Table 2*) revealed that it was a glycoglyceryl ether. Thus, the ^{1}H- and ^{13}C-NMR spectra of **2** displayed characteristic signals assignable to a terminal β-D-lyxose moiety at δ(C) 100.0 (*d*), 70.5 (*d*), 68.8 (*d*), 80.3 (*d*), and 63.3 (*t*), and δ(H) 5.05 (*d*, J = 2.2, H−C(1″)), 3.82–3.87 (*m*, H−C(2″)), 4.01 (br. *s*, H−C(3″)), 3.85–3.89 (*m*, H−C(4″)), 3.95 (br. *d*, J = 11.9, H_b−C(5″)), and 3.79 (br. *d*,

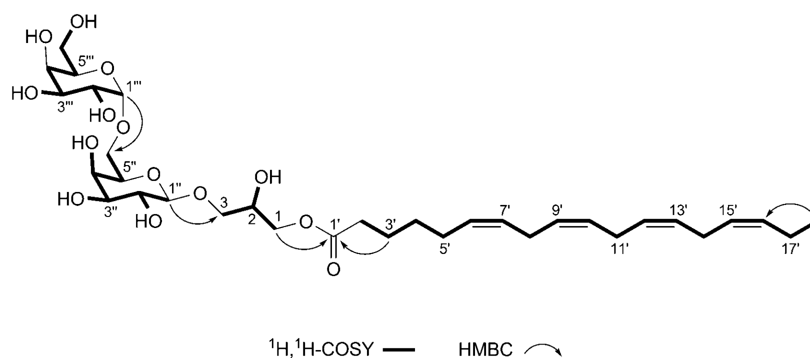

Fig. 1. *Selected ¹H,¹H-COSY correlations and HMBCs of compound* **1**

$J = 11.9$ Hz, $H_a-C(5'')$) [14] and a glycerol moiety at δ(C) 70.2 (*t*), 69.8 (*d*), and 63.6 (*t*), and δ(H) 3.52 (*d*, $J = 5.4$, $CH_2(1)$), 3.83–3.87 (*m*, H–C(2)), 3.67 (*dd*, $J = 11.4$, 3.5, $H_a-C(3)$), and 3.63 (*dd*, $J = 11.4$, 6.0, $H_b-C(3)$) [3]. Furthermore, the ¹H-NMR spectrum of **2** showed a terminal-Me signal at δ 0.87 (*t*, $J = 6.9$, Me(16′)), a broad CH_2 *s* at δ 1.26 (26 H, $CH_2(3')$ to $CH_2(15')$), a *m* at δ 1.52–1.58 ($CH_2(2')$), and another *m* at δ 3.40–3.46 ($CH_2(1')$), all asignable to the long-chain fatty alcohol moiety.

The structure of **2** was established by detailed analysis of the 1D- and 2D-NMR (¹H,¹H-COSY, HMQC, and HMBC) spectra (*Table 2*, *Fig. 2*). In particular, the location of the long-chain fatty alcohol moiety at C(1) and the β-D-lyxose moiety at C(3) was secured by the ¹H,¹³C-long-range correlations observed in the HMBC spectrum between $CH_2(1')$ and C(1), and between H–C(1″) and C(3), respectively. The NOESY correlations H–C(1″)/H–C(2″), H–C(2″)/H–C(3″), and H–C(3″)/H–C(4″) suggested that all these H-atoms are orientated on the same face (α) of the molecule (*Fig. 3*), confirming the identity of a lyxose unit. Furthermore, the β-orientation of H–C(2) was also supported by two clear NOE cross-peaks between H–C(2) and $CH_2(5'')$ in the NOESY plot (*Fig. 3*).

The absolute configuration of **2** was determined after acid hydrolysis [3]. From the reaction of **2** with 2M H_2SO_4, 3-*O*-hexadecyl-*sn*-glycerol and D-lyxose were obtained. The configuration of 3-*O*-hexadecyl-*sn*-glycerol was determined as (*R*) by comparison of its optical rotation ($[\alpha]_D^{25} = +1.2$ ($c = 0.24$, THF)) with those of authentic samples, *i.e.*, *O*-3-hexadecyl-*sn*-glycerol ($[\alpha]_D^{20} = +2.7$, THF)) and 1-*O*-hexadecyl-*sn*-glycerol ($[\alpha]_D^{20} = -2.7$, THF)) [15]. Thus, the configuration of C(2) in sarcoglycoside B was deduced as (*S*). In addition, the configuration of the obtained lyxose was determined as D by comparison of its optical rotation ($[\alpha]_D^{25} = -12.4$ ($c = 0.11$, H_2O)) with those of authentic samples, *i.e.*, D-lyxose ($[\alpha]_D^{20} = -14.8$, H_2O) and L-lyxose ($[\alpha]_D^{20} = +13.5$, H_2O) [16]. The D-lyxose was further confirmed by a co-TLC with an authentic sample (PrOH/H_2O/ammonia 60:30:2.4, R_f 0.55).

Sarcoglycoside C (**3**) was also obtained as a white amorphous powder. Its molecular formula was deduced to be $C_{24}H_{48}O_7$, identical to that of **2**. ¹H,¹H-COSY and HMBC (*Table 2*, *Fig. 2*) experiments established the same H-atom sequence and framework as

Table 2. *[1]H- (600 MHz) and ^{13}C- (150 MHz) NMR Data*[a])[b]) *of* **2** *and* **3**. δ in ppm, *J* in Hz.

	2		**3**	
	δ(H)	δ(C)[c])	δ(H)	δ(C)[c])
CH_2(1)	3.52 (*d*, *J* = 5.4)	70.2 (*t*)	3.53 (*d*, *J* = 5.6)	69.9 (*t*)
H–C(2)	3.83–3.87 (*m*)	69.8 (*d*)	3.82–3.86 (*m*)	69.5 (*d*)
CH_2(3)	3.67 (*dd*, *J* = 11.4, 3.5, H_a), 3.63 (*dd*, *J* = 11.4, 6.0, H_b)	63.6 (*t*)	3.65–3.70 (*m*), 3.63–3.67 (*m*)	63.3 (*t*)
CH_2(1′)	3.40–3.46 (*m*)	71.9 (*t*)	3.40–3.46 (*m*)	71.8 (*t*)
CH_2(2′)	1.52–1.58 (*m*)	29.5 (*t*)	1.52–1.58 (*m*)	29.5 (*t*)
CH_2(3′)	1.26 (br. *s*)	32.0 (*t*)	1.26 (br. *s*)	31.9 (*t*)
CH_2(4′) to CH_2(13′)	1.26 (br. *s*)	29.0–30.0 (*t*)	1.26 (br. *s*)	29.0–30.0 (*t*)
CH_2(14′)	1.26 (br. *s*)	26.1 (*t*)	1.26 (br. *s*)	26.0 (*t*)
CH_2(15′)	1.26 (br. *s*)	22.8 (*t*)	1.26 (br. *s*)	22.7 (*t*)
Me(16′)	0.87 (*t*, *J* = 6.9)	14.2 (*q*)	0.87 (*t*, *J* = 6.9)	14.1 (*q*)
β-D-Lyx:				
H–C(1″)	5.05 (*d*, *J* = 2.2)	100.0 (*d*)	5.06 (*d*, *J* = 2.3)	99.2 (*d*)
H–C(2″)	3.82–3.87 (*m*)	70.5 (*d*)	3.85–3.91 (*m*)	70.2 (*d*)
H–C(3″)	4.01 (br. *s*)	68.8 (*d*)	4.00 (br. *s*)	68.9 (*d*)
H–C(4″)	3.85–3.89 (*m*)	80.3 (*d*)	3.83–3.89 (*m*)	79.0 (*d*)
CH_2(5″)	3.79 (br. *d*, *J* = 11.9, H_a), 3.95 (br. *d*, *J* = 11.9, H_b)	63.3 (*t*)	3.75 (br. *d*, *J* = 11.9), 3.94 (br. *d*, *J* = 11.9)	63.2 (*t*)

[a]) In $CDCl_3$, referred to the residual $CHCl_3$ (δ(H) 7.26, δ(C) 77.0). [b]) Assignments by ^{1}H,^{1}H-COSY, HMQC, and HMBC experiments. [c]) By DEPT sequence.

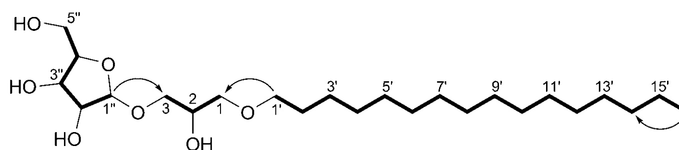

Fig. 2. *^{1}H,^{1}H-COSY correlations and key HMBCs of compounds* **2** *and* **3**

those of **2**. Careful comparison of the ^{1}H-NMR data of **3** and **2** revealed differences at C(3) and the sugar moiety. The CH_2(3) signals of **2** were splitted into two *dd* with distinct coupling constants, $J(H_a,2) = 3.5$ Hz and $J(H_b,2) = 6.0$ Hz, respectively (*Table 2*). The CH_2(3) signals of **3**, however, were splitted into two *m*, of which the coupling constants were unidentified. The δ(H) values of CH_2(5″) of the lyxose moiety were particularly diagnostic: δ 3.75 and 3.94 for **3**, and δ 3.79 and 3.95 for **2** due to the spatial interaction with H–C(2). These differences suggested the inversion of the configuration at C(2). α-Orientation of H–C(2) in **3** was further confirmed by the NOESY experiment (*Fig. 3*), where no cross-peaks H–C(2)/CH_2(5″) were observed. Furthermore, following the same method as for **2**, 1-*O*-hexadecyl-*sn*-glycerol and D-lyxose were obtained from **3** with 2M H_2SO_4. The 1-*O*-hexadecyl-*sn*-glycerol from **3** ($[\alpha]^{25}_{D} = -1.3$ ($c = 0.20$, THF)) differed from the corresponding *O*-hexadecylglycerol

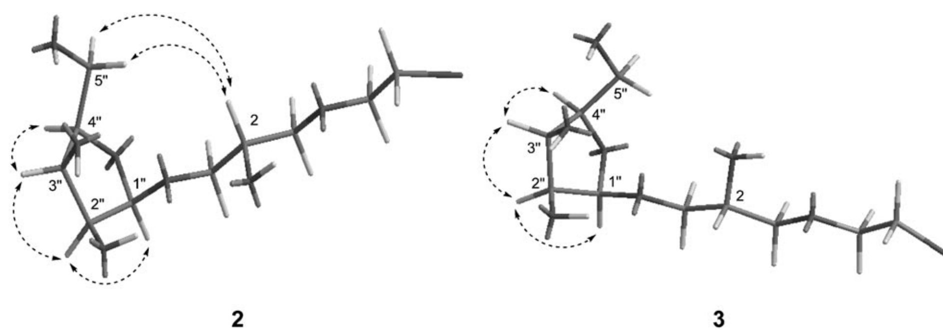

Fig. 3. *Key NOESY correlations of compounds* **2** *and* **3**

from **2** only by the sign of the optical rotation. This confirmed that the configuration at C(2) of **3** was (*R*). Thus, sarcoglycoside C was the 2-epimer of sarcoglycoside B.

Compounds **1**–**3** showed lethality to brine shrimps *A. salina* at a concentration of 50 µg/ml with lethal rates of 78.4, 44.7, and 41.5%, respectively. And the two known compounds, chimyl alcohol (**4**) and hexadecanol (**5**), also exhibited moderate lethal activities toward *A. salina*, with lethal rates of 58.9 and 32.5%, respectively.

It may be worthy to point out that sarcoglycoside A (**1**) is the first glycoglycerolipid isolated from soft corals. Sarcoglycosides B (**2**) and C (**3**), two glycoglyceryl ethers consisting of a lyxose residue and a chimyl alcohol moiety, are the first example of the co-occurrence of both C(2) epimers of a naturally occurring *O*-glycosylglycerol derivative. In addition, *O*-glycosylglycerol derivatives with lyxose residues are rare in marine materials; to the best of our knowledge, there has been only one analogue isolated before from the same genus of *Sarcophyton* (*S. solidum* [3]). These characters showed that there might be chemotaxonomic relationships between the two species. Furthermore, compounds **2**–**5** containing the same hexadecanol moiety, suggest that they are probably biogenetically related to each other. The evaluation of their physiological functions in soft coral *S. infundibuliforme* as well as the exploration of their chemoecological roles in the coral-reef ecosystem would be interesting subjects for future investigations.

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Experimental Part

General. Column chromatography (CC): commercial silica gel (SiO_2, 200–300 mesh; *Qingdao Haiyang Chemical Group Co.*), octadecylsilyl (ODS) silica gel (*Unicorn*; 45–60 µm), and *Sephadex LH-20* (*Amersham Biosciences*). TLC: precoated SiO_2 plates (*Yantai Zifu Chemical Group Co.*; *G60*, F_{254}).

Optical rotation: *Jasco-P-1020* digital polarimeter. IR Spectra: *Nicolet-Nexus-470* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Jeol-Eclips-600* spectrometer; at 600 (^{1}H) and 150 MHz (^{13}C); δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. ESI- and HR-ESI-MS: *Q-TOF-Ultima-Global-GAA076* LC mass spectrometer; in *m/z*. GC/MS System: *Agilent-6890* gas chromatograph and *Agilent-5973* mass-selective detector in the EI mode.

Animal Material. Specimen of the soft coral *S. infundibuliforme* were collected from the Wenchang coral reef at a depth of −10 m in the South China Sea, in November 2006 and were frozen immediately after collection. The animal was identified by *H. H.* of the South China Sea Institute of Oceanology, Chinese Academy of Sciences. A voucher sample (No. WCLL-1–4) is available for inspection at the Ocean University of China.

Extraction and Isolation. The frozen specimen (460.0 g, dry weight) were cut into pieces and extracted exhaustively with 95% EtOH (3 × 1000 ml) at r.t. The EtOH extract was evaporated to give a residue (18.0 g) which was partitioned between AcOEt (3 × 600 ml) and H_2O (300 ml), and then between BuOH (3 × 400 ml) and H_2O (300 ml), successively. The BuOH soln. was concentrated to give a dark green residue (4.8 g) which was fractionated by CC (SiO_2, 0 → 100% MeOH/$CHCl_3$): *Fractions A–D*. The bioactive *Fr. D* (270.0 mg) was purified by CC (*Sephadex LH-20*, $CHCl_3$/MeOH 1:1) followed by reversed-phase CC (SiO_2 (*ODS*)): **1** (12.0 mg), **2** (6.4 mg), and **3** (10.0 mg). The AcOEt-soluble portion (7.0 g) was separated by CC (SiO_2, 0 → 100% AcOEt/petroleum ether): *Frs. 1–10* (by TLC). *Fr. 7* (268 mg) was subjected to CC (*Sephadex LH-20*, $CHCl_3$) and further purified by CC (SiO_2, petroleum ether/acetone 6:1 → 7:3): **4** (38.5 mg) and **5** (160.0 mg).

Sarcoglycoside A (= *(6Z,9Z,12Z,15Z)-Octadeca-6,9,12,15-tetraenoic Acid (2R)-3-[(6-O-α-galactopyranosyl-β-D-galactopyranosyl)oxy]-2-hydroxypropyl Ester*; **1**): White amorphous powder. $[\alpha]_D^{22}$ = +20.8 (*c* = 0.30, MeOH). IR (KBr): 3350, 2926, 1739, 1693, 1534, 1076, 1023, 678. ^{1}H-NMR ((D_6)DMSO): 5.30–5.40 (*m*, H−C(6′), H−C(7′), H−C(9′), H−C(10′), H−C(12′), H−C(13′), H−C(15′), H−C(16′)); 2.75–2.80 (*m*, 2 H−C(8′), 2 H−C(11′), 2 H−C(14′)); 2.31 (*t*, *J* = 7.0, 2 H−C(2′)); 2.01–2.06 (*m*, 2 H−C(5′), 2 H−C(17′)); 1.50–1.55 (*m*, 2 H−C(3′)); 1.31–1.34 (*m*, 2 H−C(4′)); 0.92 (*t*, *J* = 7.2, Me(18′)). ^{13}C-NMR ((D_6)DMSO): 173.4 (*s*, C(1′)); 132.1 (*d*, C(16′)); 130.2, 130.1, 128.7, 128.6, 128.5, 128.4 (6*d*, C(6′), C(7′), C(9′), C(10′), C(12′), C(13′)); 127.5 (*d*, C(15′)); 33.9 (*t*, C(2′)); 29.6 (*t*, C(4′)); 29.0 (*t*, C(5′)); 27.0, 25.8, 25.7 (3*t*, C(8′), C(11′), C(14′)); 24.6 (*t*, C(3′)); 20.6 (*t*, C(17′)); 14.7 (*q*, C(18′)). ^{1}H- and ^{13}C-NMR: *Table 1*. ESI-MS: 697 ([*M* + Na]$^+$). HR-ESI-MS: 697.3413 ([*M* + Na]$^+$, $C_{33}H_{54}NaO_{14}^+$; calc. 697.3411).

Sarcoglycoside B (= *(2S)-3-(Hexadecyloxy)-2-hydroxypropyl β-D-Lyxofuranoside*; **2**): White amorphous powder. $[\alpha]_D^{25}$ = −41.2 (*c* = 0.50, $CHCl_3$). IR (KBr): 3393, 2920, 2851, 1467, 1143, 1073, 1005. ^{1}H- and ^{13}C-NMR: *Table 2*. ESI-MS: 919 ([2*M* + Na]$^+$), 471 ([*M* + Na]$^+$), 449 ([*M* + H]$^+$), 317, 299. HR-ESI-MS: 471.3307 ([*M* + Na]$^+$, $C_{24}H_{48}NaO_7^+$; calc. 471.3298).

Sarcoglycoside C (= *(2R)-3-(Hexadecyloxy)-2-hydroxypropyl β-D-Lyxofuranoside*; **3**): White amorphous powder. $[\alpha]_D^{25}$ = −58.5 (*c* = 0.50, $CHCl_3$). IR (KBr): 3393, 2920, 2851, 1467, 1143, 1073, 1005. ^{1}H- and ^{13}C-NMR: *Table 2*. ESI-MS: 471 ([*M* + Na]$^+$), 449 ([*M* + H]$^+$), 317. HR-ESI-MS: 471.3280 ([*M* + Na]$^+$, $C_{24}H_{48}NaO_7^+$; calc. 471.3298).

Methanolysis of **1**. A soln. of **1** (7.5 mg) in anh. MeOH (1.5 ml) was treated with 3% MeONa/MeOH (1.5 ml), and the mixture was stirred at r.t. for 1.5 h. The mixture was neutralized with positive-ion-exchange resin and filtered, and the filtrate partitioned between CH_2Cl_2 and H_2O. Evaporation of the solvent from the CH_2Cl_2 phase yielded fatty acid methyl ester **1b** (2.3 mg), which was identified by GC/MS to be *methyl octadeca-6,9,12,15-tetraenoate*. The aq. phase was concentrated to give a residue, which was purified by CC (*Sephadex LH-20*): *(2R)-2,3-dihydroxypropyl 6-O-α-D-galactopyranosyl-β-D-galactopyranoside* (**1**; 3.6 mg).

Acid Hydrolysis of **2** *and* **3**. A soln. of **2** (6 mg) in MeOH (1 ml) was added to 2M H_2SO_4 (1 ml) and kept for 4 h at 105° in a sealed ampule. The mixture was dried under N_2 to remove MeOH and then diluted with H_2O (3.5 ml) and extracted with CH_2Cl_2 (3 × 7 ml). The org. layer was washed with H_2O, dried (Na_2SO_4), and concentrated to give a white amorphous powder, which was identified as *3-O-hexadecyl-sn-glycerol* (= *(2R)-3-(hexadecyloxy)propane-1,2-diol*; 2.4 mg). The aq. phase was neutralized with $BaCO_3$, filtered, and concentrated to give a residue which was purified by CC (*Sephadex LH-20*, MeOH) to furnish D-lyxose (1.1 mg).

By the same hydrolysis procedure, compound **3** yielded *1*-O-*hexadecyl*-sn-*glycerol* (=*(2*S*)-3-(hexadecyloxy)propane-1,2-diol*; 2.0 mg) and D-lyxose (1.0 mg).

Bioassays. The brine-shrimp lethality assay was performed on *A. salina* according to standard protocols [17][18].

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