Tetrahedron Vol. 45, No 14, pp 4377 to 4382, 1989
Printed in Great Britain

0040-4020/89 $3 00+ 00

The Synthesis and Characterization of 2,3-Methanopyroglutamic Acid

by

Claudio Mapelli♦, Luther F. Elrod♦, Elizabeth M. Holt × and Charles H. Stammer♦*

♦School of Chemical Sciences,Department of Chemistry, University of Georgia, Athens, GA, 30602, and ×Department of Chemistry, University of Oklahoma, Oklahoma City, OK, 73019

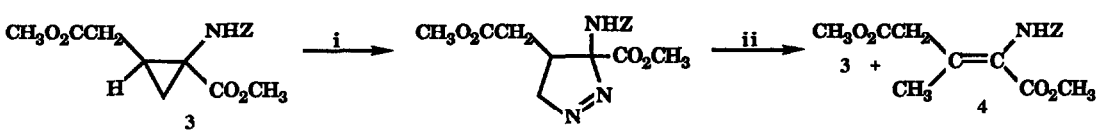
(*Received in USA* 20 *January* 1989)

Abstract: Details of the synthesis of 2,3-methanopyroglutamic acid (**1**), its N-methylamide (**7**) and N-β-naphthylamide (**6**) are reported. An NMR study of the conformation of **7** is discussed and the stability of the amide **6** to pyroglutamylaminopeptidase is detailed. The crystal structure of an alkene (**4**) formed during the pyrolysis of an intermediate pyrazoline (**2**) indicates that the (Z)-configuration is conserved during nitrogen extrusion.

The pyroglutamyl moiety is present at the N-terminus of a large number of biologically active peptides, including thyrotropin releasing hormone (TRH) and lutienizing hormone releasing hormone (LHRH). Our approach to peptide bond stabilization by the incorporation of conformationally constrained 2,3-methanoamino acids (cyclopropane amino acids) into bioactive peptides motivated us to prepare the title amino acid in order to study its biological and conformational properties. In this paper we report the details of the synthesis of this new amino acid[1] and examine the conformation of the peptide mimic, 2,3- methanopyroglutamic acid N-methyl amide using NMR spectroscopy.

The synthesis of 2,3-methanopyroglutamic acid (2,3-MeGlp,**1**) was accomplished via the decomposition of pyrazoline **2** (**Scheme 1**) prepared from the known (Z)-2,3-dehydroglutamic acid dimethyl ester[2] or the known lactone, 2-benzyloxycarbamido-5-oxo-tetrahydrofuran-2-carboxylic acid[3], via the dehydroglutamic acid derivative. The addition of diazomethane to the dehydroglutamic acid derivative gave the thermally quite stable pyrazoline **2** in excellent yields.

Scheme 1



3 2

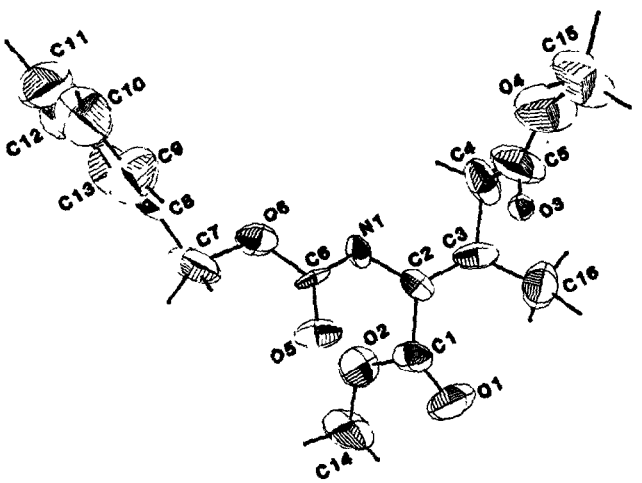
Z=PhCH$_2$OCO-

Reagents: i, hν; ii, PhH, Δ.

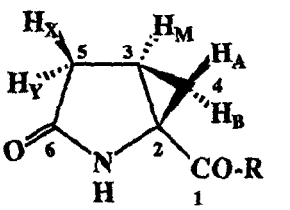
Photolysis of **2** gave the fully blocked 2,3-methanoglutamic acid **3** in excellent yield while thermolysis in boiling toluene converted **2** into an approximately 1:1 mixture of **3** and the alkene **4**. The Z-configuration of **4** was determined by X-ray crystallography (Fig. 1a). The fact that only one olefin having the same configuration as the pyrazoline[4] was formed speaks in favor of a possible concerted hydrogen migration-nitrogen extrusion mechanism[5] in which the

migrating hydrogen atom is *trans* to the leaving nitrogen atom. Since only the Z-cyclopropane **3** (as shown by pyrrolidone ring formation) is formed on photolysis of **2**, the expected 1,3-diradical intermediate[6] must ring close rapidly and without rearrangement.

Figure 1



1a



1, R = OH
5, R = OCH_3
6, R = NHβ–Naph
7, R = $NHCH_3$

1b

The cyclopropane **2** was readily converted into the cyclic ester **5** by hydrogenolysis of the N-benzyloxycarbonyl group followed by heating the free amine in refluxing in 2-butanol, since lower boiling solvents failed to cause rapid ring formation. Base catalyzed hydrolysis of **5** then gave 2,3-methanopyroglutamic acid (2,3-MeGlp, **1**) uneventfully.

The new amino acid **1** was converted into its β-naphthylamide **6**, an analog of the known pyroglutamylaminopeptidase (PAP) substrate, in order to examine its stability to PAP. Even at an amide to enzyme ratio of 10:1, no β-naphthylamine was detected in the solution of the cyclopropane after 48 hours, while the natural substrate was hydrolyzed completely in just under four hours. This result leads us to expect that peptides having 2,3-methanopyroglutamic acid at the N-terminus will have an enhanced biolifetime with increased potency and/or duration of action. The synthesis of the nicely crystalline N-methylamide **7** was accomplished by a standard mixed anhydride coupling[7] with the amine. This compound is a peptide mimic which allows an NMR study of conformations which the cyclopropane derivative may adopt when attached to a peptide chain. The X-ray structure[8] of **7** showed the expected small ψ dihedral angle which allows the carbonyl group to approach a "bisected" conformation maximizing overlap of the carbonyl π orbitals with those of the cyclopropane ring. As in the natural amino acid, the ϕ angle remains fixed by the pyrollidone ring.

The ^1H- and ^{13}C-NMR data for **1** and **7** show well-resolved first order proton spin systems. H_A and H_M are more deshielded in **1** than in **7**, whereas H_B shows the opposite behavior. This suggests that the amide carbonyl adopts slightly different conformations with respect to the cyclopropane ring in **1** and **7**. . The proton chemical shifts were readily assigned on the basis of their coupling constants and it is interesting to note that the vicinal coupling constants, J_{XM} and J_{YM}, of **1** are larger than those of **7** suggesting that the 2-pyrrolidone ring is somewhat more puckered in the N-methyl amide, **7**. These same conformational differences between **1** and **7** may explain the interesting pattern in the

cyclopropane carbon chemical shifts; i. e., C1 and C2 in **7** are downfield of those atoms in **1**, while the reverse is true of the methylenic carbon C4.

NOE Measurements. While the backbone dihedral angle ϕ (about N--C2) of the amide **7** (Fig. 2) is fixed by the bicyclic ring system, the ψ angle is variable because of free rotation about the C1--C2 bond. To gain insight into the preferred conformations of **7** we devised steady-state truncated NOE measurements based on irradiation of the amide NH proton. As can be seen from Fig. 2a, in the "extended" conformation, characterized by a large value of ψ, the amide NH is in close proximity to the H_A, H_B and H_M cyclopropane protons. In a "folded" conformation, which is adopted by 2,3-MeGlp-NHMe in the solid state, a small ψ angle promotes close interaction between the amide and the pyrrolidone NH protons. Irradiation of the amide NH proton in $CDCl_3$ resulted in enhancements of the pyrrolidone NH proton and the H_B cyclopropane proton indicating that both "folded" and "extended" conformations of **7** occur in a nonpolar solvent such as $CDCl_3$. Similar results were obtained in DMSO-d6, but, interestingly, an additional NOE enhancement of the H_A cyclopropane proton was observed indicating a slightly different y angle for the average "extended" conformation of 2,3-MeGlp-NHMe in DMSO-d_6 relative to $CDCl_3$.

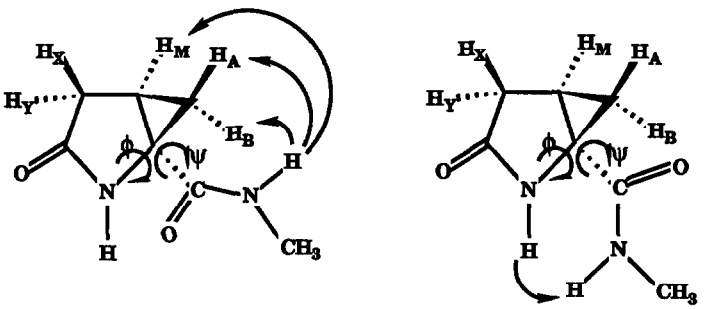


Figure 2. NOE Studies of 2,3-MeGlp.

EXPERIMENTAL

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 297 infrared spectrometer with polystyrene as the standard. ^1H- and ^{13}C-NMR spectra were recorded on a Jeol FX 90-Q, Bruker AM 250 or Varian EM-390 spectrometer, using TMS (^1H), p-dioxane or chloroform-d (^{13}C) as internal standards. DEPT 135 and Quat. Decoupled pulse sequences for determination of carbon multiplicities were run on the Bruker AM 250 spectrometer. 1-D difference proton Overhauser measurements were performed using selective irradiation pulses of 1.0 sec. and spin-recovery delays of 3.0 sec.

Solvents were HPLC grade or were distilled before use. Amino acids, N-benzyloxycarbonylglycine, dicyclohexylcarbo-diimide (DCC), N-methylmorpholine (NMM), ethyl chloroformate, isobutyl chloroformate, benzyl carbamate, and 2-ketoglutaric acid were purchased from Aldrich or Sigma Chemical Company and used without further purification. Thin layer chromatography was performed on Whatman MK6F precoated silical gel plates. TLC plates were visualized using UV light, I_2, 1% ninhydrin reagent, and chlorine-tolidine reagent. The following solvent systems were employed: (I) ethyl acetate/hexanes (1:1), (II) methylene chloride, (III) ethyl acetate, (IV) n-butanol/acetic acid/ water (4:1:5), (V) $CHCl_3$/EtOH (3:2). Flash chromatography was performed using Universal silica gel (230-400 mesh) and 60-200 mesh (Baker) silica gel was used for gravity column chromatography. Photolyses

were carried out with a medium pressure 450 watt mercury lamp and a quartz cell. A uranium glass or Vycor glass sleeve was used to restrict the shorter wavelength emission bands. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia.

Dimethyl N-Benzyloxycarbonyl-2,3-didehydroglutamate.

This compound was prepared from dimethyl 2-ketoglutarate[2,3] in 41% crude yield, m.p., 82-84° C, after silicagel chromatography; ^{1}H NMR ($CDCl_3$) δ: 7.2 (s, 5H, ArH), 6.67 (t, 1H, C=CH), 6.45 (br s, 1H, NH), 5.05 (s, 2H, $ArCH_2$), 3.74 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.28 (d, 2H, CH_2); ^{13}C NMR ($CDCl_3$) 170.6, 164.4, 153.6, 135.6, 128.4, 128.1, 128.0, 126.8, 127.2, 67.3, 52.4, 51.9, 33.5 ppm; IR (KBr) 3250, 1725, 1695, 1520 cm^{-1}; R_f (I) 0.78 and a 0.2g (2%) yield of the lactone, methyl 2-benzyloxycarbonamido-5-oxo-tetrahydrofuran-2-carboxylate : mp 136-138 °C; ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 5H, ArH), 6.34 (br s, 1H, NH), 4.95 (s, 2H, $ArCH_2$), 3.70 (s, 3H, OCH_3), 2.6 (m, 4H, CH_2CH_2); IR (KBr) 3300, 1780, 1760, 1700 cm^{-1}; R_f (I) 0.36.

Anal. Calc'd. for $C_{14}H_{15}NO_6$: C 57.34, H 5.16, N 4.78. Found: C 57.22, H 5.18, N 4.70.

Methoxycarbonylmethyl-3-benzyloxycarbamido-3-carbomethoxy-Δ^1-pyrazoline (2).

To a cold, stirred solution of 6.0 g (19.5 mmol) of dimethyl N-benzyloxycarbonyl-2,3-didehydroglatamate[2] in 200 mL of methylene chloride was added dropwise a solution of 3 g (70 mmol) of diazomethane in 150 mL of ether. After 2 hr at 0°, the reaction mixture was stirred overnight at room temperature. Excess diazomethane was quenched by addition of calcium chloride. The solution was filtered and the filtrate was evaporated under reduced pressure. The residue was triturated with ether to afford 5.4 g (80%) of **2**: mp 72-74 °C; ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 5H, ArH), 5.6 (br s, 1H, NH), 4.98 (s, 2H, $ArCH_2$), 4.7 (m, 2H, CH_2), 2.90 (t, 1H, CH), 2.41 (d, 2H, CH_2); ^{13}C NMR ($CDCl_3$) 172.6, 168.1, 154.0, 135.5, 128.6, 128.3, 128.0, 100.6, 83.8, 67.3, 54.1, 51.9, 33.3, 32.0 ppm; IR (KBr) 3370, 1730, 1510, 1450, 1440 cm^{-1}; R_f (I) 0.62.

Anal. Calc'd. for $C_{16}H_{19}N_3O_6$: C 55.01, H 5.48, N 12.03. Found C 55.10, H 5.49, N 12.00.

Dimethyl N-Benzyloxycarbonyl-2,3-methanoglutamate[2b] (3).

Method A. A solution of 3.0 g (8.6 mmol) of **2** in methylene chloride (300 mL) was photolyzed with a 450 watt Hanovia medium pressure mercury lamp for 1 h. and evaporated under reduced pressure. The residue was purified by flash chromatography using ethyl acetate-hexanes (1:1) and 2.7 g (98%) of **3** obtained as an oil: ^{1}H NMR ($CDCl_3$) δ 7.31 (s, 5H, ArH), 5.58 (br s, 1H, NH), 5.08 (s, 2H, $ArCH_2$), 3.67 (s, 3H, OCH_3), 2.4 (m, 2H, CH_2), 1.85 (m, 1H, CH), 1.1 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$) 172.6, 172.4, 156.9, 136.1, 128.2, 127.8, 66.7, 52.3, 51.7, 37.7, 23.8, 22.6 ppm; IR (NaCl) 3320, 2930, 1730, 1510 cm^{-1}; R_f (I) 0.57.

Method B. A solution of 3.0 g (8.6 mmol) of **2** was refluxed for 3 h in benzene. After thin layer chromatographic analysis (TLC) indicated that no reaction had occurred, the solvent was evaporated and the residue was dissolved in 100 mL of toluene which was refluxed overnight. TLC analysis indicated the formation of two products which, after removal of the toluene, were separated by flash chromatography using ethyl acetate-hexanes (1:2) as eluant. The first product was identified as the cyclopropane derivative **3** (43%) and the second proved to be dimethyl 3-methyl-2,3-didehydroglutamate **4**, isolated in 47% yield: mp 67-68 °C; ^{1}H NMR ($CDCl_3$) δ: 6.60 (br s, 1H, NH), 5.04 (s, 2H, $ArCH_2$), 3.70 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.20 (s, 2H, CH_2), 2.08 (s, 3H, CH_3); IR (KBr) 3290, 1730, 1690, 1520 cm^{-1}; R_f (I) 0.45.

Anal. Calc'd. for $C_{16}H_{19}NO_6$: C 59.81, H. 5.96, N 4.36. Found: C 59.57, H 5.97, N 4.29.

X-Ray Crystallography. A crystal of $C_{16}H_{19}NO_6$ (**4**) was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least squares reminement of the best angular positions for fifteen independent reflections (2θ>15°) during normal allignment procedures using molybdenum radiation (γ = 0.71069A). Data, (1261 points) were collected at room temperature using a variable scan rate, a θ 2θ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 45.0°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after

every 97 reflections and as the intensities of these reflections showed less that 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects. After removal of space group forbidden and redundent data, observed data, (728 points) ($I>3.0\sigma(I)$) were used for solution and refinement. The structures were solved for carbon, nitrogen, and oxygen positions using direct methods.[9] Least squares refinement[10] converged with anisotropic thermal parameters. The hydrogen atom bonded to N1 was not apparent from a difference Fourier synthesis. The remaining 18 hydrogen positions were calculated using appropriate geometry and a C-H distance of 0.97Å. Hydrogen positions were included in the final refinement with isotropic thermal parameters but held invariant. A difference Fourier revealed no electron density of interpretable level. Scattering factors were taken from Cromer and Mann.[11] The final cycle of refinement - function minimized $\Sigma(|F_o| - |F_c|) \times 100$. Unit weights were used until the final cycles of refinement when weights equal to $1/\sigma F$ were introduced. $R_w = 10.2\%$ analysis for the final results revealed large temperature parameters for atoms, C4, 03, 04 and C15, indicative of rotation of the ester group about the C3-C4 bond. The determined thermal ellipsoid for atom, 03, has been replaced by an isotropic sphere in the Figure to facilitate observation of the connectivity in this ester group.

Methyl 2,3-methanopyroglutamate (5).

Hydrogen gas was passed into a mixture of 2.5 g (7.8 mmol) of **3**, 0.25 g of 5% Pd/C, and acetic acid (0.3 mL) in 100 mL of methanol at atmospheric pressure for 1 h. The catalyst was removed by filtration and the residue obtained by evaporation was dissolved in 100 mL of 2-butanol and the solution was refluxed overnight. After removal of the solvent under reduced pressure, the residue was chromatographed using ethyl acetate-hexanes (5:1) as eluant. The product was triturated with ether to afford 0.9 g (75%) of **5**: mp 83-84°C; ^{1}H NMR ($CDCl_3$) δ 7.32 (s, 5H, ArH), 4.75 (s, 3H, OCH_3), 3.80 (dd, 1H, CH), 3.45 (dd, 1H, CH), 2.14 (m, 1H, CH), 1.8 (dd, 1H, HCH), 0.95 (dd, 1H, HCH); ^{13}C NMR ($CDCl_3$) 176.4, 170.9, 52.5, 40.5, 34.2, 25.8, 20.8 ppm; IR (KBr) 3410, 3215, 1730, 1695 cm^{-1}; R_f (45) 0.35.

Anal. Calc'd. for $C_7H_9NO_3$: C 54.18, H 5.85, 9.03. Found: C 54.23, H 5.89, N 8.98.

2,3-Methanopyroglutamic acid (1). To a solution of **5** (1.20g,7.7 mmol) in MeOH (5 ml) was added 4.8 ml of 2N NaOH. After 1h the methanol was evaporated and the solution was acidified to pH 2 with conc. HCl. The precipitated solid was washed with cold water and dried, to give 1.02g of crude **1** which was dissolved in hot 2-propanol (25 ml). Addition of ether (25 ml) and refrigeration afforded 0.87g (88%) of pure **1** as colorless prisms, mp 200-202° C, R_f (IV) 0.53. ^{1}H NMR (MeOH-d_4) δ: 0.86 (t, H_A, J_{AB} =-5.3, J_{AM} = 5.4), 1.69 (dd, H_B, J_{BM} = 8.8), 2.05 (dddd, H_M, J_{XM} =1.2, J_{YM} =7.3), 2.23 (dd, H_X, J_{XM} = 1.2), 2.71 (dd, H_Y, J_{XY} =18.1). ^{13}C NMR (MeOH-d_4) δ: 174.0(C_1), 43.8(C_2), 20.2(C_3), 24.4(C_4), 33.8(C_5), 179.3(C_6).

Anal. Calcd. for $C_6H_6NO_3$: C 51.06, H, 5.00, N, 9.93. Found: C, 50.94, H, 5.03, N, 9.90.

2,3-Methanopyroglutamyl-β-Naphthylamide (6)

To a solution of **1** (100 mg, 0.7 mmol) and TEA (0.7 mmol, 99 ml) in CH2Cl2 (2.0 ml) and DMF (0.2 ml) was added oxalyl chloride (0.78 mmol, 68 ml) at -30°C under a nitrogen atmosphere. The solution was stirred at 0°C for 1 h and after evaporation, solution of b-naphthylamine (Sigma, 132 mg, 0.9 mmol) and TEA (0.7 mmol, 99 ml) in DMF (1 ml) was added to the oily residue. The reaction mixture was stirred overnight at room temperature, dissolved in EtOAc (50 ml) and washed with IN KHSO4 (3 x 10 ml), brine, 10% NaHCO3 (3 x 10 ml) and brine. The solution was dried (anh. Mg SO4) filtered and evaporated to give a crude product which was purified by chromatography on silica gel (10 g) using CHCl3/EtOAc (2:1). The fractions (180-200 ml) containing the product were pooled and evaporated to give 19 mg (10%) of pure **6**, mp 194-195°C, Rf (CHCl3-EtOAc (2:1) 0.22; 1H-NMR (acetone-d6): d 0.85-0.96 (t, 1H, —H), 1.93-2.20 (m, 2H, —H), 2.42-2.89 (m, 2H, CgH2), 7.27-7.79 (m, 7H, ArH), 8.39 (br s, 1H, NH), 9.25 (br s, 1H, CONH).

FAB-MS: MH+ calcd, 267. Found: 267.

2,3-Methanopyroglutamic Acid N-methyl amide (7). To a solution of 1 (0.20g, 1.42 mmol) and 4-methylmorpholine (0.16 ml, 1.42 mmol) in DMF (2 ml), cooled to -15° C, was added i-butylchloroformate (0.20 ml, 1.56 mmol). After stirring for 30 min at -15° C, a solution of CH_3NH_2·HCl (115 mg, 1.70 mmol) and 4-methylmorpholine (0.19 ml, 1.70 mmol) in dichloromethane (2 ml) was added. The reaction mixture was stirred overnight at room temperature when evaporation of the solvents afforded a solid residue which was chromatographed using $CHCl_3$/EtOH (3:2). The fractions (100-190 ml) containing the product were pooled and evaporated to give 0.19g (88%) of 7. Recrystallization from ethyl acetate afforded 7 as colorless prisms, mp 141-142° C, R_f (V) 0.76. ^1H NMR (MeOH-d_4) δ: 0.84 (t, H_A, J_{AB} = -5.3, J_{AM} = 5.4), 1.82 (dd, H_B, J_{BM} =8.8), 1.95 (dddd, H_M, J_{XM} = 0.8, J_{YM} =6.9), 2.33 (dd, H_X, J_{XM} = 0.8), 2.81 (dd, H_Y, J_{YM} = 6.9, J_{XY} = 18.3), 2.79 (s, CH_3). ^{13}C NMR (MeOH-d_4) δ: 172.5 (C_1), 45.0 (C_2), 21.1 (C_3), 23.7 (C_4), 35.1 (C_5), 180.3 (C_6), 26.8 (CH_3).

Anal. Calcd. for $C_6H_6NO_3$: C 51.06, H 5.00, N 9.93. Found: C 50.94, H 5.03, N 9.90.

Pyroglutamyl Amino Peptides (PA) Digestion of 2,3-MeGlp-β-naphthylamide (6).

A solution of PAP (7.7 mg of lyophilizate, 0.05 units, Boehringer-Mannheim) in 200 ml of phosphate buffer (0.1 M Na2HPO4, pH 6.7), made 5% in glycerol, was incubated at 37°C for 3 min. To this buffer was added 0.5 mmol of 6 in 25 ml methanol. The reaction progress was monitored by TLC using a CHCl3/EtOH/HOAc (90:10:1) solvent system, in which the Rf's of 6 and β-naphthylamine differed by 0.3 units and uv light was used for visualization. No β-naphthylamine was detected over a period of 72 h indicating no enzymatic hydrolysis. In a simultaneous experiment, Glp-β-naphthylamide (Sigma) was hydrolyzed quantitatively in less than four hours under the same conditions.

REFERENCES

(1) The synthetic approach detailed in this paper has been previously communicated; see L. F. Elrod, Holt, E. M., Mapelli, C., Stammer, C. H., 1988, 252.

(2) (a) C. Shin, Y. Yonezawa and E. Watanabe, Tetrehedron Lett., **1985**, *26*, 85; (b) T. Wakamiya, Y. Oda and T. Shiba, *ibid.*, **1986**, *27*, 2143.

(3) J. I. Baldwin, J. D. Che and L. I. Kruse, Tetrehedron, **1985**, *41*, 5241.

(4) Even though our attempts to determine the configuration of the crystalline pyrazoline 5 by X-ray crystallography failed, the Z-configuration of 5 can be safely assumed based on the careful work of Huisgen; see Bihlmaier, W. Geittner, J., Huisgen, R. and Reissig, H-U., Heterocyles, **1978**, *10*, 147; see also Deleux, J. P., Leroy, G. and Weiler, J., Tetrahedron, **1973** *29*, 1135.

(5) (a) McGreer, D. E. and Wu, W. S.; Can. J. Chem., **1967**, *45*, 461; (b) McGreer, D. E., McKinley, J. W., *ibid.*, **1971**, *49*, 105; (c) McGreer, D. E., Masters, I. M. E., Liu, M. T. H., J. Chem. Soc., Perkin II, **1975**, 1791; (d) see Ref. 4.

(6) (a) Engel, P. S., Chem. Rev. **1980**, *80*, 99; (b) Adam, W., Oppenlander, T. and Zang, G., J. Org. Chem., **1985**, *50*, 3303.

(7) G. W. Anderson, J. E. Zimmerman, and F. M. Callahan, **1967**, *89*, 5012.

(8) C. Mapelli, L. F. Elrod, F. L. Switzer and C. H. Stammer, Biopolymers, **1989**, in press.

(9) Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., DeClerq, J. P. and Woolfson, M. M., University of York, England, 1980.

(10) Stewart, J. M., Ed., The XRAY System - Version of 1980, Technical Report TR446 of the Computer Center, University of Maryland, College Park, Maryland.

(11) Cromer, D. T. and Mann, I. B., Acta Cryst., A24, 321-324 (1968).