mp 96–97 °C. IR: ($CDCl_3$) 3616 (m), 2970 (m), 1429 (vs). MS: (FAB/DMF-KI) *m/e* 343 (M + K). NMR: (CD_3OD) δ 7.55–7.3 (m, 15 H, phenyl), 3.73 (B_2 of A_2B_2, 2 H, CH_2O), 1.78 (A_2 of A_2B_2, 2 H, CH_2Si). ^{13}C NMR: ($CDCl_3$) δ 135.5 (meta), 134.4 (ipso), 129.6 (para), 128 (ortho), 59.8 (CH_2O), 18.7 (CH_2Si). Calcd for $C_{20}H_{20}OSi·0.2\ H_2O$: C, 77.98; H, 6.67. Found: C, 77.92; H, 6.62.

1,1-Dimethyl-1-phenyl-3-acetoxy-1-silapropane (9). To a solution of 6.1 mL (40 mmol) of $PhMe_2SiH$ and 3.7 mL of vinyl acetate in 40 mL of toluene was added 61 mg (0.16 mmol) of $Rh_2Cl_2(CO)_4$. Immediately, the reaction evolved heat and gas. Within 5 min, the golden yellow reaction had turned dark brown in color. After 1 h, the reaction was complete. The reaction was worked up as in **5** to give 8.4 g of crude adduct. Proton NMR analysis showed a 9:10 addition ratio of 1.0:1.4. A 100-mg sample was purified by flash chromatography as in **5** to give 28 mg of **9** as a colorless oil. IR: ($CDCl_3$) 2960 (m), 1724 (vs), 1426 (m), 1255 (vs). MS: (DCI/NH_3) *m/e* 240 (M + NH_4). NMR: ($CDCl_3$) δ 7.6–7.3 (m, 5 H, phenyl), 4.18 (B_2 of A_2B_2, 2 H, CH_2O), 1.99 (s, 3 H, Me), 1.25 (A_2 of A_2B_2, 2 H, CH_2Si), 0.35 (s, 6 H, SiMe). ^{13}C NMR: ($CDCl_3$) δ 171.1 (CO), 138 (ipso), 133.4 (meta), 129.2 (para), 127.9 (ortho), 62.3 (CH_2O), 21.1 (Me), 16.5 (CH_2Si), –2.9 (SiMe). Anal. Calcd for $C_{12}H_{18}O_2Si$: C, 64.82; H, 8.16. Found: C, 65.02; H, 8.07.

1,1-Dimethyl-1-phenyl-1-silapropan-3-ol (11). The remaining 8.3 g of crude **9** was worked up as in the case of the (triphenylsilyl)ethanol **7** to give 1.6 g of 1,1-dimethyl-1-phenyl-1-silapropan-3-ol as a colorless oil, 23% overall. IR: ($CDCl_3$) 3616 (m), 2960 (m), 1425 (m), 1251 (s). MS: (DCI/NH_3) *m/e* 198 (M + NH_4). NMR: ($CDCl_3$) δ 7.6–7.3 (m, 5 H, phenyl), 3.75 (B_2 of A_2B_2, 2 H, CH_2O), 1.49 (s, 1.2 H, OH), 1.22 (A_2 of A_2B_2, 2 H, CH_2Si), 0.33 (s 6 H, SiMe). ^{13}C NMR: ($CDCl_3$) δ 138.5 (ipso), 133.4 (meta), 129 (para), 127.8 (ortho), 59.9 (CH_2O), 21.1 (CH_2Si), –2.8 (SiMe). Anal. Calcd for $C_{10}H_{16}OSi·0.1H_2O$: C, 65.92; H, 8.99. Found: C, 65.95; H, 8.97.

2-(Triphenylsilyl)ethyl 2-Cyanoethyl *N,N*-Diisopropylphosphoramidite (4). To a solution of 3.0 g (10 mmol) of **7**, 4.2 mL (24 mmol) of *i*-Pr_2NEt, and 5 mg of 4,4-(dimethylamino)-pyridine in 15 mL of THF at 0 °C was added 2.7 mL (12 mmol) of 2-cyanoethyl *N,N*-diisopropylchlorophosphoramidite all at once. A white precipitate formed almost immediately. Reaction was complete after 30 min at 0 °C. After solvent removal, the residue was partitioned with 200 mL of 1:1 0.1 M Na_2CO_3–EtOAc, and the phases were separated. The aqueous phase was reextracted with 50 mL of EtOAc, and the combined organic phases were concentrated and vacuum dried. Flash chromatography (10% EtOAc in cyclohexane) using a 41-mm i.d. × 150-mm long silica gel column gave 3.4 g of **4** (66%) after vacuum drying overnight as a viscous colorless oil. This material gradually crystallized in a –20 °C freezer over the course of several weeks. During the chromatography, it was necessary to add 100 μL of NEt_3 to each fraction, in order to minimize the effects of adventitious acid in the fraction tubes or in the silica gel used for flash chromatography. IR: (film) 2962 (m), 1426 (m). MS: (DCI/NH_3) *m/e* 505 (M + H). NMR: (CD_3CN) δ 7.6–7.3 (m, 15 H, phenyl), 3.9–3.7 (m, 2 H, CH_2O), 3.66 (dt, 2 H, J_{CH} = 5.9 Hz, J_{PH} = 7.7 Hz, CH_2O), 3.51 (dsept, 2 H, J_{CH} = 6.6 Hz, J_{PH} = 9.9 Hz, NH), 2.54 (t, 2 H, *J* = 5.5 Hz, CH_2CN), 1.87 (br t, 2 H, *J* = 6.3 Hz, CH_2Si), 1.07 (dd, 12 H, J_{CH} = 6.6 Hz, J_{PH} = 29.4 Hz, Me). ^{13}C NMR: (CD_3CN) δ 136.3 (meta), 135.5 (ipso), 130.7 (para), 129 (ortho), 117.7 (CN), 61.1 (d, J_{PC} = 18.3 Hz, CH_2O), 59.3 (d, J_{PC} = 18.3 Hz, CH_2O), 43.6 (d, J_{PC} = 12.2 Hz, NCH), 24.8 (virtual t, J_{PC} = 7.3 Hz, Me), 21 (d, J_{PC} = 7.3 Hz, CH_2CN), 17.2 (d, J_{PC} = 7.3 Hz, CH_2Si). ^{31}P NMR: (202 MHz, CD_3CN) δ 145.6 (s). Anal. Calcd for $C_{29}H_{37}N_2O_2PSi$: C, 69.02; H, 7.39; N, 5.55. Found: C, 69.02; H, 7.36; N, 5.42.

Use of 4 in Automated Phosphorylation of DNA. The phosphoramidite **4** was used to phosphorylate a 25-mer oligonucleotide at 1 μmol CPG loading using an ABI (Foster City, CA) 380A DNA synthesizer. The phosphoramidite couplings were run using a modified synthesis program from the manufacturer, wherein the contact time of 100 mM phosphoramidite **4** in MeCN to the column was increased to 52 s. The preparative HPLC run, showing separation of the failure sequences from full-length oligo, is shown in Figure 1. The collected material was dried in vacuo. The purified, silylated DNA was then desilylated using 200 μL of 2 M TBAF in DMSO. The reaction was performed in a 70 °C heating block for 2 h. The reaction was diluted to 500 μL with 300 μL of 1 M ammonium acetate, and the reaction mixture was desalted using a NAP-5 column (Pharmacia), following the manufacturer's instructions. The 1.0 mL eluate was dried in vacuo, and then ethanol precipitated from 100 μL of 0.2 M NaOAc to give purified, terminally phosphorylated DNA. HPLC analysis of this material is shown in Figure 2.

Acknowledgment. We gratefully acknowledge the Analytical Research department of Abbott Laboratories for all spectral measurements.

Regioselective Lithiation and Reaction of [1,2,4]Triazolo[1,5-*a*]pyridine and Pyrazolo[1,5-*a*]pyridine

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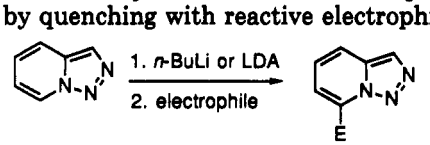
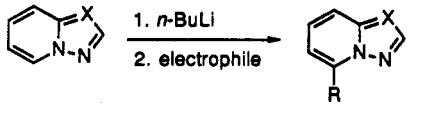
In order to probe the structure–activity relationships in a series of herbicidal 6,5-fused nitrogen heterocycles,[1] I required access to 5-substituted [1,2,4]triazolo[1,5-*a*]-pyridines. A search of the literature[2] failed to reveal methodology which would be flexible enough to allow the rapid introduction of a variety of substituents in the 5-position of this ring system. This Note reports a highly regioselective solution to this synthetic problem.

At the outset I was aware of the reports of Jones et al.[3,4] on the preparation of 7-substituted [1,2,3]triazolo[1,5-*a*]-pyridines by metalation of the parent ring system with either *n*-butyllithium or lithium diisopropylamide followed by quenching with reactive electrophiles[5] (eq 1).



Equation 1

It seemed reasonable that a similar strategy might operate in the [1,2,4]triazolo[1,5-*a*]pyridine ring system. Indeed treatment of a THF solution of [1,2,4]triazolo-[1,5-*a*]pyridine (**1**) with *n*-butyllithium at –78 °C followed by introduction of a variety of electrophiles affords 5-substituted products (**3–8**) in good yields (eq 2, X = N and



Equation 2

1 (X=N)
2 (X=CH)

3-8 (X=N)
10-13 (X=CH)

Table I). The reaction is highly regioselective; no other regioisomers were isolated. Entry 8 of Table I is worth

(1) (a) Selby, T. P. EP-A-353,902. (b) Selby, T. P.; Andrea, T. A.; Denes, L. R.; Finkelstein, B. L.; Fuesler, T. P.; Smith, B. K. In *Synthesis and Chemistry of Agrichemicals*; Baker, D. R., Feynes, J. G., Steffens, J. J., Eds.; ACS Symposium Series, in press.

(2) For a review of triazolopyridine chemistry, see: Jones, Gurnos; Sliskovic, D. R. *Adv. Heterocycl. Chem.* **1983**, *34*, 79–143.

(3) (a) Jones, Gurnos; Sliskovic, D. R. *J. Chem. Soc., Perkin Trans. 1* **1982**, 967. (b) Abaraca, B.; Ballesteros, R.; Mojarred, F.; Jones, Gurnos; Mouat, D. J. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1865.

(4) For more recent work involving lithiation of [1,2,3]triazolo[5,1-*b*]thiazoles, see: Jones, Gurnos; Ollivierre, H.; Fuller, L. S.; Young, J. H. *Tetrahedron* **1991**, *47*, 2861.

(5) Only very reactive electrophiles work in this reaction (e.g. aldehydes, chlorotrimethylsilane, but not iodomethane) since [1,2,3]triazolo-[1,5-*a*]pyridines are prone to ring opening.[2,3]

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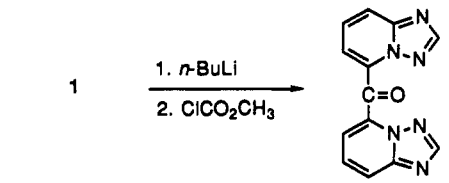
Table I. Reactions of Lithiated 1 and 2 with Electrophiles

compd	X	electrophile	R	yield (%)
3	N	$(EtS)_2$	SEt	82
4	N	MeI	Me	87
5	N	m-CF_3PhCHO	m-CF_3PhC(OH)	83
6	N	TMSCl	TMS	77
7	N	$(BrF_2C)_2$	Br	94
8	N	HCO_2Et	CHO	81
10	CH	$(EtS)_2$	SEt	84
11	CH	MeI	Me	76
12	CH	m-CF_3PhCHO	m-CF_3PhC(OH)	93
13	CH	TMSCl	TMS	87

special note. Jones et al.[3] were unable to obtain the expected aldehyde in the reaction of lithiated [1,2,3]triazolo[1,5-a]pyridine with *N,N*-dimethylformamide, instead the hydroxymethyl compound was isolated in 30% yield. In contrast, aldehyde 8 was obtained in good yield when lithiated 1 was added to ethyl formate, and the reaction was quenched with acid.[6]

The structural assignments for the products obtained from 1 are readily apparent from their proton NMR spectra. The most downfield doublet seen in the spectrum of 1 (8.62 ppm), assignable to the 5-proton, is no longer present in the spectra of 3–8. In addition the melting point for 3 is in good agreement with that previously reported[7] for this compound.

The only electrophile employed which did not give the simple substitution product was methyl chloroformate (eq 3). In this instance ketone 9 was isolated in 71% yield.[8]



Equation 3

9

No evidence of the desired ester was observed in the proton NMR of the crude reaction mixture, even when inverse addition was employed. This result suggests that the ester must be a more reactive electrophile toward lithiated 1 than methyl chloroformate.

The successful metalation of the [1,2,4]triazolo[1,5-a]pyridine ring system suggested a similar approach starting with pyrazolo[1,5-a]pyridine (2). Under similar conditions 7-substituted pyrazolo[1,5-a]pyridines (10–13) were obtained in good yields (eq 2, X = CH, Table I). Again the position of the substitution is apparent from the proton NMR spectra. The most downfield doublet seen in the spectrum of 2 (8.48 ppm), assignable to the 7-proton, is no longer present in the spectra of the products.

These results suggest that the source of regioselectivity in these reactions is chelation of the base with the nitrogen peri to the site of deprotonation.[9] It seems reasonable that this chelation-controlled selective deprotonation may operate in a variety of 1,2-diaza heterocycle systems related to 1 and 2.

(6) In one experiment when the reaction mixture was quenched with water rather than acid a 23% yield of of the hydroxymethyl compound along with a 45% yield of the aldehyde was obtained. The hydroxymethyl compound is most likely formed by a facile Cannizzaro reaction. No attempt was made to isolate any acid from this reaction.

(7) Potts, K. T.; Burton, H. R.; Bhattacharyya, J. *J. Org. Chem.* **1966**, *31*, 260.

(8) In the reaction of lithiated [1,2,3]triazolo[1,5-a]pyridine with ethyl chloroformate Jones et al.[3] isolated the analogous ketone in 19% yield.

(9) A similar suggestion has been made by Jones[3] to explain the selectivity in the lithiation of [1,2,3]triazolo[1,5-a]pyridines.

In conclusion, a simple method has been developed which provides ready access to a variety of 5-substituted [1,2,4]triazolo[1,5-a]pyridines and 7-substituted pyrazolo[1,5-a]pyridines in good yield.

Experimental Section

General. Unless otherwise noted, materials were obtained from commercial supplies and used without further purification. Chlorotrimethylsilane and ethyl formate were distilled from CaH_2 immediately prior to use. 1 and 2 were prepared by literature[10,11] procedures. Melting points (Pyrex capillary) are uncorrected. All NMR spectra were measured in $CDCl_3$ solution unless otherwise noted. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. *J* values are in hertz. Flash chromatography refers to the procedure of Still, Kahn, and Mitra.[12]

General Procedure for the Metalation of 1. To a solution of 1.0 g (8.4 mmol) of 1 in 50 mL of THF at −78 °C was added dropwise 3.7 mL of a 2.5 M solution of *n*-butyllithium in hexanes (9.2 mmol). After 30 min 9.2 mmol of the electrophile was added. After 5 min the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. The reaction was quenched with 5 mL of water and extracted with 100 mL of ethyl acetate. The organic layer was dried (Na_2SO_4), and the solvent was removed with a rotary evaporator. The residue was purified by flash chromatography to afford the product.

5-(Ethylthio)[1,2,4]triazolo[1,5-a]pyridine (3). ^1H NMR: δ 1.46 (t, 3, *J* = 7.3), 3.19 (q, 2, *J* = 7.3), 6.89 (d, 1, *J* = 7.2), 7.48 (dd, 1, *J* = 8.8, 7.2), 7.60 (d, 1, *J* = 8.8), 8.39 (s, 1). IR (KBr): 1610, 1485, 1300, 1200, 775 cm^{-1}. Chromatography solvent: 25% ethyl acetate in hexanes. An analytical sample was obtained by recrystallization from petroleum ether, mp 57–58 °C. Anal. Calcd for $C_8H_9N_3S$: C, 53.61; H, 5.06; N, 23.44. Found: C, 53.57; H, 4.98; N, 23.48.

5-Methyl[1,2,4]triazolo[1,5-a]pyridine (4). ^1H NMR: δ 2.81 (s, 3), 6.88 (d, 1, *J* = 7.0), 7.46 (dd, 1, *J* = 9.0, 7.0), 7.66 (d, 1, *J* = 9.0), 8.37 (s, 1). IR (KBr): 1640, 1555, 1515, 1305, 1195 cm^{-1}. Chromatography solvent: 40% ethyl acetate in hexanes. Mp: 57–58.5 °C (lit.[7] mp 58–59 °C).

α-[3-(Trifluoromethyl)phenyl][1,2,4]triazolo[1,5-a]pyridine-5-methanol (5). ^1H NMR: δ 4.93 (d, 1, *J* = 5.5), 6.42 (d, 1, *J* = 5.5), 6.75 (d, 1, *J* = 7.2), 7.70 (m, 6), 8.39 (s, 1). IR (KBr): 3165, 1325, 1185, 1110 cm^{-1}. Chromatography solvent: 50% ethyl acetate in hexanes. An analytical sample was obtained be recrystallization from hexanes, mp 114–115 °C. Anal. Calcd for $C_{14}H_{10}F_3N_3O$: C, 57.34; H, 3.44; N, 14.33. Found: C, 57.27; H, 3.43; N, 14.17.

5-(Trimethylsilyl)[1,2,4]triazolo[1,5-a]pyridine (6). ^1H NMR: δ 0.48 (s, 9), 7.09 (d, 1, *J* = 6.6), 7.46 (dd, 1, *J* = 9.0, 6.6), 7.75 (d, 1, *J* = 9.0), 8.34 (s, 1). IR (KBr): 3165, 1300, 1245, 815, 795, 760 cm^{-1}. Chromatography solvent: 15% ethyl acetate in hexanes. An analytical sample was obtained by recrystallization from petroleum ether, mp 58–59 °C. Anal. Calcd for $C_9H_{13}N_3Si$: C, 56.51; H, 6.85; N, 21.96. Found: C, 56.41; H, 6.90; N, 22.07.

5-Bromo[1,2,4]triazolo[1,5-a]pyridine (7). ^1H NMR: δ 7.33 (d, 1, *J* = 7.4), 7.46 (dd, 1, *J* = 8.7, 7.4), 7.79 (d, 1, *J* = 8.4), 8.44 (s, 1). IR (KBr): 1625, 1490, 1300, 1190, 785 cm^{-1}. Chromatography solvent: 35% ethyl acetate in hexanes. An analytical sample was obtained by recrystallization from cyclohexane, mp 146–146.5 °C. Anal. Calcd for $C_6H_4N_3Br$: C, 36.39; H, 2.04; N, 21.22. Found: C, 36.33; H, 1.97; N, 20.88.

[1,2,4]Triazolo[1,5-a]pyridine-5-carboxaldehyde (8). In this instance the general procedure was employed with the following changes: Lithiated 1 was added by cannula to a solution of ethyl formate in 10 mL of THF at −78 °C. The reaction was stirred at −78 °C for 1 h and then poured into 50 mL of 1 N HCl. It was necessary to extract the aqueous layer with a liquid–liquid continuous extractor overnight with dichloromethane to obtain the crude product. ^1H NMR: δ 7.69 (dd, 1, *J* = 8.7, 7.0), 7.74 (d, 1, *J* = 7.0), 8.07 (d, 1, *J* = 8.4), 8.51 (s, 1), 10.83 (s, 1). IR (KBr) 1705, 1620, 1305, 1250, 1195 cm^{-1}. Chromatography solvent: 15% 2-propanol in cyclohexane. An analytical sample was obtained

(10) Lin, Y.-i.; Lang, S., Jr. *J. Org. Chem.* **1981**, *46*, 3123.

(11) Bower, J. D.; Ramage, G. R. *J. Chem. Soc.* **1957**, 4506.

(12) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

by recrystallization from cyclohexane/ethyl acetate, mp 168–169 °C. Anal. Calcd for $C_7H_5N_3O$: C, 57.14; H, 3.43; N, 28.56. Found: C, 57.05; H, 3.27; N, 28.44.

Bis([1,2,4]triazolo[1,5-*a*]pyridin-5-yl)methanone (9). The procedure employed was the same as for compound 8. ^{1}H NMR: δ 7.75 (m, 4), 7.94 (s, 2), 8.05 (m, 2). ^{13}C NMR (CD_3SOCD_3): δ 117.52, 120.78, 129.99, 136.20, 149.99, 153.55, 179.65. IR (KBr): 1660, 1615, 1305, 1185 cm^{-1}. Chromatography solvent: 80% ethyl acetate in hexanes. An analytical sample was obtained by recrystallization from ethyl acetate, mp 234.5–236 °C. Anal. Calcd for $C_{13}H_8N_6O$: C, 59.09; H, 3.05; N, 31.80. Found: C, 58.85; H, 2.85; N, 31.45.

Pyrazolo[1,5-*a*]pyridines (10–13) were obtained by a procedure analogous to the general procedure.

7-(Ethylthio)pyrazolo[1,5-*a*]pyridine (10). ^{1}H NMR: δ 1.46 (t, 3, J = 7.4), 3.16 (q, 2, J = 7.4), 6.56 (d, 1, J = 2.2), 6.67 (d, 1, J = 7.0), 7.11 (dd, 1, J = 8.6, 7.0), 7.42 (d, 1, J = 8.6), 8.03 (d, 1, J = 2.2). IR (film): 1615, 1500, 1310, 1210, 775 cm^{-1}. Chromatography solvent: 5% ethyl acetate in hexanes. This compound was obtained as an oil. Anal. Calcd for $C_9H_{10}N_2S$: C, 60.64; H, 5.65; N, 15.71. Found: C, 60.36; H, 5.56; N, 15.70.

7-Methylpyrazolo[1,5-*a*]pyridine (11). ^{1}H NMR: δ 2.76 (s, 3), 6.56 (s, 1), 6.63 (d, 1, J = 6.6), 7.07 (dd, 1, J = 8.3, 6.6), 7.47 (d, 1, J = 8.3), 8.00 (s, 1). IR (film): 1550, 1310, 1185, 780 cm^{-1}. Chromatography solvent: 5% ethyl acetate in hexanes. This compound was obtained as an oil. Satisfactory analytical data could not be obtained for this compound. HRMS: calcd for $C_8H_8N_2$ 132.0687, found 132.0686.

α-[3-(Trifluoromethyl)phenyl]pyrazolo[1,5-*a*]pyridine-7-methanol (12). ^{1}H NMR: δ 6.00 (d, 1, J = 5.6), 6.34 (m, 2), 6.60 (d, 1, J = 2.3), 7.09 (dd, 1, J = 8.9, 7.0), 7.60 (m, 4), 7.84 (s, 1), 7.99 (d, 1, J = 2.3). IR (KBr): 3140, 1330, 1165, 1120, 790 cm^{-1}. Chromatography solvent: 5% ethyl acetate in hexanes. An analytical sample was obtained by recrystallization from hexanes, mp 74–75 °C. Anal. Calcd for $C_{15}H_{11}F_3N_2O$: C, 61.65; H, 3.79; N, 9.59. Found: C, 61.57; H, 3.70; N, 9.56.

7-(Trimethylsilyl)pyrazolo[1,5-*a*]pyridine (13). ^{1}H NMR: δ 0.46, (s, 9), 6.49 (d, 1, J = 2.4), 6.84 (dd, 1, J = 6.7, 1.6), 7.13 (dd, 1 J = 9.0, 6.7), 7.53 (dd, 1, J = 9.0, 1.6), 7.94 (d, 1, J = 2.4). IR (KBr): 1305, 845 cm^{-1}. Chromatography solvent: 1% ethyl acetate in hexanes. This compound was obtained as an oil. Anal. Calcd for $C_{10}H_{14}N_2Si$: C, 63.11; H, 7.41; N, 14.72. Found: C, 63.02; H, 7.25; N, 14.47.

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Keramamide F, a New Thiazole-Containing Peptide from the Okinawan Marine Sponge *Theonella* sp.

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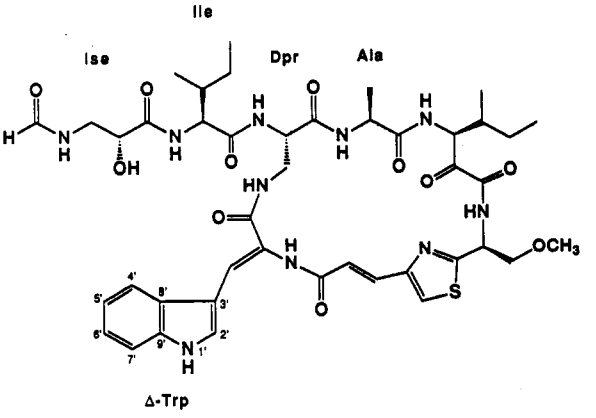
Recently, unique peptides have been isolated from marine sponges[2] and tunicates.[3] We have also reported new cyclic peptides, konbamide[4] and keramamides A–D,[5,6] from Okinawan marine sponges of the genus *Theonella*. Further investigation of extracts of the *Theonella* sponge, from which keramamides B–D have been obtained, resulted in isolation of a novel peptide, named keramamide F (1), containing unusual amino acids such as (*O*-methylseryl)thiazole, α,β-dehydrotryptophan, isoserine, 2,3-diaminopropionic acid, and 3-amino-4-methyl-2-oxohexanoic acid. Here we describe the isolation and structure elucidation of 1.

The MeOH/toluene (3:1) extract of the sponge *Theonella* sp. collected off Kerama Islands, Okinawa, was partitioned between toluene and water. The $CHCl_3$ extract of the aqueous phase was subjected to flash chromatography on a silica gel column followed by gel filtration on a Sephadex LH-20 column and reversed-phase HPLC on ODS to afford keramamide F (1, 0.0001% wet weight) as a colorless solid.



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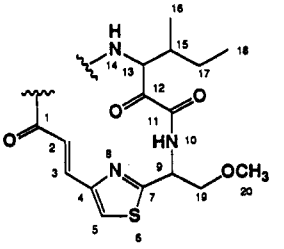

2

The molecular formula of keramamide F (1) was established to be $C_{43}H_{56}N_{10}O_{11}S$ by the HRFABMS data [m/z 921.3912 $(M + H)^+$ for $C_{43}H_{57}N_{10}O_{11}S$, Δ +1.7 mmu]. Its peptide nature was suggested by the ^{1}H NMR spectrum of 1, and the amino acid analysis of the hydrolysate of 1 showed the presence of 1 mol each of alanine (Ala), isoserine (Ise), isoleucine (Ile), and 2,3-diaminopropionic acid

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