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Pentaporins A, B and C: disulfides from the marine bryozoan *Pentapora fascialis*

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Abstract—Three new disulfides, pentaporins A, B and C, with anthelmintic in vitro activity have been isolated from the mediterranean bryozoan *Pentapora fascialis*. The structures of these compounds were determined by 1D and 2D NMR spectroscopy, mass spectrometry and EDX-analysis. The pentaporins show activity against *Trichinella spiralis*. © 2002 Published by Elsevier Science Ltd.

1. Introduction

Recent studies have demonstrated that bryozoans are a rich and excellent source of novel and biologically active secondary metabolites.[1] The most well known of these compounds are the bryostatins,[2a–c] other examples include the flustramines,[3a,b] the securamines and securines,[4a,b] the tambjamines,[5a,b] the amathamides,[6a–c] the amathaspiramides,[7] the convolutamydines[8a,b] and the alternatamides.[9]

In the course of our screening program for anthelmintic active natural products, we found that the extract of the bryozoan *Pentapora fascialis* shows bioactivity against *Trichinella spiralis*. Bioassay-guided fractionation of the toluene phase and of the 2-butanol phase afforded three active substances, the pentaporins A, B and C. Now we report on their structures.

2. Results and discussion

The frozen red bryozoan *P. fascialis*, collected in the Mediterranean at depths of 35–45 m, was completely extracted and partitioned. Chromatography of the toluene phase and of the 2-butanol phase on Sephadex LH-20 yielded the pentaporins A (**1**), B (**2**) and C (**3**), respectively, as faint yellow oils.

The structures of **1**, **2** and **3** were determined by spectroscopic analysis. The high-resolution mass spectrum (HR-ESI) of the main compound pentaporin B (**2**) shows a molecular ion at m/z=321.09 $[M]^{3-}$, indicating the molecular formula $C_{42}H_{59}S_5O_{15}$.

The ^{1}H NMR spectrum of pentaporin B (**2**) displays the signals of two different 1,3,5-substituted benzyl moieties (δ 6.66–6.11). The chemical shift values in the ^{1}H and ^{13}C NMR spectra show that one is an 5-alkyl-1,3-benzenediole, the other one differs in position 1, which has a shift value of an ether. ^{1}H–^{1}H COSY and ^{1}H–^{1}H TOCSY experiments show a decyl side chain (δ 2.54–1.67) including two asymmetric centers (δ 2.93, 4.58), which are separated by a diasteretopic methylene group (δ 2.57). This carbon chain is connected to a *trans* diene system (δ 6.10–5.60; $^3J_{H,H}$=14.6 and 14.5 Hz) and a methyl group (δ 1.73). Integration of the ^{1}H NMR signals indicate that this carbon chain occur twice in comparison to the two 1,3,5-substituted benzene systems. Long-range couplings in the HMBC experiment suggest that each benzyl moiety is linked to one of these carbon chains. The presence of sulfur was proven by EDX (energy-dispersive X-ray) analysis. Taking into account the molecular formula and the chemical shift values, it is obvious that a sulfate group is attached to one of the benzyl moieties. Two other sulfate groups are connected to one of the carbon chains respectively. The two chains are linked by a disulfide bond to give the asymmetric dimeric structure of pentaporin B (**2**).

Pentaporin A (**1**) and C (**3**) are symmetric dimers, the three compounds differ in the number of sulfate ester groups.

Acetylation of pentaporin B (**2**) with acetic anhydride in pyridine yielded the triacetate **4**, methylation of **2** with methyl iodide and potassium carbonate in

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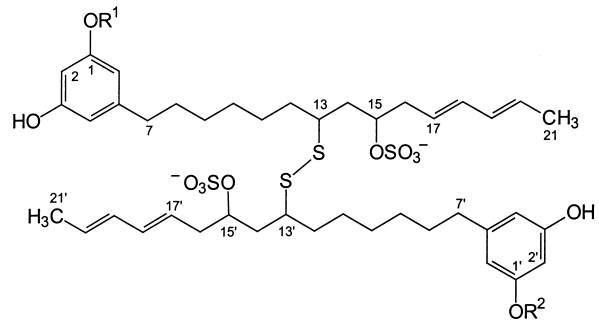
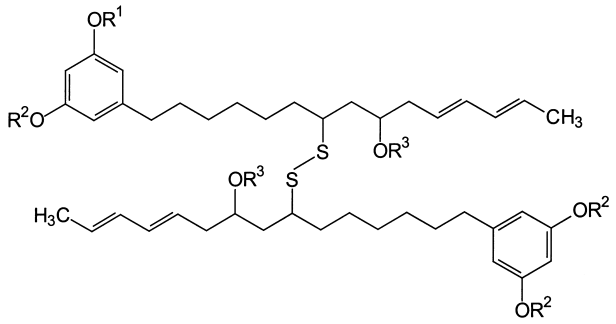


1 R^1 = H, R^2 = H
2 R^1 = SO_3^-, R^2 = H
3 R^1 = SO_3^-, R^2 = SO_3^-



4 R^1 = SO_3^-, R^2 = Ac; R^3 = SO_3^-
5 R^1 = SO_3^-, R^2 = Me; R^3 = SO_3^-
6 R^1 = H, R^2 = H, R^3 = H

dimethylformamide gave the trimethyl ether **5** and solvolysis of **2** with pyridine–dioxane (1:1, v/v) gave **6**.

The derivative **6** does not show activity against *T. spiralis* any more. So it can be assumed that the sulfate ester groups are responsible for the anthelmintic activity of the pentaporins **1**, **2** and **3**.

To determine the absolute configuration at position C-13 and C-15 vibrational circular dichroism (VCD) spectroscopy was carried out with pentaporin B (**2**). This compound is not VCD-active because of its conformative flexibility.

Other known marine disulfides are the polycarpamines[10] and polycarpine[11a,b] from some species of the tunicate *Polycarpa*, nereistoxin[12] and metabolites from the algae *Dictyopteris*.[13] Similar aliphatic sulfates have been isolated from the marine sponge *Toxadocia cylindrica*. The tetrasulfates toxadocials A, B and C and toxadocic acid A show thrombin inhibitory activity.[14]

The panosialins wA~wD from *Streptomyces* sp. OH-5186 are compounds with a similar substituted benzene system, which inhibit several glycosidases.[15]

Examples for sulfur-containing metabolites from bryozoans are the perfragilins,[16a,b] the (2-hydroxyethyl)dimethylsulfoxonium ion from *Alcyonidium gelatinosum*[17] and the euthyroideones.[18]

3. Experimental

3.1. General

NMR: Bruker AMX2-600 (600.13 MHz for ^{1}H and 150.9 MHz for ^{13}C; chemical shifts are given relative to the residual solvent signal CD_3OD: δ_H=3.35, δ_C=49.0). HR-ESI MS: Finnigan MAT 95Q (250°C, 2.5 kV). IR: Perkin–Elmer Spectrum 1000. UV/Vis: Perkin–Elmer Lambda 16 Spectrometer. Optical rotations: Perkin–Elmer 241. CD: Instruments S. A. Jobin Yvon CD-6-Dichrograph. Analytical TLC: aluminium sheets silica gel 60 F_{254} (Merck), 0.2 mm, 1-butanol/acetic acid/water 5:1:4 (v/v/v) and benzene/ethyl formate/formic acid 10:5:3 (v/v/v). CC: Sephadex LH-20 (Pharmacia); eluent: methanol and methanol/chloroform 1:1 (v/v). EDX (energy-dispersive X-ray) analysis: Field-emission scanning electron microscope (FESEM): Hitachi S-4100; EDX analysis system: Vantage, Noran Instruments (acceleration voltage 15 kV). A small amount of the pentaporins A, B and C, each dissolved in methanol was put on Melinex® foil (DuPont), dried and the foil was mounted on aluminium stubs.

3.1.1. Extraction and isolation of pentaporins A (1), B (2) and C (3). The wet biomass (485 g) of the frozen bryozoan, collected from the Mediterranean at depths of 35–45 m in July 1999, was completely extracted with methanol/chloroform 1:1 (v/v) in a blender at room temperature, and the solvent was removed by evaporation. The crude extract (25 g, oil) was partitioned first between water and toluene. The water layers were combined, the solvent was evaporated, and the residue was dissolved again in water and extracted with 2-butanol. Chromatography of the toluene phase (1.56 g) on Sephadex LH-20 with methanol/chloroform 1:1 (v/v) (80 cm×6 cm, i.d.) yielded three faint yellow fractions, which gave on evaporation pentaporin A (**1**) (23 mg, 0.0474‰), pentaporin B (**2**) (62 mg, 0.1278‰) and pentaporin C (**3**) (1 mg, 0.0021‰) respectively as a yellow oil. Chromatography of the 2-butanol phase (229 mg) on Sephadex LH-20 with methanol (43 cm×3 cm, i.d.) yielded pentaporin A (**1**) (7 mg, 0.0144‰), pentaporin B (**2**) (24 mg, 0.0495‰) and pentaporin C (**3**) (6 mg, 0.0124‰).

3.1.2. Pentaporin A (1). $[\alpha]_D^{25}$=−13.1 (*c* 0.0065, MeOH). TLC (1-butanol/acetic acid/water 5:1:4 (v/v/v)): R_f=0.54. UV/Vis (MeOH): λ_{max} (log ε)=202 nm (7.95), 223 (7.77), 274 (6.59). CD (MeOH): λ_{max} ($\Delta\varepsilon$)=204 nm (−6.38), 217 (−4.16), 219 (−4.24), 232 (−3.06). ^{1}H NMR and ^{13}C NMR: see Table 1 (2′-H–21′-H and C-1′–C-21′). IR (KBr): $\tilde{\nu}$=3436 cm^{-1} (s, br), 2926 (s), 2853 (m), 1599 (s), 1454 (m), 1216 (s), 1150 (m), 1058 (m), 989 (m). ESI MS: *m*/*z*=907 $[M+Na]^-$, 885 $[M+H]^-$, 805 $[M+H-SO_3]^-$, 725 $[M+H-2SO_3]^-$, 442 $[M]^{2-}$. HR-ESI MS: *m*/*z*=442.1484 (442.1491 calcd for $C_{42}H_{60}S_4O_{12}$) $[M]^{2-}$.

3.1.3. Pentaporin B (2). $[\alpha]_D^{25}$=−13 (*c* 0.006, MeOH). TLC (1-butanol/acetic acid/water 5:1:4 (v/v/v)): R_f=0.27. UV/Vis (MeOH): λ_{max} (log ε)=202 nm (8.19), 224 (7.95), 271 (6.83). CD (MeOH): λ_{max} ($\Delta\varepsilon$)=203 nm (−1.71), 208 (−6.24), 219 (−2.92), 224 (−4.69), 234 (−1.25). ^{1}H NMR and ^{13}C NMR: see Table 1. IR (KBr): $\tilde{\nu}$=3436 cm^{-1} (s), 2929 (s), 2855 (m), 1628 (s), 1451 (m), 1331 (m), 1245 (s), 1154 (w), 1061 (m), 990 (m). ESI MS: *m*/*z*=965 $[M+2H]^-$,

Table 1. NMR data of pentaporin B (**2**) in CD_3OD

^1H	δ_H (ppm)	$J_{H,H}$ (Hz)	^{13}C	δ_C (ppm)
			C-1	158.9
			C-1′	159.2
2-H (1H)	6.66 (d)	2.3	C-2	107.0
2′-H (1H)	6.11 (t)	2.1	C-2′	101.0
			C-3	154.7
			C-3′	159.2
4-H (1H)	6.65 (d)	2.3	C-4	113.6
4′-H (1H)	6.19 (d)	2.1	C-4′	108.0
			C-5	146.1
			C-5′	146.4
6-H (1H)	6.50 (d)	2.3	C-6	113.0
6′-H (1H)	6.19 (d)	2.1	C-6′	108.0
7-H (2H)	2.54 (t)	7.8	C-7	36.9
7′-H (2H)	2.47 (t)	7.9	C-7′	37.0
8-H (2H), 8′-H (2H)	1.60 (m)		C-8	32.3
			C-8′	32.4
9-H (2H), 9′-H (2H)	1.37 (m)		C-9, C-9′	30.5
10-H (2H), 10′-H (2H)	1.37 (m)		C-10, C-10′	30.3
11-H (2H), 11′-H (2H)	1.45 (m)		C-11, C-11′	27.5
12-H (2H), 12′-H (2H)	1.76 (m)		C-12, C-12′	34.5
	1.67 (m)			
13-H (1H), 13′-H (1H)	2.93 (m)	8.0, 5.8	C-13, C-13′	49.9
14-H (2H), 14′-H (2H)	1.99 (ddd)	14.5, 7.9, 5.8	C-14, C-14′	40.2
	1.87 (ddd)	14.5, 8.0, 5.0		
15-H (1H), 15′-H (1H)	4.58 (m)	7.9, 5.0	C-15, C-15′	77.6
16-H (2H), 16′-H (2H)	2.57 (m)		C-16, C-16′	38.5
17-H (1H), 17′-H (1H)	5.60 (m)	14.5	C-17, C-17′	127.0
18-H (1H), 18′-H (1H)	6.10 (m)	14.5, 10.8	C-18, C-18′	135.0
19-H (1H), 19′-H (1H)	6.05 (m)	14.6, 10.8	C-19, C-19′	132.9
20-H (1H), 20′-H (1H)	5.61 (m)	14.6, 6.7	C-20, C-20′	128.6
21-H (3H), 21′-H (3H)	1.73 (d)	6.7	C-21, C-21′	18.2

885 $[M+2H-SO_3]^-$, 805 $[M+2H-2SO_3]^-$, 482 $[M+H]^{2-}$, 321 $[M]^{3-}$. HR-ESI MS: m/z=482.1267 (482.1268 calcd for $C_{42}H_{60}S_5O_{15}$) $[M+H]^{2-}$, 321.0862 (321.0819 calcd for $C_{42}H_{59}S_5O_{15}$) $[M]^{3-}$.

3.1.4. Pentaporin C (3). $[\alpha]_D^{25}=-11$ (c 0.0021, MeOH). TLC (1-butanol/acetic acid/water 5:1:4 (v/v/v)): R_f=0.06. UV/Vis (MeOH): λ_{max} (log ε)=202 nm (6.97), 222 (6.75), 272 (6.01). CD (MeOH): λ_{max} ($\Delta\varepsilon$)=203 nm (0), 206 (−5.42), 209 (−4.77), 220 (−8.37), 233 (−4.44). ^1H NMR and ^{13}C NMR: see Table 1 (2-H–21-H and C-1–C-21). IR (KBr): $\tilde{\nu}$=3435 cm^{-1} (s), 2929 (m), 2855 (m), 1623 (s), 1457 (m), 1244 (s), 1153 (w), 1057 (s), 991 (m). ESI MS: m/z=965 $[M+3H-SO_3]^-$, 885 $[M+3H-2SO_3]^-$, 522 $[M+2H]^{2-}$, 348 $[M+H]^{3-}$, 260 $[M]^{4-}$. HR-ESI MS: m/z= 522.1015 (522.1052 calcd for $C_{42}H_{60}S_6O_{18}$) $[M+2H]^{2-}$, 347.7466 (347.7342 calcd for $C_{42}H_{59}S_6O_{18}$) $[M+H]^{3-}$.

3.1.5. Acetylation of pentaporin B (2). Compound **2** (1 mg) was acetylated with an excess of acetic anhydride (1 ml) and 0.1 ml pyridine at room temperature for 20 min. The triacetate **4** was obtained after evaporation in quantitative yield. $[\alpha]_D^{25}=-14$ (c 0.002, MeOH). TLC (1-butanol/acetic acid/water 5:1:4 (v/v/v)): R_f=0.20. UV/Vis (MeOH): λ_{max} (log ε)= 222 nm (7.60), 228 (7.59), 265 (6.37). ^1H NMR (CD_3OD): δ=1.37 (m, 8 H, 9-H, 10-H, 9′-H, 10′-H), 1.46 (m, 4 H, 11-H, 11′-H), 1.60 (m, 4 H, 8-H, 8′-H), 1.67 (m, 2 H, 12-H_b, 12′-H_b), 1.74 (d, $^3J_{H,H}$=6.6 Hz, 6 H, 21-H, 21′-H), 1.76 (m, 2 H, 12-H_a, 12′-H_a), 1.87 (m, 2 H, 14-H_b, 14′-H_b), 1.99 (m, 2 H, 14-H_a, 14′-H_a), 2.28 (s, 3 H, 23-H), 2.29 (s, 6 H, 23′-H, 25′-H), 2.59 (m, 4 H, 16-H, 16′-H), 2.63 (t, $^3J_{H,H}$=7.9 Hz, 2 H, 7-H), 2.66 (t, $^3J_{H,H}$=7.7 Hz, 2 H, 7′-H), 2.94 (m, 2 H, 13-H, 13′-H), 4.58 (m, 2 H, 15-H, 15′-H), 5.60 (m, $^3J_{H,H}$=14.5 Hz, 2 H, 17-H, 17′-H), 5.61 (m, $^3J_{H,H}$=14.6 and 6.6 Hz, 2 H, 20-H, 20′-H), 6.05 (m, $^3J_{H,H}$=14.6 and 10.8 Hz, 2 H, 19-H, 19′-H), 6.10 (m, $^3J_{H,H}$=14.5 and 10.8 Hz, 2 H, 18-H, 18′-H), 6.76 (t, $^4J_{H,H}$=2.1 Hz, 1 H, 2′-H), 6.80 (t, $^4J_{H,H}$=1.7 Hz, 1 H, 4-H), 6.88 (d, $^4J_{H,H}$=2.1 Hz, 2 H, 4′-H, 6′-H), 6.95 (t, $^4J_{H,H}$=2.1 Hz, 1 H, 2-H), 7.05 (t, $^4J_{H,H}$=1.7 Hz, 1 H, 6-H). ^{13}C NMR (CD_3OD): δ=18.2 (C-21, C-21′), 21.0 (C-23, C-23′, C-25′), 27.6 (C-11′), 27.7 (C-11), 30.2 (C-10′), 30.3 (C-10), 30.5 (C-9, C-9′), 32.1 (C-8′), 32.3 (C-8), 34.5 (C-12′), 34.6 (C-12), 36.5 (C-7′), 36.8 (C-7), 38.5 (C-16), 38.6 (C-16′), 40.3 (C-14), 40.4 (C-14′), 49.7 (C-13, C-13′), 77.5 (C-15, C-15′), 113.3 (C-2), 113.9 (C-2′), 119.0 (C-4), 119.7 (C-6), 120.1 (C-4′, C-6′), 127.1 (C-17, C-17′), 128.5 (C-20, C-20′), 132.9 (C-18, C-18′), 134.9 (C-19, C-19′), 146.3 (C-5), 146.8 (C-5′), 152.3 (C-3), 152.5 (C-1′, C-3′), 154.4 (C-1), 170.9 (C-22′, C-24′), 171.0 (C-22). IR (KBr): $\tilde{\nu}$=3480 cm^{-1} (s, br), 3019 (m), 2930 (s), 2856 (m), 1767 (s), 1745 (m), 1620 (m), 1591 (m), 1450 (m), 1370 (m), 1224 (s), 1154 (w), 1125 (m), 1061 (s), 1022 (w), 990 (s). ESI MS: m/z=1129 $[M+H+K]^-$, 545 $[M+H]^{2-}$, 363 $[M]^{3-}$. HR-ESI MS: m/z=545.1403 (545.1427 calcd for $C_{48}H_{65}S_5O_{18}$) $[M+H]^{2-}$.

3.1.6. Methylation of pentaporin B (2). Compound **2** (3 mg) was dissolved in dimethylformamide (2 ml). Potassium carbonate (30 mg) and methyl iodide (30 μl) were added and the mixture was stirred at 35°C for 24 h. Excess K_2CO_3 was filtered off, the solvent was evaporated, and the residue was partitioned between H_2O-saturated 2-butanol and H_2O. The organic layer was evaporated to give the trimethyl ether **5** (1.8 mg, 58%). TLC (1-butanol/acetic acid/water 5:1:4 (v/v/v)): R_f=0.37. UV/Vis (MeOH): λ_{max} (log ε)=221 nm (8.16), 269 (7.02), 279 (6.98). ^1H NMR (CD_3OD): δ=1.37 (m, 8 H, 9-H, 10-H, 9′-H, 10′-H), 1.45 (m, 4 H, 11-H, 11′-H), 1.63 (m, 4 H, 8-H, 8′-H), 1.67 (m, 2 H, 12-H_b, 12′-H_b), 1.73 (d, $^3J_{H,H}$=6.7 Hz, 6 H, 21-H, 21′-H), 1.76 (m, 2 H, 12-H_a, 12′-H_a), 1.87 (m, 2 H, 14-H_b, 14′-H_b), 1.99 (m, 2 H, 14-H_a, 14′-H_a), 2.57 (m, 4 H, 7-H, 7′H), 2.58 (m, 4 H, 16-H, 16′H), 2.92 (m, 2 H, 13-H, 13′H), 3.78 (s, 6 H, 22′-H, 23′H), 3.80 (s, 3 H, 22-H), 4.58 (m, 2 H, 15-H, 15′-H), 5.60 (m, $^3J_{H,H}$=14.5 Hz, 2 H, 17-H, 17′-H), 5.61 (m, $^3J_{H,H}$=14.6 and 6.7 Hz, 2 H, 20-H, 20′-H), 6.05 (m, $^3J_{H,H}$=14.6 and 10.8 Hz, 2 H, 19-H, 19′-H), 6.10 (m, $^3J_{H,H}$=14.5 and 10.8 Hz, 2 H, 18-H, 18′-H), 6.31 (s, 1 H, 2′-H), 6.38 (s, 2 H, 4′-H, 6′-H), 6.61 (s, 1 H, 2-H), 6.76 (s, 1 H, 6-H), 6.77 (s, 1 H, 4-H). ^{13}C NMR (CD_3OD): δ=18.2 (C-21, C-21′), 27.5 (C-11, C-11′), 30.4 (C-10, C-10′), 30.8 (C-9, C-9′), 32.4 (C-8, C-8′), 34.5 (C-12, C-12′), 37.1 (C-7), 37.2 (C-7′), 38.5 (C-16, C-16′), 40.3 (C-14, C-14′), 49.7 (C-13, C-13′), 55.7 (C-22), 55.9 (C-22′, C-23′), 77.6 (C-15, C-15′), 98.6 (C-2′), 105.6 (C-4), 107.5 (C-4′, C-6′), 111.8 (C-2), 114.9 (C-6), 127.0 (C-17, C-17′), 128.6 (C-20, C-20′), 132.9 (C-19, C-19′), 135.0 (C-18, C-18′), 146.2 (C-5), 146.5 (C-5′), 154.8 (C-1), 161.4 (C-3), 162.2 (C-1′ C-3′). IR (KBr): $\tilde{\nu}$=3436 cm^{-1} (s, br), 2928 (s), 2854 (s), 1594 (s), 1463 (w), 1349 (m), 1244 (s), 1151 (m), 1056 (m), 990 (m). ESI MS: m/z=335 $[M]^{3-}$. HR-ESI MS: m/z=335.0997 (335.0976 calcd for $C_{45}H_{65}S_5O_{15}$) $[M]^{3-}$.

3.1.7. Solvolysis of pentaporin B (2). Compound **2** (5 mg) was heated at 110°C overnight in pyridine-dioxane (1:1)

(6 ml). Evaporation of solvent afforded a brown residue which was dissolved in MeOH, filtered off and the filtrate was purified by Sephadex LH-20 chromatography (22 cm×2 cm, i.d.) using MeOH to yield **6** (3 mg, 79%) as a dark yellow oil. $[\alpha]_D^{25}=-6.7$ (*c* 0.006, MeOH). TLC (benzene/ethyl formate/formic acid 10:5:3 (v/v/v)): R_f=0.29. UV/Vis (MeOH): λ_{max} (log ε)=203 nm (7.90), 224 (7.66), 275 (6.54). CD (MeOH): λ_{max} ($\Delta\varepsilon$)=204 nm (−0.20), 208 (−3.72), 213 (−1.27), 217 (−2.14), 231 (−0.11), 242 (−0.76). ^{1}H NMR (CD_3OD): δ=1.38 (m, 8 H, 9-H, 10-H), 1.47 (m, 4 H, 11-H), 1.61 (m, 4 H, 8-H), 1.65 (m, 2 H, 12-H_a), 1.69 (m, 2 H, 12-H_b), 1.74 (d, $^3J_{H,H}$=6.7 Hz, 6 H, 21-H), 1.74 (m, 2 H, 14-H_a), 1.79 (m, 2 H, 14-H_a), 2.27 (m, 4 H, 16-H), 2.48 (t, $^3J_{H,H}$=7.6 Hz, 4 H, 7-H), 2.87 (m, 2 H, 13-H), 3.82 (m, 2 H, 15-H), 5.61 (m, $^3J_{H,H}$=14.5 Hz, 2 H, 17-H), 5.62 (m, $^3J_{H,H}$=14.6 and 6.7 Hz, 2 H, 20-H), 6.07 (m, $^3J_{H,H}$=14.6 and 10.8 Hz, 2 H, 19-H), 6.07 (m, $^3J_{H,H}$=14.5 and 10.8 Hz, 2 H, 18-H), 6.12 (s, 2 H, 2-H), 6.17 (s, 4 H, 4-H, 6-H). ^{13}C NMR (CD_3OD): δ=18.2 (C-21), 27.5 (C-11), 30.2 (C-10), 30.5 (C-9), 32.3 (C-8), 34.7 (C-12), 37.0 (C-7), 41.7 (C-16), 42.8 (C-14), 49.6 (C-13), 69.8 (C-15), 101.0 (C-2), 108.0 (C-4, C-6), 128.2 (C-17), 128.3 (C-20), 132.9 (C-18), 134.4 (C-19), 146.3 (C-5), 159.3 (C-1, C-3). IR (KBr): $\tilde{\nu}$=3341 cm^{-1} (s, br), 2928 (s), 2854 (s), 1600 (s), 1451 (m), 1344 (w), 1301 (w), 1147 (m), 991 (m). ESI MS: *m*/*z*=725 $[M-H]^+$, 761 $[M-H+HCl]^+$. HR-ESI MS: *m*/*z*=725.3888 (725.3909 calcd for $C_{42}H_{62}S_2O_6$) $[M-H]^+$.

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