Experimental. The preparation of I and its reduction with sodium-ethanol has been described earlier.[1] The electrolyses were carried out at a mercury pool cathode in a cell of conventional design equipped with a ceramic cup for separation of anode and cathode compartments. The anolyte was 0.1 M tetrabutylammonium tetrafluoroborate in ethanol/water solution (9/1 by volume). The catholyte contained 2 mmol (538 mg) of the oxime I in 50 ml of the same solvent-supporting electrolyte system as the anolyte. The electrolyses were run at a constant current of 0.25 A until 6 *F*/mol of substrate had passed. On work-up the catholyte was made weakly acidic with dilute hydrochloric acid and the solvent evaporated. The residue was diluted with a sodium hydrogen carbonate solution and repeatedly extracted with ether. Drying and evaporation of the ether solution yielded the crude amine II. This could be purified by extraction of the amines from the ether solution with 0.1 M hydrochloric acid, precipitation with dilute alkali and isolation of the product by extraction with ether, drying and evaporation.

The *endo*/*exo*-ratios (IIa/IIb) were determined either directly from the PMR-spectrum of the product II by integration of the peak-areas corresponding to the α-methine proton and cyclopentadienyl ring proton resonance signals, or by means of a chromatographic separation of IIa and IIb.[5]

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5-Amino-2-formylimidazo [1,2-a]pyridine

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In an attempt to synthesize 1,4-diazacycl[3.2.2]azine, *7*, in a "one-step" reaction (*cf.* Chart 1), 2,6-diaminopyridine, *1*, was condensed with bromomalondialdehyde, *2* (X = Br). A yellow solid with the composition $C_8H_7N_3O$ was obtained in 17 % yield. Its IR spectrum shows aldehydic C–H absorption at 3730 and 2820 cm^{-1}

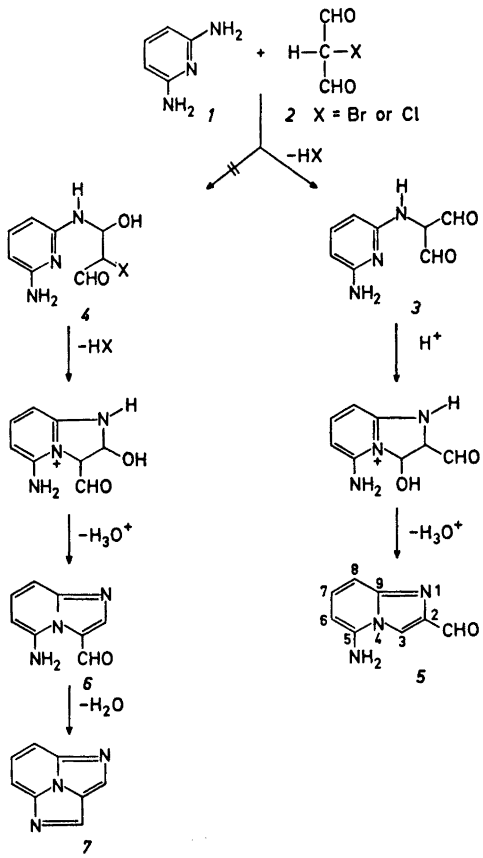

Chart 1.

and a carbonyl band at 1650 cm^{-1}; the NMR spectrum contains an unsplit aldehyde signal at 9.21 ppm and a broad NH_2 absorption at 8.30 ppm, which vanished on addition of deuterium oxide. The aromatic region displays a one-proton singlet at 8.42 ppm and an ABX pattern between 6.27 and 7.48 ppm (*cf.* Experimental). These observations indicate that the reaction product has structure *5* or *6*. The chemical-shift values for the aromatic proton singlets, H-2 in *6* and H-3 in *5*, are probably too close to allow a distinction between the two isomers. Infrared dilution studies on the yellow product demonstrated the presence of inter- but no intramolecular hydrogen bonds, which is in support of structure *5*. Recently [1] compound *6* was obtained by acid hydrolysis of *7* and was proved to have properties different from our product, which therefore possesses structure *5*.

In *2*, C-2 is thus more susceptible to nucleophilic attack than are the carbonyl-carbon atoms. Attempts to reverse this order of reactivity by substituting bromomalondialdehyde (*2*:X = Br) for its chloro-analog (*2*:X = Cl) also led to *5* and not to the desired compound *6*. Similarly, *5* was obtained in less than 10 % yield from *1* and 2,3-dibromopropionaldehyde, *8*,[2] in dilute hydrochloric acid solution. The title compound probably arose from aerial oxidation of the intermediate *9* (*cf.* Chart 2).

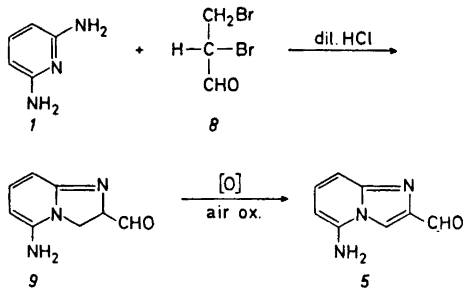

Chart 2.

The chemical-shift values for the ring protons in *5* were assigned by using the shift-change suffered by an aromatic proton on acetylation of an adjacent amino group.[3–5] Treatment of *5* with acetic anhydride in *p*-xylene yielded an *N*-acetyl derivative. In its NMR spectrum the one-proton doublet, which appeared at 6.27 ppm in *5*, was shifted 115 Hz to 8.19 ppm. These resonances are thus assigned to H-6, and in the spectrum of *5*, the triplet at 7.48 ppm to H-7, and the doublet at 6.81 ppm to H-8. Paudler *et al.*[1] have made shift assignments which are in agreement with our results, but they have not given any basis for their choice.

Experimental. Nuclear magnetic resonance (NMR) spectra were recorded with a Varian Model A-60 spectrometer, using tetramethylsilane as internal standard. Mass spectra were determined with a GEC-AEI MS 902 instrument at the Department of Medical Biochemistry, University of Göteborg. Thin-layer chromatography (TLC) was performed on Silica Gel GF_{254} (Merck) according to Stahl and the spots were visualized by means of short-wave ultraviolet light. For column chromatography, silica gel (0.05–0.2 mm; Merck) was used. Elemental analyses were carried out at Mikroanalytisches Laboratorium, Institut für Physikalische Chemie, Universität Wien.

5-Amino-2-formylimidazo[1,2-a]pyridine, 5, from bromomalondialdehyde. To a solution of 1.1 g (0.01 mol) of 2,6-diaminopyridine, *1*, in 50 ml of 1,2-dimethoxyethane was added 1.5 g (0.01 mol) of bromomalondialdehyde (*2*:X = Br), whereupon a solid precipitated. The suspension was heated at 50° for 12 h and then poured into 25 ml of a saturated aqueous sodium bicarbonate solution. All volatile materials were removed *in vacuo* and the residue was extracted with chloroform. The chloroform extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The brown residue was chromatographed on 30 g of silica gel with chloroform-methanol (9:1), giving 300 mg (17 %) of a bright yellow solid, m.p. 198°. MS: $M^+ = 161$. NMR (dimethyl sulfoxide-d_6): aldehyde singlet at 9.21 (1H), broad NH_2 at 8.30 (2H), aromatic singlet at 8.42 (1H, H-3), triplet ($J = 8$ Hz) at 7.48 (1H, H-7), doublet ($J = 8$ Hz) at 6.81 (1H, H-8), doublet ($J = 8$ Hz) at 6.27 (1H, H-6) ppm; IR (KBr): 3200–3400 (NH), 3730 and 2820 (aldehydic C-H) 1650 cm^{-1} (C=O). (Found: C 59.52; H 4.42; N 25.95. Calc. for $C_8H_7N_3O$: C 59.62; H 4.38; N 26.07).

5-Amino-2-formylimidazo[1,2-a]pyridine, 5, from chlomalondialdehyde.[6] The reaction conditions were the same as those described above, except that the solution was stirred for 15 h at 65–70°. The yield was 173 mg (9 %).

Acetylation of 5 to 5-acetamido-2-formylimidazo[1,2-]pyridine. To a solution of 26 mg of *5* in 5 ml of *p*-xylene was added 0.7 ml of freshly distilled acetic anhydride. The mixture

was heated to reflux for 96 h. The solvent was evaporated under reduced pressure and the residue was chromatographed on a silica gel column, eluted with chloroform-ethyl acetate (3:1). Yield: 25 mg (77 %). MS: $M^+ = 203$; NMR (dimethyl sulfoxide-d_6): broad NH at 13.07 (1H), aldehyde singlet at 9.42 (1H), aromatic singlet at 8.36 (1H, H-3), doublet ($J = 7$ Hz) at 8.19 (1H, H-6), triplet ($J = 7$ Hz) at 7.75 (1H, H-7), doublet ($J = 7$ Hz) at 7.40 (1H, H-8), and singlet at 2.35 (3H, CH_3) ppm.

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Methylation Studies on Levans

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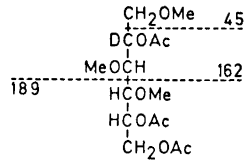
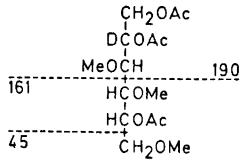
Levan, which is an essentially (2→6)-linked β-fructan, is antigenic in man and is precipitated by some myeloma proteins.[1] Different preparations show variations in their immunochemical behaviour[1,2] which must be due to structural differences. We now report methylation studies on some levan preparations of different origins.

Qualitative and quantitative analysis of the methylated sugars obtained on hydrolysis of a methylated polysaccharide is preferably performed by GLC-MS of the derived alditol acetates.[3,4] Some difficulties might be expected in working with ketoses since reduction of each partially methylated ketose should give rise to two alditol derivatives. None of the pairs of D-glucitol and D-mannitol derivatives obtained from 1,3,4,6-tetra-*O*-methyl-, 1,3,4-tri-*O*-methyl-, or 3,4-di-*O*-methyl-D-fructose separated, however, on the chromatographic columns used. Another possible source of difficulty is that the alditols derived from the 1,3,4- and 3,4,6-isomers of tri-*O*-methyl-D-fructose might not be distinguishable. When the conversion to





alditols is carried out with sodium borodeuteride, however, these substances give different mass spectra. The origin of some pertinent primary fragments is indicated above for the D-glucitol derivatives. When this method is used, a small proportion of 3,4,6-tri-*O*-methyl-D-fructose in the 1,3,4-tri-*O*-methyl-D-fructose might be overlooked. Therefore GLC was used to compare the acetates of the free sugars obtained on hydrolysis of methylated inulin with those obtained from the methylated levans B512 PP2, "Coryne", "Hestrin", and "Rye grass". The 1,3,4- and 3,4,6-tri-*O*-methyl-D-fructose acetates gave only one peak each on GLC and these were well separated (retention times relative to 1,5-di-*O*-acetyl-2,3,4,6-tetra-

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