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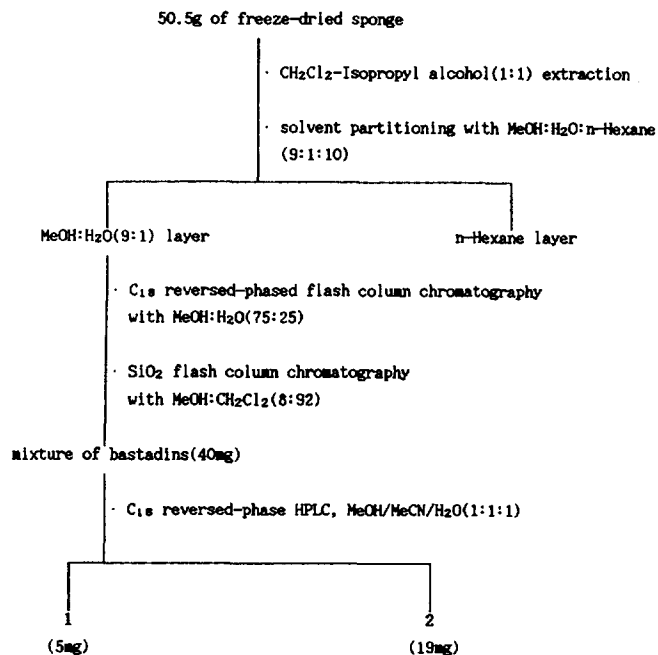
Scheme 1.

structure determination of a new bastadin 17 and the previously reported compound, bastadin 3,[4] from the Marine sponge *Ianthella basta* Pallas collected in October, 1992 at Manado Bay, Sulawesi Indonesia.

The *Ianthella basta* extract was partitioned between $MeOH/H_2O$ (9 : 1) and *n*-hexane and the $MeOH/H_2O$ (9 : 1) layer residue was subjected to C_{18} reversed-phase followed by Silica gel normal-phase flash column chromatography to yield a fraction whose ^1H NMR spectrum revealed structural features of bastadins. The mixture of bastadins was sepa-

Isolation and Structure Determination of a New Bastadin from an Indonesian Sponge *Ianthella basta*

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The bastadins are series of predominantly macrocyclic sponge metabolites, which are biogenetically derived from four tyrosines by oxidative phenolic coupling of two tyramine-tyrosine units.[1~8] We now report the isolation and
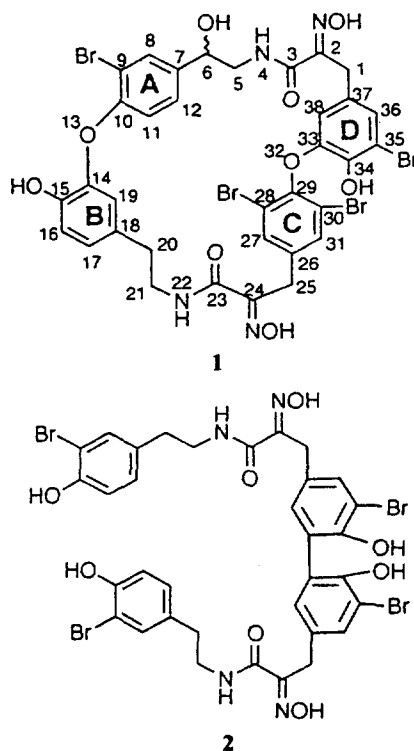
Table 1. Nmr Data for 1 (DMSO-d₆) at 500 MHz

position	¹H NMR	¹³C NMR	HMBC	NOE
1	3.52(2H, s)	27.4	2, 3, 36, 38	36, 38
2(NOH)	11.77(1H, s)	151.0	1, NOH-2	
3		162.9	1, 4, 5	
4(NH)	7.77(1H, t, J=6.3 Hz)			
5	2.92(1H, m)	47.7	OH-6	
	3.38(1H, m)			
6	4.58(1H, m)	70.5	OH-6, 8, 12	5, 8, 12
6(OH)	5.53(1H, d, J=4.4 Hz)			
7		139.3	OH-6, 11	
8	7.62(1H, d, J=1.9 Hz)	129.8	12	
9		111.4	8, 11	
10		153.1	8, 11, 12	
11	6.73(1H, d, J=8.5 Hz)	117.4		
12	7.13(1H, dd, J=8.5, 1.9 Hz)	126.2	8	
14		142.5	OH-15, 16, 19	
15		146.9	17, 19	
15(OH)	9.36(1H, s)			
16	6.83(1H, d, J=8.2 Hz)	116.5	OH-15	
17	6.81(1H, dd, J=8.2, 1.9 Hz)	126.1	19, 20	
18		130.6	16, 19, 20	
19	6.76(1H, d, J=1.9 Hz)	121.1	17, 20	
20	2.65(2H, t, J=6.3 Hz)	34.1	17, 19	17, 19, 21
21	3.40(2H, m)	39.2	22	
22(NH)	7.95(1H, t, J=6.3 Hz)			
23		163.0	22, 25	
24(NOH)	11.91(1H, s)	150.4	NOH-24, 25	
25	3.51(1H, d, J=12.9 Hz)	28.7	27, 31	27, 31
	3.56(1H, d, J=12.9 Hz)			
26		137.6	25	
27	7.58(1H, s)	133.6	25, 31	
28		117.2	27	
29		146.0	27, 31	
30		117.2	31	
31	7.58(1H, s)	133.6	25, 27	
33		144.6	38	
34		141.8	36, 38	
34(OH)	9.98(1H, s)			
35		109.7	36	
36	7.03(1H, d, J=1.9 Hz)	126.8	1, 38	
37		128.0	1, 38	
38	6.24(1H, d, J=1.9 Hz)	113.1	1, 36	

rated by C_{18} reversed-phase hplc[ODS column, MeOH/H₂O /MeCN (1:1:1), 2 mL/min] to give 5 mg of 1 as a pure white solid, and 19 mg of 2 as shown in Scheme 1.

The presence of a one-proton multiplet at δ 4.58 (H-6) in the ¹H NMR spectrum of 1 suggested that, by analogy with bastadins 8[1~2] and 10,[1] it contained a benzylic alcohol. A molecular formula of $C_{34}H_{29}Br_4N_4O_9$, determined by High resolution fast atom bombardment mass spectroscopy (hrfa-

bms), supported this and indicated that 1 was isomeric with bastadin 10. The ¹H NMR spectrum indicated the presence of two trisubstituted and two tetrasubstituted aromatic rings, one symmetric and one dissymmetric. Extensive ¹H-¹³C (1 bond) Heteronuclear Multiple Quantum Coherence Spectroscopy (HMQC) and ¹H-¹³C (2 and 3 bond) Heteronuclear Multiple Bond Correlation Spectrosopy (HMBC) data (Table 1) revealed that 1 shared the entire sequence O-13 to C-23 with bastadin 8,[1~2] leaving trisubstituted ring B to be elucidated. A one-proton doublet at δ 6.83 (J=8.2 Hz, H-16), ortho-coupled to a proton at δ 6.81 (J=8.2 and 1.9 Hz, H-17), which was in turn meta-coupled to a proton at δ 6.76 (J=1.9 Hz, H-19), showed H-C correlations to C-14 (δ 142.5), C-15 (δ 146.9), and C-18 (δ 130.6). Correlations of H-19 (δ 6.76) to carbon signals at δ 126.1 (C-17), δ 142.5(C-14), δ 130.6 (C-18), δ 146.9 (C-15) and δ 34.1 (C-20) established the structure of the remaining portion, and HMBC cross peaks from NH-22 to C-21 and C-23 completed the macrocycle.

The characteristic ion fragment at m/z 500 for the eastern part of the molecule was not obserbed in the ei mass spectrum of 1, but an ion cluster at m/z 418/420/422 (1:2:1) was prominent. The isotope pattern suggested that the fragment contained two bromines instead of the expected three, and High resolution electron impact mass spectroscopy (hreims) of the ion at m/z 418 corresponded to a formula of $C_{16}H_8Br_2N_2O_2$, indicating 13 double bond equivalents and a loss of HBr from the expected fragment. The ei mass spectrum of bastadin 13, which has the eastern hemisphere in common with 1, gave rise to the same fragment and composition as determined by hreims.[5]

The chemical shifts of C-1 and C-25 indicated that both oximes in 1 also had E geometry. The expected three-bond correlations of OH-15 to C-14 and C-16 were observed in the HMBC experiment, thus demonstrating that 1 contained the common C-10 to C-14 bastadin ether linkage found in all bastadins except bastadin 13.[5] The ¹H NMR signal for OH-34 was too broad to observe the desired couplings; attempts at sharpening this signal by adding Trifluoroacetic acid (TFA) to the nmr sample and by variable temperature nmr experiments were unsuccessful, but all available data were consistent with a C-29 to C-33 ether linkage found in all bastadin reported to data.

Irradiation of benzylic protons in 1 [δ 3.52 (H-1), and 3.51 (H-25), 3.56 (H-25)] induced nuclear Overhauser enhancement (nOe) in two aromatic resonances (H-36, 38 and H-27, 31), respectively, showing that the carbon containing the benzylic proton was adjacent to this ring.

Irradiation of the one-proton multiplet signal at δ 4.58 (H-6) induced nOe in these aromatic signals at δ 7.62 (H-8), 7.13 (H-12), and methylene proton signal at δ 2.92, 3.38 (H-5).

Exprimental

General Experimental Procedures. Ir spectra were recorded on a Perkin-Elmer model 1420 spectrophotometer and UV spectra were obtained on a Hewlett-Packard Model 8452A diode array detector. NMR spectra were measured on a General Electric GN OMEGA 500 at 500 MHz (¹H) 125 MHz (¹³C). ¹H NMR chemical shifts are reported in ppm

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with the chemical shift of the residual protons of the solvent used as internal standard. ^{13}C NMR chemical shifts are reported in ppm by using the natural abundance of ^{12}C of the solvent as an internal standard. Mass spectra were provided by the University of Illinois mass spectrometry facility. YMC RP and Silica gel (230-400 mesh) were used for flash column chromatography. YMC ODS 30×10 mm column was used for hplc separation.

Collection and Isolation. The sponge was collected Oct., 1992 from Manado bay north along the coast of Sulawesi up to Bunaken Island in Indonesia. The sponge was idetified by Dr. Peter Karuso, University of Macquarie. The freeze-dried sponge (50.5 g) was extracted for 2 days with 400 mL of CH_2Cl_2-iPrOH (1 : 1), and the residue (3.02 g) was partitioned between $MeOH/H_2O$ (9 : 1) and n-hexane. The $MeOH/H_2O$ layer yielded 2.03 g of red solid. The $MeOH/H_2O$ layer was subjected to RP-C_{18} flash column chromatography and Si gel flash column chromatography sequentially using $MeOH$-H_2O (75 : 25) and $MeOH$-CH_2Cl_2 (8 : 92), yielding 40 mg of mixture of bastadins. The mixture was separated by C_{18} reversed-phase hplc [ODS column, $MeOH/H_2O/MeCN$ (1 : 1 : 1), 2 mL/min] to give 5 mg of **1** as a pure white solid and 19 mg of **2** as shown in scheme 1.

HMBC condition for **1**: concentration of sample, 5 mg/ DMSO-d_6, 0.6 mL, 256 of blocks x 2048 data matrix with 64 of scan per t_1 increment, 3.0 delay period for long-range couplings, 100° shifted since bell squared filtering for t_1 and 5100 MHz line broadening for it.

Bastadin (1). Hrfabms m/z $[M+H]^+$ 956.8606 (calcd for $C_{34}H_{29}N_4O_9{}^{79}Br_2{}^{81}Br_2$, 956.8627); hreims m/z 417.8925 (calcd for $C_{16}H_8N_2O_2{}^{79}Br_2$, 417.8953); ir ν_{max} (Nujol) 3600-3100, 1660, 1640, 1490, 1470, 1285, 1220 cm^{-1}; UV ν_{max} (MeOH) (logε) 278 (4.1) nm; ^1H and ^{13}C nmr see Table 1.

Bastadin 3(2)/^{4}. ^1H NMR (in MeOH-d_4); δ 7.36 (2H, d, $J=2.2$ Hz), 7.28 (2H, d, $J=2.2$ Hz), 7.12 (2H, d, $J=2.2$ Hz), 6.89 (2H, dd, $J=8.3$, 2.2 Hz), 6.72 (2H, d, $J=8.3$ Hz), 3.80 (4H, s), 3.37 (4H, t, $J=6.9$ Hz), 2.66 (4H, t, $J=7.3$ Hz); ^{13}C NMR, δ 165.91, 153.92, 153.74, 153.61, 134.16, 133.29, 133.01, 132.27, 130.31, 130.07, 128.80, 117.21, 114.09, 110.67, 42.09, 35.19, 28.83; Irradiation at δ 3.80 (H-1) induced nuclear Overhauser enhancement (nOe) at δ 7.28 and 7.12. Irradiation at δ 2.62 (H-6) induced nOe at δ 3.37, 7.36 and 6.89. Irradiation at δ 3.37 (H-5) induced nOe at δ 2.62, 7.36 and 6.89.

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Structure of Bis(N,N-dimethyl-2-thiophenemeth-ylammonium)Tetrachlorocobaltate(II)

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2-(dimethylaminomethyl)thiophene (DMAT) ligand usually provides an [NS] donor set to form a delocalized five membered chelate ring with metal(II) ions and the structural characteristics of (DMAT)CuX$_2$ and (DMAT)NiX$_2$ where $X^- =$ Cl^- or Br^- have been characterized and reported (1). However, when cobalt(II)chloride reacts with DMAT in similar condition in ethanol, it does not produce a 1:1 complex of type (DMAT)CoCl$_2$. Instead, bis(N,N-dimethyl-2-thiophenemethylammonium)tetra-chlorocobaltate(II), (DMTMAH)$_2$ CoCl$_4$ is formed. We isolated the single crystals of this cobalt (II) complex and conducted X-ray crystallographic studies on it.

Experimental

The (DMTMAH)$_2$CoCl$_4$ was prepared by the direct reaction of DMAT (0.3 g, 2.0 mmol) with dried CoCl$_2$·6H$_2$O (0.4 g, 1.7 mmol) in ethanol (50 mL) and triethylorthoformate (10 mL). The mixture was stirred for two hours at warm (yield, 54%). Dark blue single crystals were obtained by slow recrystallization in acetonitrile. A flat crystal of size 0.80×0.60× 0.20 mm was used for intensity measurements on an Enraf-Nonius CAD-4 diffractometer using the ω-θ scan technique; lattice parameters from setting angles of 23 reflections in the range $8<\theta<10°$; scan width (0.8+0.350 tanθ) and with variable scan rate 1 to 7°min^{-1}; 2θmax=45.0°; $0<h<10$, 0 $<k<18$, $-14<l<14$. Intensity data for 3175 reflections were collected; 2858 unique observed reflections; 2621 included reflections with Fo$^2>1.5$ (Fo^2). Lorentz and polarization corrections were applied. The linear absorption coefficient is 14.6 cm^{-1} for Mo Kα radiation. An empirical absorption correction based on a series of psi-scans was applied to the data. Relative transmission coefficients ranged from 0.937 to 0.999. A secondary extinction correction was applied (2).