Dihydroxystyrene Metabolites from an Association of the Sponges *Poecillastra wondoensis* and *Jaspis* sp.

Yong Ha Chang,[†] Daehyun Shin,[†] Zeyei Na,[†] Hyi-Seung Lee,[‡] Dae-Duk Kim,[†] Ki-Bong Oh,*[,§] and Jongheon Shin*[,†]

College of Pharmacy, Seoul National University, 599 Gwanangno, Gwanak-gu, Seoul 151-742, Korea, Marine Natural Products Laboratory, Korea Ocean Research and Development Institute, Ansan P.O. Box 29, Seoul 425-600, Korea, and School of Agricultural Biotechnology, Seoul National University, 599 Gwanangno, Gwanak-gu, Seoul 151-921, Korea

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Five new dihydroxystyrene metabolites and six known compounds of the same structural class were isolated from an association of the sponges *Poecillatra wondoensis* and *Jaspis* sp., collected from Keomun Island, Korea. The structures of novel compounds were determined to be the sodium or *N*,*N*-dimethyl guanidinium salts of a dihydroxystyrene dimer (**5**) and two trimers (**6**, **7**). Two dimers (**10**, **11**) containing imidazole moieties were also identified on the basis of the results of combined spectroscopic analyses. Several compounds exhibited weak to moderate inhibitory effects against isocitrate lyase and sortase A enzymes derived from microorganisms.

Marine sponges of the genus *Jaspis* are widely recognized as a rich source of bioactive compounds of diverse skeletal classes, including amino acid derivatives, aromatics, macrolides, modified nucleosides, peptides, sphingosines, terpenoids, and mixed biogenetic products.[1,2] During the course of our search for bioactive metabolites from Korean waters, we reported the structures of the wondonins, novel antiangiogenic bis(dihydroxystyrenyl) imidazole alkaloids from an association of the sponges *Poecillatra wondoensis* and *Jaspis* sp.[3] Although these compounds were isolated from a two-sponge association, the structural relationship of the wondonins with the previously reported jaspisins and narains suggested that *Jaspis* sp. may have been their biogenic source.[4–7] In our continuing search for enzyme-inhibiting compounds from sponges, we recollected these sponges from the same area. Bioactivity-guided separation yielded several secondary metabolites.

Here, we report the isolation and structural characterization of five new hydroxystyrene compounds and six known metabolites of the same structural class. Compound **5** (**5a**, **5b**) was a bis(dihydroxystyrene) metabolite possessing a cyclic acetal moiety, while compounds **6** (**6a**, **6b**) and **7** belonged to a new tris(dihydroxystyrene) class. Compounds **10** and **11** were geometric isomers of the wondonins.[3] The new compounds exhibited weak to moderate inhibitory activity against isocitrate lyase and sortase A, key enzymes in microbial metabolism.

Results and Discussion

Freeze-dried specimens were extracted with CH_2Cl_2 and MeOH. Guided by the combined results of bioactivity tests and ^{1}H NMR analysis, the crude extracts were separated by sequential solvent-partitioning, ODS vacuum flash chromatography, HP20 adsorption chromatography, silica flash chromatography, and ODS HPLC, to yield 11 compounds.

Compounds **1**, **2**, and **3** were determined to be jaspisin, isojaspisin, and 1,1,2-trimethoxy-2-(3,4-dihydroxyphenyl)ethane, respectively, by combined spectroscopic analyses and comparison of NMR data with those reported previously.[4–6] The spectroscopic data for compound **4** were also very similar to those of a bis(dihydroxystyrene) metabolite isolated from *Jaspis* sp. However, the presence of *N*,*N*-dimethylguanidinium as the counterion of a sulfate group at C-1 or C-1′ was revealed by NMR: δ_H 2.93 (6H, s); δ_C 156.9 (C), 37.9 (CH_3) (Tables 1, 2). The geometry at the C-1 double bond was assigned as *E* by the large proton coupling constant ($J_{1,2}$ = 12.8 Hz) and comparison with other dihydroxystyryl enol sulfates.[3–7] Due to the small coupling constant ($J_{1',2'}$ = 1.7 Hz) and lack of reliable NOE correlations, however, the stereochemistry at the C-1′ and C-2′ asymmetric centers was not assigned.[7]

The molecular formula of compound **5a** was deduced to be $C_{16}H_{13}O_9S$ by HRFABMS, consistent with the ^{13}C NMR data (Table 1). The spectroscopic data for this compound were very similar to those of **4**. However, the carbon and proton signals at C-1′ and C-2′ were significantly shifted in the ^{1}H and ^{13}C NMR spectra (Table 2). These spectroscopic differences could be explained by a five-membered cyclic acetal, consistent with combined 2D NMR data, and in particular, long-range correlations of H-1′ at δ 6.12 with C-5, C-6, C-2′, and C-3′ at δ 148.2, 146.4, 72.6, and 130.3, respectively, in the gHMBC spectrum. In addition, placement of the hydroxyl groups at C-2′, C-5′, and C-6′ was supported by the long-range couplings between these protons and neighboring aromatic carbons (Table 2).

A closely related congener, compound **5b**, was isolated as a yellow gum. The ^{1}H and ^{13}C NMR data of this compound were very similar to those of **5a**, with the presence of *N*,*N*-dimethylguanidinium as the only difference in the NMR data, confirmed by a combination of 2D NMR experiments. It is unclear whether the significant difference in the H-2′ and 2′-OH between **5a** and **5b** (J = ~0 and 4.4 Hz, respectively) was the result of the change in counterion (Table 2). It is possible that **5a** was an ion-exchange product of **5b**, which was formed during the isolation process. However, the isolation of narains and jaspisins, dihydroxystyryl sulfates with different counterions, from different specimens of *Jaspis* sp. suggests that **5a** and **5b** were both natural products.[4–6]

The molecular formula of compound **6a** was shown to be $C_{24}H_{18}O_{14}S_2$ by combined HRFABMS and ^{13}C NMR spectroscopic analyses. The styrene nature of this compound was evident from the NMR data (Tables 1, 2) and comparison of spectroscopic data with those of **4** and **5**. However, the occurrence of eight more carbon signals in the ^{13}C NMR spectra suggested that **6a** possessed a more complex structure. A combination of 2D NMR experiments showed that the bis(dihydroxystyrene) moiety of **4** was intact in **6a**, leaving eight extra carbons to form a partial structure to be connected at an oxygenated functionality in **4**.

As found in other compounds, the characteristic signals at δ 7.07 and 5.86, coupled with large vicinal coupling constants (J = 12.8

* To whom correspondence should be addressed. (J.S.) Tel.: 82 2 740 8919. Fax: 82 2 762 8322. E-mail: shinj@snu.ac.kr. (K.-B.O.) Tel.: 82 2 880 4646. Fax: 82 2 873 3112. E-mail: ohkibong@snu.ac.kr.
[†] College of Pharmacy, Seoul National University.
[‡] Korea Ocean Research and Development Institute.
[§] School of Agricultural Biotechnology, Seoul National University.

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Chart 1

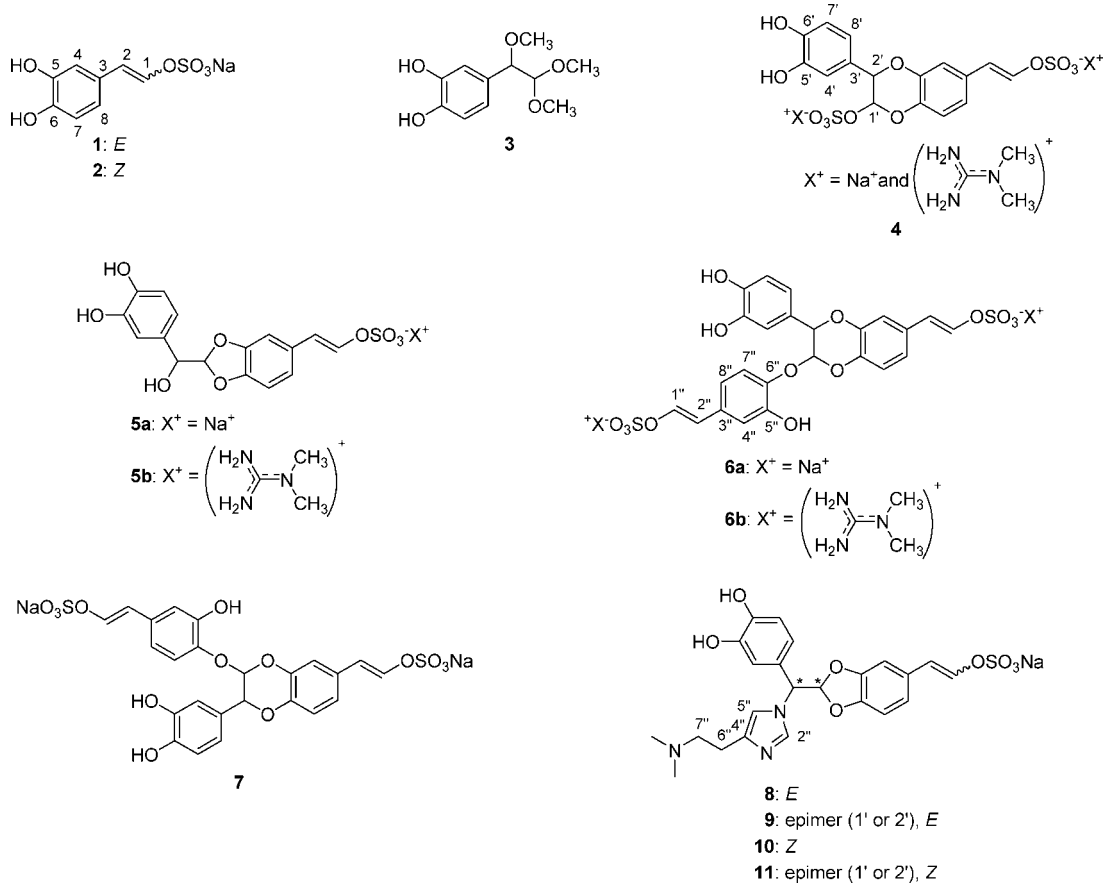

Table 1. ^{13}C NMR Assignments for Compounds **4**−**7**, **10**, and **11**[a]

position	4	5a	5b	6a	6b	7	10	11
1	140.7	140.3	140.3	140.79	140.86	140.6	137.9	137.9
2	110.3	111.0	111.0	110.4	110.5	110.3	110.8	110.6
3	130.1	129.3	129.3	130.3	130.4	129.3	130.3	130.3
4	113.2	104.5	104.4	113.4	113.5	114.22	109.8	109.6
5	142.5	148.2	148.3	142.6	142.7	140.1	148.5	148.3
6	138.9	146.4	146.3	138.4	138.6	141.0	147.1	147.2
7	117.6	107.9	108.0	117.6	117.7	117.0	108.5	108.6
8	118.3	118.8	118.9	118.5	118.6	119.3	123.8	123.6
1′	92.7	112.4	112.4	95.1	95.2	95.3	110.9	110.8
2′	75.5	72.6	72.5	74.9	75.1	75.1	64.4	64.4
3′	127.9	130.3	130.3	127.5	127.6	127.5	126.6	126.3
4′	113.6	115.0	115.0	114.0	114.1	114.18	116.9	116.9
5′	145.4	145.0	145.0	145.3	145.3	145.6	146.9	146.8
6′	145.4	145.0	145.0	145.5	145.5	145.3	147.5	147.3
7′	115.7	115.2	115.2	115.6	115.7	115.6	116.6	116.5
8′	117.4	118.5	118.4	117.8	117.9	118.1	121.6	121.5
1″				140.76	140.83	140.8		
2″				110.1	110.2	110.1	139.2	139.0
3″				131.7	131.8	131.7		
4″				113.0	113.0	112.9	134.5	137.5
5″				148.2	148.2	148.2	118.3	119.3
6″				141.9	142.0	142.0	25.3	24.4
7″				120.0	120.1	119.9	59.4	59.0
8″				116.7	116.8	116.8		
guanidium	156.9		156.9		156.8			
N-Me	37.9		38.0		38.0		44.4	43.9

[a] Data were obtained in DMSO-d_6 (**4**−**7**) and MeOH-d_4 (**10**, **11**) solutions.

Hz), in the ^{1}H NMR spectrum revealed the presence of an arylenol sulfate. The ABX-type protons at δ 6.81, 6.77, and 6.62 showed a 1,2,4-trisubstituted benzene moiety that was consistent with the HMBC correlations of these protons with neighboring carbons. The attachment of the enol sulfate at the C-3″ position of the extra benzene ring was also confirmed by long-range coupling between the olefinic protons and aromatic carbons. Similarly, the linkage between C-6″ and C-1′ of the distyrene moiety was determined on the basis of coupling between H-1′ at δ 5.93 and C-6″ at δ 141.9 in the gHMBC spectrum (Figure 1). The locations of the hydroxyl groups at C-5′, C-6′, and C-5″ were also confirmed by long-range coupling of these protons with the aromatic carbons. Thus, the structure of compound **6a** was determined to be a tris(dihydroxystyrenyl) sulfate, belonging to a previously unknown class of sponge metabolites.

The spectroscopic data of compound **6b** were very similar to those of its congener, **6a**. A combination of 2D NMR experiments showed that **6b** had the same tris(dihydroxystyrene) structure as **6a**. The presence of two *N*,*N*-dimethylguanidinium ions in the NMR data, coupled with the negative MS data containing an *N*,*N*,-dimethylguanidinium, revealed that **6b** possessed two of these units instead of sodium in **6a**, as the counterions of the sulfates.

The molecular formula of compound **7** was deduced to be $C_{24}H_{18}O_{14}S_2$ by HRFABMS and ^{13}C NMR analyses. Although its spectroscopic data were very similar to those of **6a**, careful examination of the ^{1}H and ^{13}C NMR spectra revealed noticeable shifts in several signals (Tables 1 and 2). Extensive 2D NMR analyses showed that **7** consisted of the same tris(dihydroxystyrene) moiety as **6a**. However, the gHMBC data showed long-range correlations of H-1′ and H-2′ with C-5 and C-6, respectively, the opposite of the diether linkage between the two dihydroxystyrene units in **6a** (Figure 1). Furthermore, an additional ether linkage was determined between C-1′ and C-6″ based on a long-range coupling of H-1′ with C-6″ (Figure 1). Thus, the structure of **7** was determined to be an analogue of **6a**, containing switched ether linkages.

Four additional compounds, **8**−**11**, were also isolated along with the dihydroxystyrene metabolites. On the basis of the results of spectroscopic analyses, the structures of **8** and **9** were identified as

Table 2. ^{1}H MMR Assignments for Compounds **4**−**7**, **10**, and **11**[a]

position	4	5a	5b	6a	6b	7	10	11
1	7.10, d (12.8)	7.07, d (12.7)	7.06, d (12.8)	7.13, d (12.8)	7.13, d (12.9)	7.10, d (12.8)	6.64, d (7.1)	6.65, d (7.1)
2	5.90, d (12.8)	5.90, d (12.7)	5.89, d (12.8)	5.94, d (12.8)	5.94, d (12.9)	5.90, d (12.8)	5.44, d (7.1)	5.44, d (7.1)
4	6.82, d (1.6)	6.78, br s	6.76, br s	6.91, br s	6.90, d (1.5)	6.78, br s	7.31, d (1.3)	7.17, d (1.1)
7	6.71, d (8.4)	6.67, d (8.1)	6.70, d (8.0)	6.75, d (8.3)	6.75, d (8.4)	6.87	6.60, d (8.1)	6.67, d (8.2)
8	6.76, dd (8.4, 1.6) (8.0, 1.2)	6.63, br d (8.1)	6.64, dd	6.79	6.79	6.88	6.80, br d (8.1)	6.88, br d (8.2)
1′	5.79, d (1.7)	6.12, d (3.6)	6.12, d (4.0)	5.93, br s	5.93, d (2.1)	5.90, d (1.2)	6.79, d (1.7)	6.82, d (2.1)
2′	5.12, br s	4.58, br s	4.58, dd (4.4, 4.0)	5.38, br s	5.37, d (2.1)	5.34, d (1.2)	5.57, d (1.7)	5.61, d (2.1)
4′	6.67, br s	6.83, s	6.83, s	6.78, s	6.78, s	6.78, s	7.04, d (1.9)	7.03, br s
7′	6.66, d (8.3)	6.66, ND	6.66, ND	6.69, ND	6.69, ND	6.68, ND	6.81, d (8.1)	6.82, d (8.0)
8′	6.53, dd	6.65, ND	6.66, ND	6.68, ND	6.68, ND (8.1, 1.9) (8.2, 2.1)	6.70, ND	6.91, dd	6.93, dd
1″				7.07, d (12.8)	7.07, d (12.9)	7.07, d (12.8)		
2″				5.86, d (12.8)	5.86, d (12.9)	5.85, d (12.8)	7.60, s	7.53, s
4″				6.77, br s	6.77, br s	6.77, br s		
5″							6.92, s	7.03, s
6″							2.64, m; 2.70, m	2.76, m; 2.71, m
7″				6.81, d (8.4)	6.81, d (8.5)	6.85, d (8.0)	2.70, t (7.1)	2.88, m
8”				6.62, br d (8.4)	6.62, dd	6.63, br d (8.0)		
2′-OH		5.75, s	5.73, d (4.4)					
5′-OH		8.83, s	8.84, s	9.00, s				
6′-OH		8.80, s	8.77, s	8.98, s				
5″-OH				9.32, s				
N-Me	2.93, s (6H)		2.93, s (6H)		2.93, s (12H)		2.50, s (6H)	2.64, s (6H)

[a] Data were obtained in DMSO-d_6 (**4**−**7**) and MeOH-d_4 (**10**, **11**) solutions. ND: Due to the signal overlapping, splitting patterns were not measured.

Table 3. Results of Bioacitivity Tests for Compounds **1**−**11**

compound	isocitrate lyase IC_{50} (μg/mL)	sortase A IC_{50} (μg/mL)
1	>200	14.6
2	>200	34.2
3	28.7	>200
4	172.8	>200
5a	123.9	>200
5b	>200	82.4
6a	173.3	163.5
6b	>200	>200
7	41.1	>200
8	>200	>200
9	>200	>200
10	48.0	>200
11	92.1	68.3
itaconicacid	5.8	
PHMB		40.6

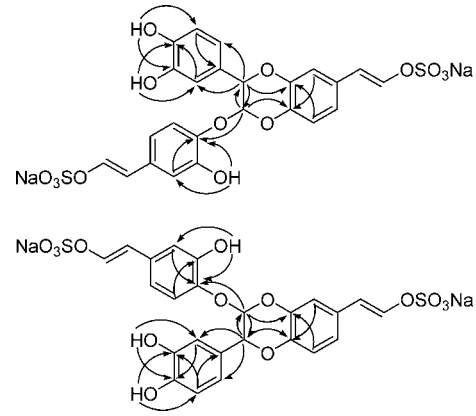

Figure 1. Key HMBC correlations (H→C) for **6a** (top) and **7** (bottom).

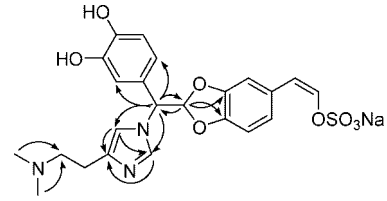

Figure 2. Key HMBC correlations (H→C) for **10**.

wondonins A and B, isolated previously from the same sponges *Poecillastra wondoensis* and *Jaspis* sp., respectively. The molecular formula of isowondonin A, compound **10**, was shown to be $C_{23}H_{24}N_3O_8S$, identical to **8** and **9**, by HRFABMS. The spectroscopic data of this compound were very similar to those of **8**, with shifts in the NMR signals for the C-1 double bond as the only noticeable difference, confirmed by combined 2D NMR experiments. The 1*Z* configuration was assigned on the basis of the small coupling constant ($J_{1,2}$ = 7.1 Hz) between the olefinic protons. Thus, isowondonin A was defined as a configurational isomer of wondonin A. Similarly, the structure of isowondonin B, compound **11**, was also determined to be the 1*Z* configurational isomer of wondonin B on the basis of the combined results of NMR analyses and comparison of NMR data with those of wondonin B. All of the wondonins, **8**−**11**, possessed asymmetric carbon centers at C-1′ and C-2′. Identical planar structures, defined by extensive spectral experiments, first suggested diastereomeric relations between these compounds. However, because of the lack of reliable NOE correlations among the key protons, the stereochemistry at the asymmetric centers could not be assigned. A simple 3D energy-minimized model study showed that the spatial environment around the C-2′ center was very crowded, with three rings: acetal, benzene, and imidazole. Thus, these rings were not placed in a plane and tilted significantly toward each other, probably explaining the lack of NOE correlations among the protons in the different rings. Alternatively, compounds **8** and **10** and **9** and **11** could be not diastereomers but conformers with very high rotational barriers. This problem was solved by variable-temperature ^{1}H and ^{13}C NMR experiments in which these compounds were intact at given condition (60 °C, 3 h). Thus, compounds **9** and **11** were defined to be the diastereomers of **8** and **10**, respectively.

Dihydroxystyrenes derived from *Jaspis* sp. exhibited diverse bioactivities, including cytotoxicity, antiangiogenic activity, inhibition of fertilization of sea urchin gametes, and induction of metamorphosis in ascidian larvae.[3–7] In our measurements of bioactivity against isocitrate lyase (ICL) and sortase A (Srt A),

important enzymes in microbial metabolism, derived from *Candida albicans* and *Staphylococcus aureus*, respectively,[8–11] these compounds showed weak to moderate inhibition (IC_{50} 28.7 to >200 and 14.6 to >200 μg/mL for ICL and Srt A, respectively) (Supporting Information). The new dihydroxystyrenes were also inactive against diverse bacterial and fungal strains and the tumor cell lines K-562 and A-549 (data not shown).

Experimental Section

General Experimental Procedures. Optical rotations were measured on a JASCO P-1020 polarimeter using a 1 cm cell. IR spectra were recorded on a JASCO 300E FT-IR spectrometer, using a NaCl cell. UV spectra were recorded on a Hitachi U-3010 spectrophotometer. NMR spectra were recorded in D_2O, DMSO-d_6, and CD_3OD solutions, containing Me_4Si as an internal standard, on Bruker Advance 500 and 600 spectrometers. ESI and FAB mass spectra were obtained on Finnigan MS:LCQ DECA XP and JEOL JMS-700 high-resolution mass spectrometers, provided by the Basic Science Research Institute, Seoul Branch, Seoul, Korea. All solvents used were spectral grade or were distilled from glass prior to use.

Animal Material. Specimens of a two-sponge association of *Poecillastra wondoensis* and *Jaspis* sp. (voucher number 04K-5) were collected by hand using scuba equipment at a depth of 25 m off the shore of Keomun Island, Korea, in August 2004. On the basis of the comparison of gross morphological characters, the thin and bright yellow outer layer was identified as *P. wondoensis,* while the golden yellow inner layer was identified as *Jaspis* sp., as reported previously (Registry No. Por. 32 at National History Museum, Hannam University, Korea). Voucher specimens are on deposit at the Sponge Collection, Seoul National University.

Extraction and Isolation. The fresh collected specimens were immediately frozen and kept at −25 °C until chemical investigations. The specimens were lyophilized (dry weight 5.0 kg), macerated, and extracted repeatedly with MeOH (4 L × 5) and CH_2Cl_2 (4 L × 2). The combined crude extract (568.2 g) was partitioned between *n*-BuOH and H_2O, and then the *n*-BuOH layer (117.2 g) was repartitioned between 15% aqueous MeOH (38.1 g) and *n*-hexane (74.4 g). An aliquot of the aqueous MeOH layer (24.0 g) was subjected to C_{18} reversed-phase vacuum flash chromatography using sequential mixtures of MeOH and H_2O as eluents (elution order: 50%, 40%, 30%, 20%, 10% aqueous MeOH, 100% MeOH) and finally acetone. The first fraction (6.18 g) was subjected to HP20 adsorption chromatography, with sequential elution with 100% H_2O, 50% aqueous MeOH, 50% aqueous acetone, 100% MeOH, and finally 100% acetone. The 50% aqueous MeOH fraction (2.05 g) was separated by normal-phase vacuum flash chromatography, using 5% gradient mixtures of CH_2Cl_2 and MeOH as eluents. Guided by the results of bioassay and ^{1}H NMR analyses, two fractions (75% CH_2Cl_2/25% MeOH and 70% CH_2Cl_2/30% MeOH, 236.1 and 279.2 mg, respectively) were combined and separated by C_{18} reversed-phase semipreparative HPLC (YMC ODS-A column, 1 cm × 25 cm, 85% aqueous MeOH) to yield, in order of elution, compounds **1**, **2**, **5b**, **5a**, **4**, **6b**, **6a**, and **7**.

The aqueous acetone fraction (1.98 g) from HP20 adsorption chromatography was separated by C_{18} reversed-phase HPLC (60% aqueous MeOH) to yield, in order of elution, compounds **3**, **9**, **11**, **8**, and **10**. Proton NMR analysis revealed that compounds **6**−**9** contained significant amounts of impurities. Further purification of these compounds was then accomplished by reversed-phase HPLC (75% aqueous MeCN) to yield these compounds as yellow gums. Final purifications of these metabolites afforded the following amounts of compounds **1**−**11** (in mg; compounds indicated in parentheses): 68.0 (**1**), 27.6 (**2**), 35.7 (**3**), 14.0 (**4**), 25.1 (**5a**), 7.9 (**5b**), 64.5 (**6a**), 23.6 (**6b**), 19.6 (**7**), 68.2 (**8**), 53.4 (**9**), 18.6 (**10**), and 8.9 (**11**).

Compound 1: yellow gum; IR (NaCl) ν_{max} 3500, 2960, 1730, 1515, 1460, 1275, 1125, 1070, 1000 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 210 (3.78), 290 (3.61) nm; HRFABMS (negative, glycerol) *m/z* 230.9968 (calculated for $C_8H_7O_6S^-$, *m/z* 230.9936).

Compound 2: yellow gum; IR (NaCl) ν_{max} 3500, 2960, 1730, 1520, 1455, 1380, 1280, 1125, 1070, 1020 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 208 (4.00), 260 (3.74), 290 (3.28) nm; HRFABMS (negative, glycerol) *m/z* 230.9981 (calculated for $C_8H_7O_6S$, 230.9936).

Compound 3: yellow gum; $[\alpha]^{25}_D$ −0.8 (*c* 0.5, MeOH); IR (NaCl) ν_{max} 3465, 2960, 2925, 1730, 1515, 1460, 1380, 1125, 1075 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 209 (3.96), 281 (3.41) nm; HRFABMS (negative, TEA) *m/z* 227.0913 (calculated for $C_{11}H_{15}O_5$, 227.0925).

Compound 4: yellow gum; $[\alpha]^{25}_D$ +1.3 (*c* 0.55, MeOH); IR (NaCl) ν_{max} 3465, 2925, 1730, 1650, 1510, 1460, 1270, 1125, 1070, 1040 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 207 (4.46), 260 (3.98) nm; ^{1}H and ^{13}C NMR data (DMSO-d_6), see Tables 1 and 2; HRFABMS (negative, TEA) *m/z* 482.9653 (calculated for $C_{16}H_{12}O_{12}S_2Na$, 482.9673).

Compound 5a: yellow gum; $[\alpha]^{25}_D$ −2.8 (*c* 0.40, MeOH); IR (NaCl) ν_{max} 3565, 2925, 1730, 1640, 1500, 1455, 1275, 1125, 1070 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 207 (4.40), 264 (3.88) nm; ^{1}H and ^{13}C NMR data (DMSO-d_6), see Tables 1 and 2; ESIMS *m/z* 381.15 [M]$^-$, HRFABMS (negative, PEG 400) *m/z* 381.0287 (calculated for $C_{16}H_{13}O_9S$, 381.0286).

Compound 5b: yellow gum; $[\alpha]^{25}_D$ −2.4 (*c* 0.55, MeOH); IR (NaCl) ν_{max} 3565, 2925, 1730, 1645, 1500, 1455, 1275, 1125, 1070 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 207 (4.40), 264 (3.88) nm; ^{1}H and ^{13}C NMR data (DMSO-d_6), see Tables 1 and 2; ESIMS *m/z* 381.13 [M]$^-$, HRFABMS (negative, PEG 400) *m/z* 381.0280 (calculated for $C_{16}H_{13}O_9S$, 381.0286).

Compound 6a: yellow gum; $[\alpha]^{25}_D$ −2.2 (*c* 0.45, MeOH); IR (NaCl) ν_{max} 3500 (br), 2960, 1730, 1650, 1510, 1460, 1270, 1125, 1040 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 211 (4.52), 261 (4.27) nm; ^{1}H and ^{13}C NMR data (DMSO-d_6), see Tables 1 and 2; ESIMS *m/z* 617.0 [M]$^-$, HRFABMS (negative, PEG 400) *m/z* 617.0037 (calculated for $C_{24}H_{18}O_{14}S_2Na$, 617.0041).

Compound 6b: yellow gum; $[\alpha]^{25}_D$ −1.6 (*c* 0.45, MeOH); IR (NaCl) ν_{max} 3500 (br), 2960, 1730, 1650, 1510, 1455, 1270, 1125 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 211 (4.51), 261 (4.27) nm; ^{1}H and ^{13}C NMR data (DMSO-d_6), see Tables 1 and 2; ESIMS *m/z* 681.094 [M]$^-$, HRFABMS (negative, PEG400) *m/z* 681.0944 (calculated for $C_{27}H_{27}N_3O_{14}S_2$, 681.0934).

Compound 7: yellow gum; $[\alpha]^{25}_D$ −1.1 (*c* 0.35, MeOH); IR (NaCl) ν_{max} 3500 (br), 2955, 1730, 1645, 1510, 1460, 1270, 1120, 1040 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 209 (4.47), 260 (4.32) nm; ^{1}H and ^{13}C NMR data (DMSO-d_6), see Tables 1 and 2; ESIMS *m/z* 617.0 [M]$^-$, HRFABMS (negative, PEG 400) *m/z* 617.0129 (calculated for $C_{24}H_{18}O_{14}S_2Na$, 617.0041).

Compound 8: yellow gum; $[\alpha]^{25}_D$ −4.8 (*c* 0.12, MeOH); IR (NaCl) ν_{max} 3400 (br), 1650, 1495, 1245, 1035 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 210 (4.16), 264 (3.94) nm; HRFABMS *m/z* 502.1291 [M]$^-$ (calculated for $C_{23}H_{24}N_3O_8S$, 502.1284).

Compound 9: yellow gum; $[\alpha]^{25}_D$ +2.4 (*c* 0.42, MeOH); IR (NaCl) ν_{max} 3400 (br), 1645, 1495, 1245, 1035 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 211 (4.23), 264 (3.25) nm; HRFABMS *m/z* 502.1297 [M]$^-$ (calculated for $C_{23}H_{24}N_3O_8S$, 502.1284).

Compound 10: yellow gum; $[\alpha]^{25}_D$ −4.0 (*c* 0.72, MeOH); IR (NaCl) ν_{max} 3465 (br), 2925, 1730, 1650, 1500, 1270, 1125, 1015 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 209 (4.66), 268 (4.03) nm; ^{1}H and ^{13}C NMR data (DMSO-d_6), see Tables 1 and 2; HRFABMS *m/z* 502.1291 [M]$^-$ (calculated for $C_{23}H_{24}N_3O_8S$, 502.1284).

Compound 11: yellow gum; $[\alpha]^{25}_D$ −3.7 (*c* 0.65, MeOH); IR (NaCl) ν_{max} 3465 (br), 2925, 1730, 1560, 1495, 1275, 1125, 1015 cm^{-1}; UV (MeOH) λ_{max} (log ϵ) 212 (4.33), 263 (3.99) nm; ^{1}H and ^{13}C NMR data (DMSO-d_6), see Tables 1 and 2; HRFABMS *m/z* 502.1291 [M]$^-$ (calculated for $C_{23}H_{24}N_3O_8S$, 502.1284).

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Supporting Information Available: Inhibitory activities against isocitrate lyase and sortase A. This material is available free of charge via the Internet at http://pubs.acs.org.

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