

ammonia lyase) which operate with the removal of  $\beta$ -protons. A general method has been investigated for the synthesis of the required stereospecifically-labelled substrates which involves the stereospecific ring fission of an aziridine intermediate. This approach is illustrated by a new method for the synthesis of (2SR, 3SR)-[3- $^2$ H<sub>1</sub>]phenylalanine.

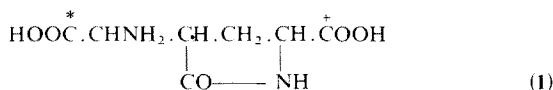
### *Penmacric Acid: a New Dicarboxylic Amino Acid from Seeds of the tropical Legume*

#### *Pentaclethra macrophylla\**

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Aqueous extract of endosperm subjected to analysis by Moore and Stein cation-exchange chromatography showed a novel ninhydrin-reactive zone close to aspartic acid. This is a major free amino acid *ca* 0.03% of endosperm dry matter. Successive displacement (ammonia on Dowex-50) and gradient-elution (Dowex-1 with acetic acid gradient) chromatography of extract on a preparative scale yielded a crystalline product. The proposed structure (I)



is supported by evidence as follows. High-resolution mass spectrometry of the *N*-acetyl dimethyl ester indicated  $M = C_{11}H_{16}N_2O_6$ . The low-resolution MS of the free acid had common features with that of pyrrolidonecarboxylate. Permethylation introduced two further methyl groups. IR spectra of the free amino acid and pyrrolidonecarboxylic acid showed similarities. Electrophoretic behaviour and PMR spectrum ( $D_2O$ ) of the free amino acid were consistent with above structure. On acid-alkali titration, chemical shifts for the  $\alpha$ -H atoms changed with ionization of  $-\text{COOH}$  ( $pK \sim 2.4$ ) and  $-\text{COOH}$  ( $pK \sim 3.4$ ). Accompanying  $[\alpha]_D$  changes suggest L-configuration of both  $\alpha$ -C atoms.

\* See also following abstract.

### *New Free Amino acids from Leguminosae\**

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From the legume, *Pentaclethra macrophylla*, a Mimosaceae from Central Africa, we have isolated a new acid with a very unexpected structure: 3(R) [1(S)-aminocarboxymethyl]-2-pyrrolidone-5(S)-carboxylic acid [1]. Some years ago, Krauss and Reinbothe detected only by TLC a large quantity of dichrostachinic acid in these seeds. As we wanted to isolate this amino acid, an extract of the seeds was subjected to 2D chromatography on paper and to HVE. On a 2D chromatogram, we found at the same place as dichrostachinic acid a grey-blue nin-

hydrin spot but this compound reacted only weakly with the reagent for sulfur amino acids. Also, on electrophoresis at pH 3.6, the substance moved between aspartic and dichrostachinic acid added as markers. From the results, we decided to isolate this compound on a basic ion-exchange resin. The structure has been established by chemical and spectroscopic methods (IR,  $^{13}C$  and  $^1H$  NMR). The absolute configuration at C1' is  $-S$  and is inferred from the results of the circular dichroism measurements. The absolute configuration of C3 and C5 was established by X-ray diffraction [2].

Treatment of this amino acid with HCl transforms it to three new compounds which have been isolated. Their structures are: 2,5-diamino-3-carboxyadipic acid, 3-amino-4,6-carboxypiperidone carboxylic acid and 3-amino-5,6-carboxy-2-piperidone carboxylic acid.

Two years ago, we isolated from leaves of *Calliandra haematocephalla* (Mimosaceae) a disubstituted derivative of pipecolic acid: 2(S)-carboxy-4(R),5(S)-dihydroxypiperidine or *cis*-4,5-dihydroxypipecolic acid [3]. Its absolute configuration was determined by X-ray diffraction [4]. This imino acid coexists with proline, pipecolic acid, *trans*-4-hydroxypipecolic acid and with a new imino acid which has now been isolated in relatively large quantities. This compound gives a red ninhydrin color and it moves on a 2D chromatogram just near 4-hydroxypipecolic acid. By HCl hydrolysis, this neutral compound is transformed to acetic acid and to a basic imino acid which has now been separated and identified as 4-aminopipecolic acid, by 2-DPC and NMR spectroscopy. On deamination, this pipecolic acid derivative gives 4-hydroxypipecolic acid. From these results, this new compound was identified as 4-acetylaminopipecolic acid. The configuration at C(4) has been tentatively assigned as *trans* by NMR and IR spectroscopy. This is the fourth amino derivative of an imino acid found in the plant kingdom.

Recently we have identified a large number of imino acids in the leaves of the legume, *Derris elliptica*. This legume contains proline, pipecolic acid, *trans*-5-hydroxypipecolic acid, *trans*-4-hydroxypipecolic acid and two other isatin-reacting compounds which give a blue-green color with ninhydrin. The mixture of imino acids has been isolated through the ether soluble *N*-nitroso acids. Hydrolysis of the mixture following by separation on cation exchange resin gives first the two new imino acids. One of them has been identified as *cis*-4,5-dihydroxypipecolic acid isolated also from *Calliandra*. The second compound was expected to be a diastereoisomer. In order to confirm this hypothesis we synthesized the four stereoisomers of 4,5-dihydroxypipecolic acid. This was achieved by specific hydroxylation of L-baikaine (4,5-dehydropipecolic acid). We used for the *cis* isomers:  $H_2O_2$ - $OsO_4$  and for the *trans* isomers  $H_2O_2$  performic acid. These four isomers have been studied by IR and NMR spectroscopy. One of the *trans* isomers has been studied by X-ray diffraction. Comparisons with the synthetic compounds showed that the second new natural imino acid was 2(S)-carboxy-4-(S)-dihydroxypiperidine or *trans*-4,5-dihydroxypipecolic acid.

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2. Dupont, L., Dideberg, O. and Welter, A. *Acta Cryst.* sous presse.
3. Marlier, M., Dardenne, G. and Casimir, T. (1972) *Phytochemistry* **11**, 2597.
4. Evrard, G., Durant, F. and Marlier, M. (1972) *Cryst. Struct. Comm.* **1**, 215.

\* See also preceding abstract.