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Isolation and Structure of an Unusual Cyclic Amino Alditol from a Legume

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Summary 1,5-Dideoxy-1,5-imino-D-mannitol, (**1**), has been isolated as an unusual constituent of *Lonchocarpus sericeus* and *L. costaricensis*; its relative conformation has been determined by ^1H and ^{13}C n.m.r. spectroscopy and its absolute configuration determined by the benzoate chirality method.

VARIOUS parts of the legume *Lonchocarpus sericeus* (Poir), H.B. and K., a native of the West Indies and tropical America, are reported to have insecticidal and piscicidal properties, and bark extracts are used to treat parasitic skin infections.¹ The seeds were examined (L. F. and E. A. B.) as part of a programme concerned with the distribution of potentially physiologically active compounds in Leguminosae. Preliminary screening produced two unusual guanidinium compounds² along with a third component which gave a characteristic pale yellow colour with ninhydrin.

The crude extract obtained on extracting 170 g ground seed with 0.1 N HCl in methanol (1 l) for 48 h was concentrated to 0.5 l, diluted with 1 l H_2O , and centrifuged. The supernatant was applied to an Amberlite i.r.-120 column (100—200 mesh, H^+ form, 15×5 cm) prepared in 50% methanol. The resin was eluted successively with 0.1 N HCl in 50% methanol (1 l), H_2O (1 l), and 0.25 M HCl

(0.5 l). The brown oil obtained by concentration of the 0.25 M HCl eluate was applied to an i.r.-120 column (H^+ form, 10×1.2 cm) which was washed with water and was then eluted with 0.5 M NH_4OH (50 ml). The residue of the ammonia eluate was dissolved in 10 ml H_2O and purified by passage through Amberlite CG-400 (100—200 mesh, OH^- form, 10×1.2 cm). Adjustment of the pH to 5.0, evaporation to dryness, dissolution in methanol, and addition of a few drops of ethanol and acetone gave 400 mg of a crystalline monohydrochloride, which gave satisfactory elemental analyses.

The hygroscopic material showed strong ammonium i.r. bands, end absorption in the u.v., and a weak c.d. extremum at 225 nm ($\Delta\epsilon_{225} -0.025$, assignment not known) accompanied by a strong positive Cotton effect(s) below 200 nm. The electron impact mass spectrum (70 eV) showed peaks at m/e 164 (25%, corresponding to $M+1$ of the free amine) and 132 (100%, $M-31$ or $M-\text{CH}_2\text{OH}$). The chemical ionisation mass spectrum CI-MS (iso-butane) likewise showed peaks at m/e 164 (100%, $M+1$) and 146 ($M-\text{H}_2\text{O}+\text{H}$). The structure was derived by the ^1H -n.m.r. (100 MHz) and ^{13}C n.m.r. data: ^{13}C n.m.r. (relative to Me_4Si) δ 58.9 (CH_2O), 48.4 (CH_2N), 66.5, 66.7, and 73.2 (CHO), and 61.1 p.p.m. (CHN); for ^1H n.m.r. assignments see Figure. The well resolved contiguous eight proton system allowed the full configurational structure to be established as (**1**).

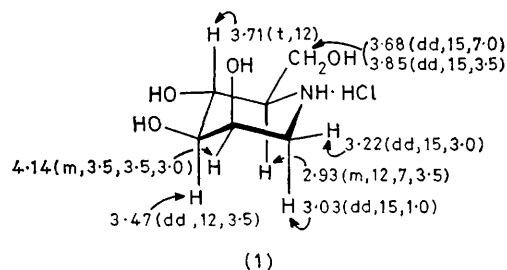
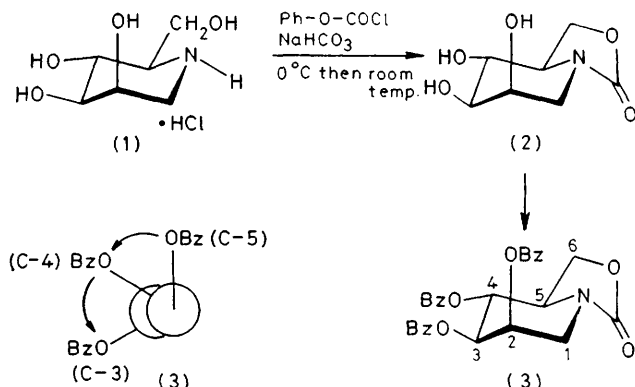


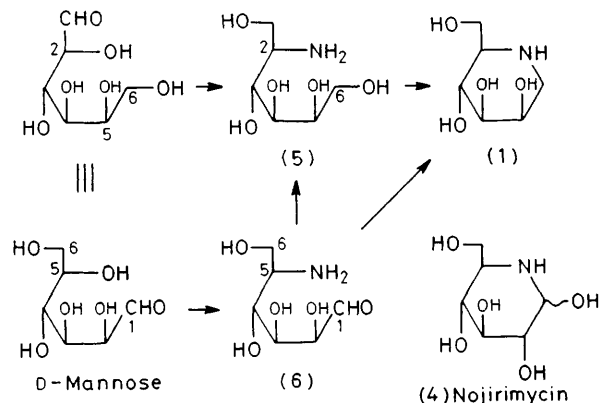
FIGURE. ^1H N.M.R. assignments in D_2O for (1). Coupling constants J in Hz are given in parentheses.

Since the three vicinal *sec*-hydroxy functions are arranged in either a clockwise [see structures (2) and (3)] or counterclockwise manner on the ring, the absolute configuration should be assignable by use of the benzoate chirality method.³ Blockage of the annular imino group and the freely rotating primary hydroxy group was achieved by formation of the cyclic carbamate (2) by treating (1) (1 mg) with phenyl chloroformate in aqueous NaHCO_3 at 0°C for 12 h followed by warming to room temperature for 4 h.



SCHEME 1. Preparation of the tribenzoate (3)

Benzoylation of the carbamate (2) (benzoyl chloride, pyridine, 0°C , 12 h) gave the tribenzoate (3) in 59% yield from (1) (0.63 mg) which was purified by silica gel chromatography (CI-MS m/e 502, $M+2$) (see Scheme 1). The intense negatively split Cotton effect extrema, $\Delta\epsilon_{237} - 68$ and $\Delta\epsilon_{222} + 10^\circ$ (MeCN) established the chiral arrangements of the hydroxy functions as depicted in the stereochemical drawing of (3). The structure of the compound is thus fully established as 1,5-dideoxy-1,5-imino-D-mannitol (1). It is the first naturally occurring amino alditol, cyclic or acyclic,⁴ and the second example of a sugar derivative containing a nitrogen atom instead of an oxygen atom in the ring [the first example being nojirimycin (4)].⁵



SCHEME 2. Possible precursors of 1,5-dideoxy-1,5-imido-D-mannitol (1).

Two biogenetic precursors are conceivable for this unusual compound (1) (Scheme 2). One is 2-amino-2-deoxy-D-mannitol (5) which can cyclize to (1). The alternative is 5-amino-5-deoxy-D-mannose (6) which could cyclize as in nojirimycin (4) and then be reduced at the anomeric carbon.

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⁴ 'Rodd's Chemistry of Carbon Compounds,' ed. S. Coffey, Elsevier, Amsterdam, 1967, 2nd edn, vol. 7, Pt. F, p. 58.

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