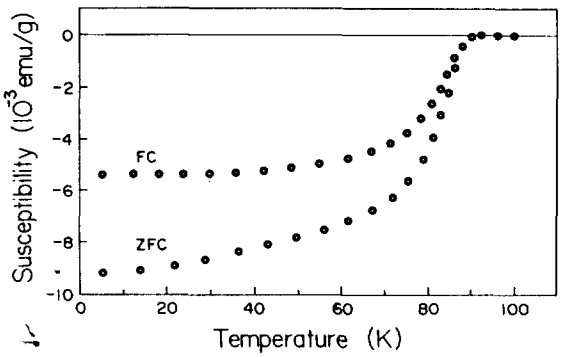

Figure 2. Magnetic susceptibility versus temperature for $HgBa_2CuO_{4+x}$ material with an applied magnetic field of 20 G.

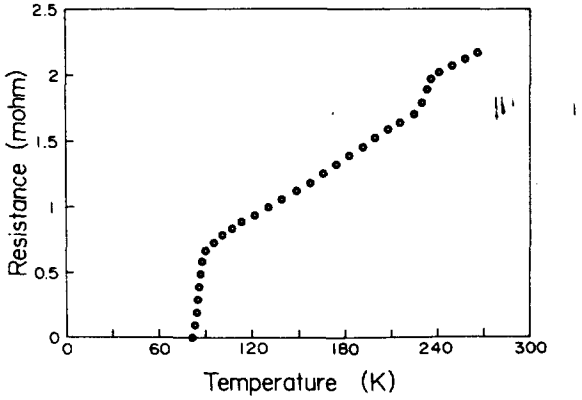

Figure 3. Resistance versus temperature for $HgBa_2CuO_{4+x}$ compound.

reaches about 42%. The resistance versus temperature for the same $HgBa_2CuO_{4+x}$ compound which was measured with use of a standard four probe method is shown in Figure 3. This displays a superconducting transition at 92 K and reaches zero at 84 K, which is agree well with the magnetic susceptibility data.

In summary, we have synthesized superconducting $HgBa_2CuO_{4+x}$ compound with use of Ba_2CuO_{3+x} precursor. Isolation of pure $HgBa_2CuO_{4+x}$ samples largely depends on precursor materials and synthetic conditions, especially on moisture in air. We found that the $HgBa_2CuO_{4+x}$ has a tetragonal *P4/mmm* symmetry with lattice parameters $a=3.8868$ (2) Å and $c=9.4886$ (1) Å, and shows a bulk T_c of about 92 K. Currently, we are attempting to isolate structurally homologous series of $HgBa_2Ca_{n-1}Cu_nO_{2n+2+x}$ ($n=2$ and 3) compounds.

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A Synthetic Approach to 2-Piperidylglycine (II)[1]

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Heterocyclic derivatives of amino acids show some interesting pharmacologic properties. 2-Piperidylglycine (**1**) will be a model compound for the synthesis of streptolutin (**2**) and antitumor agent 593A (**3**).[2] Diastereoisomeric 2-piperidylglycine has been synthesized by extending Lowe's method for preparing nuclear analogues of penicillins,[3] and by alkylation of glycine equivalent to C-2 position of piperidine ring.[1]

We now report a straight forward synthesis of both diastereoisomers of α-amino-2-piperidineacetonitrile **8**. Protected 2-piperidinecarbaldehydes (**5**) were obtained by the protections of 2-piperidinemethanol (**4a**) with benzyl (Bn), benzyloxycarbonyl (Cbz) and t-butoxycarbonyl (t-Boc) group followed by Swern oxidation.[5] Treatment of 2-piperidinecarbaldehyde **5** with KCN[6] afforded α-hydroxy-2-piperidineacetonitrile **6**.[7]

The α-hydroxy-2-piperidineacetonitrile **6** was reacted with ammonia in methanol to give α-amino-2-piperidineacetonitrile **8**.

In Cbz case, the formation of bicyclic carbamate **7** was observed in THF-H_2O, and suppressed in the presence of ammonium chloride. The ratio of threo to erythro was about

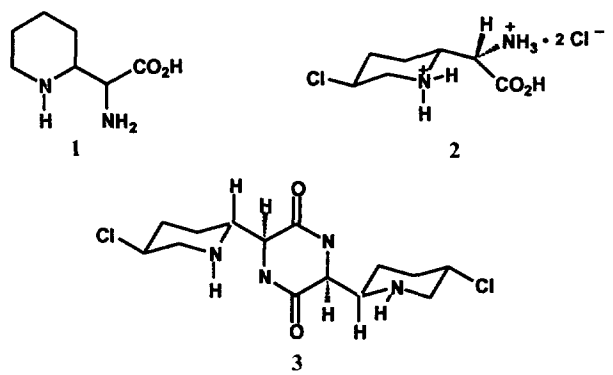

Figure 1.

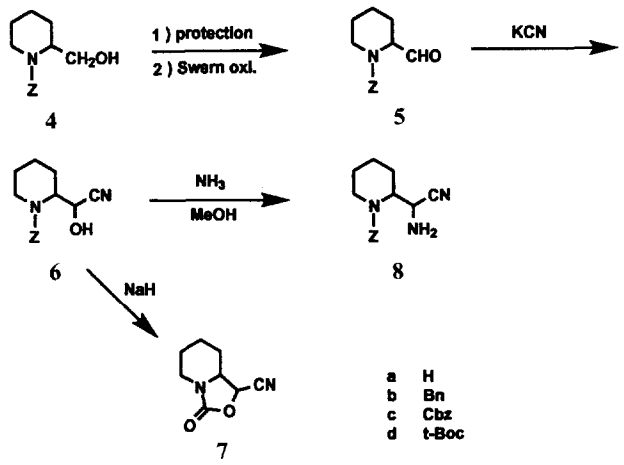

Figure 2.

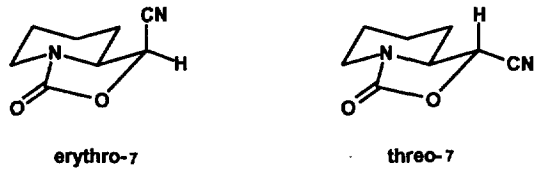

Figure 3.

1 : 2 in the case of cyanohydrin **6**.[8] This result is different from the fact that the threo isomer was major in the reaction of piperidinecarbaldehyde **5** with phenyl magnesium bromide.[7,9] The stereochemistry was assigned by the chemical shift of the proton next to cyano in bicyclic carbamate **7**, which was formed in the reaction of cyanohydrin **6** with sodium hydride. The major isomer shown 5.2 ppm (equatorial) was expected to be the erythro isomer, while the minor isomer shown 4.7 ppm (axial) was the threo one.

The addition of Grignard reagent was rationalized in terms of chelation control, while the addition of cyanide was interpreted in terms of Cram's rule. The difference in reactivity depends on the solvent effect; the Grignard reaction carried out in ether so the chelation was possible, while the cyanide addition ran in THF-H_2O so the chelation was ineffective.

The stereochemistry of the diastereoisomer **8b** was characterized by comparing their proton nmr spectra in 2M DCl/D_2-O with spectra for threo- and erythro-2-piperidylglycine respectively.[3] One isomer shown a narrow doublet (J=3.5 Hz) for α-H was expected to be the threo isomer, while the other shown a relatively wide doublet (J=6.5 Hz) was the erythro one.[10]

Extending of this work and stereoselective synthesis of 2-piperidylglycine are in progress.

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8. The diastereoisomeric ratio was checked by HPLC for acylated cyanohydrin **6c**, and aminocyanide **8c**.
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10. **Experiment.**
[1]H-NMR spectra were recorded with a Varian EM-360L 60-MHz instrument with $CDCl_3$ as solvent and TMS as an internal standard.
***N*-Benzyl-2-piperidinemethanol (4b)**; [1]H-NMR δ 1.2-2.0 (m, 6H), 2.1-3.0 (m, 4H), 3.2, 4.0 (ABq, J=13 Hz, 2H), 3.55 (d, 1H), 3.7 (d, 1H), 7.2 (s, 5H). ***N*-Benzyloxycarbonyl-2-piperidinemethanol (4c)**; [1]H-NMR δ 1.55 (m, 6H), 2.3 (t, 1H), 2.6-3.3 (m, 1H), 3.4-4.5 (m, 4H), 5.06 (s, 2H), 7.25 (s, 5H). ***N*-(*tert*-Butoxycarbonyl)-2-piperidinemethanol (4d)**; [1]H-NMR δ 1.45 (s, 9H), 1.6 (bs, 6H), 2.4 (t, 1H), 2.6-3.2 (m, 1H), 3.4-4.5 (m, 4H).
General Procedure for the Preparation of Aldehyde 5. To a solution of oxalyl chloride in CH_2Cl_2 was added dropwise a mixture of DMSO and CH_2Cl_2 at −60 ℃. The reaction mixture was stirred for 10 min and a solution of alcohol **4** was added dropwise. After stirring for 15 min at −60℃, triethylamine was added dropwise. The reaction mixture was allowed to warm to room temperature. A standard work-up gave aldehyde **5**.
***N*-Benzyl-2-piperidinecarbaldehyde (5b**, 85%); [1]H-NMR δ 1.1-1.9 (m, 6H), 2.0 (m, 1H), 2.8 (m, 2H), 3.25, 3.70 (ABq, J=13 Hz, 2H), 7.2 (s, 5H), 9.45 (d, 1H). ***N*-Benzyloxycarbonyl-2-piperidinecarbaldehyde (5c**, 87%); [1]H-NMR δ 1.2-2.4 (m, 6H), 2.6-3.3 (m, 1H), 4.05 (bd, 1H), 4.7 (m, 1H), 5.1 (s, 2H), 7.25 (s, 5H), 9.46 (s, 1H). ***N*-(*tert*-Butoxycarbonyl)-2-piperidinecarbaldehyde (5d**, 89%); [1]H-NMR δ 1.4-2.3 (m, 15H), 2.6-3.2 (m, 1H), 3.9 (bd, 1H), 4.5 (m, 1H), 9.46 (s, 1H).
General Procedure for the Preparation of Cyanohydrin 6. To a solution of KCN and NH_4Cl in H_2O was added dropwise a solution of aldehyde **5** in THF at 0℃. After stirring for 30 min at 0℃, a standard work-up gave cyanohydrin **6**.
***N*-Benzyl-α-hydroxy-2-piperidineacetonitrile (6b**, 72 %); [1]H-NMR δ 1.3-2.0 (m, 6H), 2.4-3.1 (m, 2H), 3.1-4.1 (m, 4H), 4.4-4.7 (m, 1H), 7.2 (s, 5H). ***N*-Benzyloxycarbonyl-α-hydroxy-2-piperidineacetonitrile (6c**, 94%); [1]H-NMR δ 1.3-2.1 (m, 6H), 2.6-3.3 (m, 1H), 3.8-4.9 (m, 4H), 5.1 (s, 2H), 7.25 (s, 5H). ***N*-(*tert*-Butoxycarbonyl)-α-hydroxy-2-piperidineacetonitrile (6d**, 93%); [1]H-NNR δ 1.2-2.2 (m, 15H), 2.5-3.1 (m, 1H), 4.0 (bd, 1H), 4.2-4.9 (m, 2H), 5.1 (d, 1H).
Formation of Bicyclic Carbamate 7. To a slurry of sodium hydride (prewashed) in THF was added a solu-

tion of cyanohydrin **6** in THF at room temperature. After stirring for 2h, a standard work-up gave a mixture of erythro-7 and threo-7 in 42% yield.

threo-8-Oxa-7-cyano-1-azabicyclo[4.3.0]nonan-9-one (threo-7); ^{1}H-NMR δ 1.0-2.4 (m, 6H), 2.9 (m, 1H), 3.6-4.1 (m, 2H), 4.7 (d, J=5 Hz, 1H). **erythro-8-Oxa-7-cyano-1-azabicyclo[4.3.0]nonan-9-one (erythro-7)**; ^{1}H-NMR δ 1.0-2.3 (m, 6H), 2.8 (m, 1H), 3.5-4.2 (m, 2H), 5.2 (d, J=8 Hz, 1H).

General Procedure for the Preparation of Aminocyanide 8. A solution of cyanohydrin **3** in methanol was cooled and saturated with ammonia gas. After stirring for 2 days at room temperature, the excess ammonia was expelled by N_2, and the methanol was evaporated. **threo-*N*-Benzyl-α-amino-2-piperidineacetonitrile (threo-8b**, 35%); ^{1}H-NMR (2M DCl/D_2O) δ 1.3-2.3 (m, 6H), 2.8-3.3 (m, 2H), 3.8 (m, 1H), 4.1, 4.6 (ABq, J=12 Hz, 2H), 5.4 (d, J=3.5 Hz, 1H), 7.25 (s, 5H). **erythro-*N*-Benzyl-α-amino-2-piperidineacetonitrile (erythro-8b**, 17%); ^{1}H-NMR (2M DCl/D_2O) δ 1.3-2.3 (m, 6H), 2.8-3.3 (m, 2H), 3.85 (m, 1H), 4.15, 4.65 (ABq, J=12 Hz, 2H), 5.25 (d, J=6.5 Hz, 1H), 7.30 (s, 5H). ***N*-Benzyloxycarbonyl-α-amino-2-piperidineacetonitrile (diastereoisomer, 8b**, 29%); ^{1}H-NMR δ 1.2-2.1 (m, 8H), 2.4-3.1 (m, 1H), 3.8-4.7 (m, 3H), 5.1 (s, 2H), 7.3 (s, 5H).

NMR Studies of the Psoralen Photobinding Sites of the d(GGGTACCC) and d(GGGATCCC) Duplex in Solution

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The interactions between psoralen and DNA take place in the formation of covalent photobinding of complexed psoralens to pyrimidine bases of DNA.[1,2] There is an optimal site for these interactions. Chart I shows the sequences of the two octamers which are referred to as 5′-TA or 5′-AT where they are distinguished from each other by the difference in their sequences. Although it is generally known that both 5′-TA and 5′-AT sequences are psoralen-DNA interstrand photo-cross-linked sites,[3,4] it has been found that 5′-TA sequences are highly preferred over 5′-AT sequences.[5,6] The

5′-TA	5′-AT
GGGTACCC	GGGATCCC
12344321	12344321
CCCATGGG	CCCTAGGG

Chart 1.

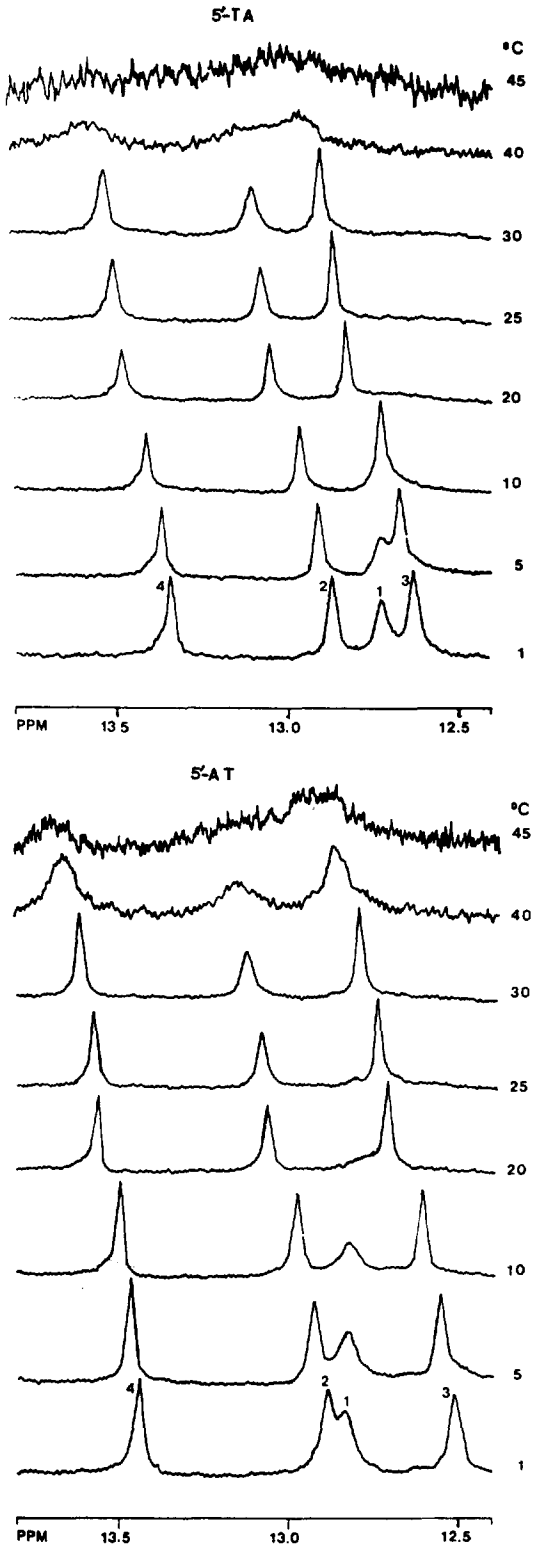

Figure 1. The 500-MHz imino proton spectra of the d(GGGTACCC)(left) and d(GGGATCCC)(right) in 2 mM phosphate, 200 mM NaCl, H_2O, pH 7 between 1 and 45℃. The imino proton assignments to specific base pairs are designated over the resonances.

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