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REACTION OF 2-AMINO-2-DEOXYHEPTOSES WITH CYCLIC β-DICARBONYL COMPOUNDS*

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ABSTRACT

The reaction between 2-amino-2-deoxyaldoses and β-dicarbonyl compounds yields polyhydroxyalkylpyrroles. Thus, 6,6-dimethyl-2-(D-*galacto*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**4a**), 6,6-dimethyl-2-(D-*gluco*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**4b**), and 6,6-dimethyl-2-(D-*manno*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**4c**) have been obtained from 5,5-dimethylcyclohexane-1,3-dione (**2**) and 2-amino-2-deoxyheptoses having D-*glycero*-L-*gluco* (**1a**), D-*glycero*-D-*ido* (**1b**), and D-*glycero*-D-*talo* (**1c**) configurations, respectively. 2-Amino-2-deoxy-D-*glycero*-L-*manno*-heptose (**1d**), the epimer of **1a**, also reacts with **2**, to yield **4a**. In a similar way, **1a**, **1b**, and **1c** react with cyclohexane-1,3-dione (**3**), to give 2-(D-*galacto*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**5a**), 2-(D-*gluco*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**5b**), and 2-(D-*manno*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**5c**), respectively.

INTRODUCTION

The reaction between amino sugars and β-dicarbonyl compounds has been widely studied by García González and co-workers[1,2]. The final products are pyrrole derivatives having a polyhydroxylated chain joined to one carbon atom of the ring, though intermediate keto-enamines have been isolated in certain cases. With cyclic β-dicarbonyl compounds, *e.g.*, cyclohexane-1,3-dione, the final products contain the pyrrole ring fused with another ring. This reaction has been studied for 2-amino-2-deoxy-D-glucose or 1-amino-1-deoxy-D-*arabino*-hexulose, and has yielded several D-*arabino*-tetrahydroxybutyl-4,5,6,7-tetrahydroindol-4-ones[3,4].

We now report on the preparation of pentahydroxypentyl-4,5,6,7-tetrahydroindol-4-ones from 2-amino-2-deoxyheptoses.

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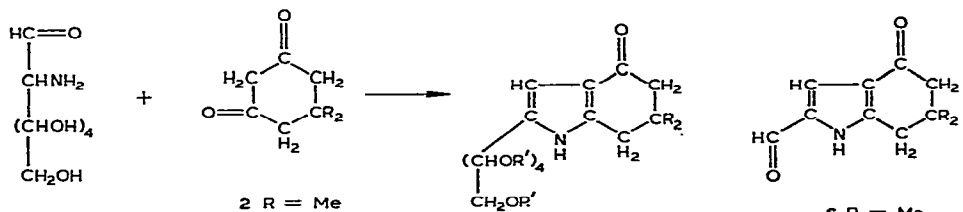
RESULTS AND DISCUSSION

2-Amino-2-deoxyheptoses having the D-*glycero*-L-*gluco* (**1a**), D-*glycero*-D-*ido* (**1b**), D-*glycero*-D-*talo* (**1c**), and D-*glycero*-L-*manno* (**1d**) configurations have been used. Compounds **1a**, **1b**, and **1c** were prepared by the aminonitrile synthesis[5], while **1d** was obtained by the nitromethane synthesis[6,7]. As β-dicarbonyl compounds, 5,5-dimethylcyclohexane-1,3-dione (**2**) and cyclohexane-1,3-dione (**3**) were used.

Both **1a** and **1d** reacted with **2** in aqueous acetone at pH 7–8 and room temperature, to yield 6,6-dimethyl-2-(D-*galacto*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**4a**). Likewise, compounds **1b** and **1c** gave 6,6-dimethyl-2-(D-*gluco*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**4b**) and 6,6-dimethyl-2-(D-*manno*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**4c**), respectively.



Configuration
1a D-*glycero*-L-*gluco*
1b D-*glycero*-D-*ido*
1c D-*glycero*-D-*talo*
1d D-*glycero*-L-*manno*

2 R = Me
3 R = H

4 R = Me, R′ = H
5 R = R′ = H
8 R = Me, R′ = Ac
9 R = H, R′ = Ac

Chain configuration
a D-*galacto*
b D-*gluco*
c D-*manno*

6 R = Me
7 R = H

The reactions of cyclohexane-1,3-dione (**3**) with the amino sugars **1a**, **1b**, and **1c** gave 2-(D-*galacto*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**5a**), 2-(D-*gluco*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**5b**), and 2-(D-*manno*-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one (**5c**), respectively. The reactions were performed under similar conditions, in aqueous solution at pH 7–8 and at room temperature.

The structures proposed for **4a**, **4b**, **4c**, **5a**, and **5c** were demonstrated by elemental analysis and spectral data (u.v., i.r., and p.m.r.). The presence of the pentahydroxypentyl side-chain was proved by periodate oxidation[8]; ~4 molar equivalents of periodate were consumed in each case. Assignment of D-*galacto*, D-*gluco*, or D-*manno* configurations is based on the respective configurations of the parent amino sugars, and is consistent with the Richtmyer–Hudson rules[9]. The structure of the heterocyclic ring-system was established by degradation of the polyhydroxyalkyl side-chain with sodium metaperiodate. By this reaction, compounds **4a**, **4b**, and **4c** gave known[3] 6,6-dimethyl-4-oxo-4,5,6,7-tetrahydroindole-2-carbaldehyde (**6**). Likewise, **5a**, **5b**, and **5c** gave known[4] 4-oxo-4,5,6,7-tetrahydroindole-2-carbaldehyde (**7**).

Treatment of **4a**, **4b**, **5a**, **5b**, and **5c** with acetic anhydride in pyridine gave the corresponding penta-*O*-acetyl derivatives **8a**, **8b**, **9a**, **9b**, and **9c**.

The new compounds described are of interest, because they can be converted into *C*-nucleosides by intramolecular dehydration of the pentahydroxypentyl chains[10]; these anhydro derivatives are analogous to some of D-ribose, which exhibit a variety of interesting biological properties[11].

EXPERIMENTAL

General methods. — Solutions were evaporated *in vacuo* at temperatures below 40°. Melting points were determined by using a Gallenkamp apparatus, and are uncorrected. Optical rotations were measured at 20 ±2° with a Perkin–Elmer 141 polarimeter and a 10-cm cell. Infrared spectra were recorded, for potassium bromide discs, with a Beckman IR-33 grating spectrophotometer, and u.v. spectra with a Unicam SP-8000. N.m.r. spectra were recorded at 90 MHz with a Perkin–Elmer R-32 spectrometer for solutions in $CDCl_3$ (internal tetramethylsilane) and D_2O (internal sodium 4,4-dimethyl-4-silapentane-1-sulphonate). T.l.c. was performed on silica gel (Merck GF_{254}) with benzene–ethanol (3:1) or ethyl acetate–ethanol (3:1) as eluant, and detection with u.v. light, iodine vapour, or Ehrlich's reagent for pyrroles. Paper chromatography was performed on Whatman No. 1 paper, by the horizontal technique, with 1-butanol–pyridine–water (1:1:1) as eluant, and silver nitrate–sodium hydroxide or Ehrlich's reagent as indicator. Column chromatography was performed on silica gel (Merck No. 60, 0.063–0.200 mm) with an ethyl acetate–ethanol gradient.

Consumption of periodate was determined by the method described by García González *et al.*[12], based on the Fleury and Lange[13] procedure.

6,6-Dimethyl-2-(D-galacto-*pentitol-1-yl*)*-4,5,6,7-tetrahydroindol-4-one* (**4a**). — (*a*) A solution of 2-amino-2-deoxy-D-*glycero*-L-*manno*-heptose hydrochloride[6,7] (2.45 g, 10 mmol) in water (15 ml) was treated with 5,5-dimethylcyclohexane-1,3-dione (1.40 g, 10 mmol) in acetone–water (11:4, 15 ml). The mixture was neutralized with sodium carbonate (0.53 g, 5 mmol) and kept at room temperature for 10 days, and then the acetone was evaporated under diminished pressure. The resulting solution was extracted with chloroform (8 × 10 ml), and the aqueous layer was evaporated to yield **4a** (0.73 g, 23%), m.p. 185–187° (from 96% ethanol), $[\alpha]_D$ +22° (*c* 0.5, water); $\lambda_{max}^{H_2O}$ 211, 246, and 288 nm (ε 13,100, 6,300, and 5,000); ν_{max} 3460–3230 (OH, NH), 1640 (C=O), 1617 and 1480 cm^{-1} (C=C pyrrole).

Anal. Calc. for $C_{15}H_{23}NO_6$: C, 57.51; H, 7.35; N, 4.47. Found: C, 57.26; H, 7.65; N, 4.17. Periodate consumption: 7.83 equivalents.

(*b*) The product **4a** was also obtained from 2-amino-2-deoxy-D-*glycero*-L-*gluco*-heptose hydrochloride[5] by the procedure described in (*a*). Yield: 18%.

6,6-Dimethyl-2-(*penta*-O-*acetyl*-D-galacto-*pentitol-1-yl*)*-4,5,6,7-tetrahydroindol-4-one* (**8a**). — A solution of **4a** (0.1 g, 0.32 mmol) in pyridine (1 ml) and acetic anhydride (0.5 ml) was kept at 0° for 24 h. The mixture was poured into ice–water (15 ml), yielding **8a** (117 mg, 70%), m.p. 148–150° (from ethanol–water, 3:1),

$[\alpha]_D$ +74° (*c* 0.25, chloroform); λ_{max}^{EtOH} 238 and 273 nm (ε 18,200 and 18,800); ν_{max} 3190 (NH), 1750 (C=O ester), 1640 (C=O ketone), 1610 and 1480 cm^{-1} (C=C pyrrole); p.m.r. data ($CDCl_3$): δ 1.10 (s, 6 H, CMe_2), 2.00, 2.03, 2.06, 2.07, and 2.08 (5 s, 15 H, 5 OAc), 2.32 (s, 2 H, CH_2-7), 2.63 (s, 2 H, CH_2-5), 3.88 (dd, 1 H, H-5′), 4.27 (dd, 1 H, $J_{5',5''}$ 12.0 Hz, H-5″), 5.31 (m, 1 H, $J_{4',5'}$ 7.0, $J_{4',5''}$ 5.0 Hz, H-4′), 5.39 (dd, 1 H, $J_{3',4'}$ 1.5 Hz, H-3′), 5.52 (dd, 1 H, $J_{2',3'}$ 9.0 Hz, H-2′), 5.93 (d, 1 H, $J_{1',2'}$ 2.5 Hz, H-1′), 6.47 (d, 1 H, $J_{1,3}$ 2.0 Hz, H-3), and 8.96 (m, 1 H, H-1).

Anal. Calc. for $C_{25}H_{33}NO_{11}$: C, 57.35; H, 6.35; N, 2.67. Found: C, 57.12; H, 6.60; N, 2.73.

6,6-Dimethyl-2-(D-gluco-*pentitol-1-yl*)*-4,5,6,7-tetrahydroindol-4-one* (**4b**). — A solution of 2-amino-2-deoxy-D-*glycero*-D-*ido*-heptose hydrochloride[5] (10 g, 40.7 mmol) in water (50 ml) was treated with 5,5-dimethylcyclohexane-1,3-dione (5.7 g, 40.7 mmol) in acetone–water (3:1, 60 ml), as described above for **4a**, to give **4b** (2.85 g, 22%), m.p. 192–194° (from water), $[\alpha]_D$ +22° (*c* 0.5, water); $\lambda_{max}^{H_2O}$ 211, 245, and 287 nm (ε 13,100, 5,500, and 4,500); ν_{max} 3425–3275 (NH, OH), 1635 (C=O), 1620 and 1480 cm^{-1} (C=C pyrrole).

Anal. Calc. for $C_{15}H_{23}NO_6$: C, 57.51; H, 7.35; N, 4.47. Found: C, 57.48; H, 7.43; N. 4.57. Periodate consumption: 7.99 equivalents.

*6,6-Dimethyl-2-(penta-*O*-acetyl-*D*-gluco-pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one* (**8b**). — Acetylation of **4b** (0.1 g, 0.32 mmol), as described for **4a**, gave the penta-acetate **8b** (146 mg, 87%), m.p. 177–179° (from water–ethanol, 3:1), $[\alpha]_D$ +127° (*c* 0.5 pyridine); λ_{max}^{EtOH} 238 and 274 nm (ε 17,800 and 18,400); ν_{max} 3220 (NH), 1740 (C=O ester), 1635 (C=O ketone), 1605 and 1475 cm^{-1} (C=C pyrrole); p.m.r. data ($CDCl_3$): δ 1.11 (s, 6 H, CMe_2), 1.99, 2.02, 2.09, 2.13 (4 s, 15 H, 5 OAc), 2.36 (s, 2 H, CH_2-7), 2.66 (s, 2 H, CH_2-5), 4.05 (dd, 1 H, H-5′), 4.25 (dd, 1 H, $J_{5',5''}$ 12.0 Hz, H-5″), 5.10 (m, 1 H, $J_{4',5'}$ 5.0, $J_{4',5''}$ 3.0 Hz, H-4′), 5.25 (dd, 1 H, $J_{3',4'}$ 8.0 Hz, H-3′), 5.64 (dd, 1 H, $J_{2',3'}$ 2.5 Hz, H-2′), 5.77 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 6.58 (d, 1 H, $J_{1,3}$ 2.0 Hz, H-3), and 9.30 (m, 1 H, H-1).

Anal. Calc. for $C_{25}H_{33}NO_{11}$: C, 57.35; H, 6.35; N, 2.67. Found: C, 57.45; H, 6.42; N, 2.88.

6,6-Dimethyl-2-(D-manno-*pentitol-1-yl*)*-4,5,6,7-tetrahydroindol-4-one* (**4c**). — A solution of 2-amino-2-deoxy-D-*glycero*-D-*talo*-heptose hydrochloride[5] (24.55 g, 0.1 mol) in water (100 ml) was treated with 5,5-dimethylcyclohexane-1,3-dione (14.0 g, 0.1 mol) in acetone–water (3:1) (110 ml). The mixture was neutralized with sodium carbonate (5.3 g, 0.05 mol) and kept at room temperature for 10 days, and then the acetone was evaporated under diminished pressure. The resulting solution was extracted with chloroform (5 × 50 ml), and the aqueous layer was evaporated, to give a syrup that was treated with boiling ethanol (250 ml). The ethanolic solution was again evaporated, and the residual brownish syrup was treated with boiling acetone (500 ml). The acetonic solution was discarded and the syrupy residue was treated with ethyl ether, to give an amorphous solid that was collected by filtration and washed on the filter with cold ethanol; **4c** (6.8 g, 22%) had m.p. 149–151° (from 96% ethanol), $[\alpha]_D$ −19° (*c* 0.5, water); $\lambda_{max}^{H_2O}$ 211, 246, and 288 nm (ε 13,100, 5,700,

and 4,800); ν_{max} 3350–3265 (NH, OH), 1640 (C=O), 1620 and 1472 cm^{-1} (C=C pyrrole); p.m.r. data (D_2O): δ 1.07 (s, 6 H, CMe_2), 2.32 (s, 2 H, CH_2-7), 2.69 (s, 2 H, CH_2-5), and 3.60–4.68 (several complex multiplets, 6 H, pentahydroxypentyl chain), and 6.42 (s, 1 H, H-3).

Anal. Calc. for $C_{15}H_{23}NO_6$: C, 57.51; H, 7.35; N, 4.47. Found: C, 57.20; H, 7.44; N, 4.34. Periodate consumption: 7.89 equivalents.

6,6-Dimethyl-4-oxo-4,5,6,7-tetrahydroindole-2-carbaldehyde (**6**). — An ice-cold solution of **4a**, **4b**, or **4c** (0.156 g, 0.5 mmol) in the minimum amount of cold water was treated with a cold, aqueous solution (~1 ml) of sodium periodate (0.428 g, 2 mmol) under continuous stirring. The product **6** began to crystallize after a few minutes and then was left for 1 h in a refrigerator. The crystals (68–72 mg, 71–75%) were collected, and recrystallized from water–ethanol (2:1), to give **6**, m.p. 195–196°. This product was identified by i.r. spectrum and mixture m.p. with the product already described[3].

2-(D-galacto-*Pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one* (**5a**). — A solution of 2-amino-2-deoxy-D-*glycero*-L-*gluco*-heptose hydrochloride[5] (24.55 g, 0.1 mol) in water (30 ml) was treated with cyclohexane-1,3-dione (11.2 g, 0.1 mol). The mixture was neutralized with sodium carbonate (5.3 g, 0.05 mol) and kept at room temperature for 10 days. The solution was concentrated to small volume and partitioned between acetone (6 × 25 ml) and water. The acetonic layer was evaporated, to give a syrup that was dried by azeotropic distillation with ethanol and benzene. The yellow residue (5.6 g, 20%) was crystallized from 99% ethanol (using activated charcoal) to give **5a**, m.p. 138–140°, $[\alpha]_D$ +22.3°, $[\alpha]_{578}$ +23.7°, $[\alpha]_{546}$ +27.6°, $[\alpha]_{436}$ +53.7° (*c* 0.5, water); $\lambda_{max}^{H_2O}$ 212, 247, and 288 nm (ε 13,200, 6,700, and 6,450); ν_{max} 3260 (NH, OH), 1620 (C=O), 1600 and 1470 cm^{-1} (C=C pyrrole).

Anal. Calc. for $C_{13}H_{19}NO_6$: C, 54.74; H, 6.66; N, 4.91. Found: C, 54.46; H, 6.85; N, 4.66. Periodate consumption: 8.07 equivalents.

*2-(Penta-*O*-acetyl-*D-galacto-*pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one* (**9a**). — By the procedure described for the synthesis of **8a**, **5a** (0.1 g, 0.35 mmol) was converted into **9a** (115 mg, 67%), m.p. 181–183° (from ethanol–water, 3:1), $[\alpha]_D$ +95.3°, $[\alpha]_{578}$ +100.8°, $[\alpha]_{546}$ +116.2°, $[\alpha]_{436}$ +216.0°, $[\alpha]_{365}$ +385.0° (*c* 0.5, pyridine); λ_{max}^{EtOH} 237 and 273 nm (ε 17,300 and 17,900); ν_{max} 3270 (NH), 1735 (C=O ester), 1650 (C=O ketone), 1620 and 1475 cm^{-1} (C=C pyrrole); p.m.r. data (in $CDCl_3$): δ 2.02, 2.06, 2.07 (3 s, 15 H, 5 OAc), 2.50, 2.80 (2 t, 6 H, CH_2-5,6,7), 3.85 (dd, 1 H, H-5′), 4.25 (dd, 1 H, $J_{5',5''}$ 12.0 Hz, H-5″), 5.29 (m, 1 H, $J_{4',5'}$ 7.0, $J_{4',5''}$ 5.0 Hz, H-4′), 5.39 (dd, 1 H, $J_{3',4'}$ 1.5 Hz, H-3′), 5.52 (dd, 1 H, $J_{2',3'}$ 9.0 Hz, H-2′), 5.92 (d, 1 H, $J_{1',2'}$ 2.5 Hz, H-1′), 6.45 (d, 1 H, $J_{1,3}$ 2.0 Hz, H-3), and 9.46 (m, 1 H, H-1).

Anal. Calc. for $C_{23}H_{29}NO_{11}$: C, 55.75; H, 5.86; N, 2.83. Found: C, 55.51; H, 5.79; N, 2.83.

2-(D-gluco-*Pentitol-1-yl)-4,5,6,7-tetrahydroindol-4-one* (**5b**). — A solution of 2-amino-2-deoxy-D-*glycero*-D-*ido*-heptose hydrochloride[5] (13.5 g, 55 mmol) in water (50 ml) was treated with cyclohexane-1,3-dione (6.10 g, 55 mmol). The mixture was

neutralized with sodium carbonate (2.9 g, 27.5 mmol), kept at room temperature for 10 days, concentrated to ~25 ml, and extracted with ethyl acetate (5 × 40 ml). The aqueous layer was discarded, and the organic layer was dried (Na_2SO_4) and then evaporated *in vacuo*. The resulting syrup was eluted from a column of silica gel with an ethyl acetate–ethanol gradient, to give amorphous **5b** (1.56 g, 15%), R_F 0.10 (t.l.c.; ethyl acetate–ethanol, 3:1).

The penta-acetate (**9b**) of **5b** (52% yield) had m.p. 179–181° (from methanol), $[\alpha]_D$ +147.2°, $[\alpha]_{578}$ +150.0°, $[\alpha]_{546}$ +192.4° (*c* 0.5, chloroform); λ_{max}^{EtOH} 236 and 274 nm (ε 19,100 and 19,700); ν_{max} 3220–3140 (NH), 1740 (C=O ester), 1625 (C=O ketone), 1600 and 1480 cm^{-1} (C=C pyrrole); p.m.r. data (in $CDCl_3$): δ 1.97, 2.05, 2.06 (3 s, 15 H, 5 OAc), 2.45, 2.79 (2 t, 6 H, CH_2-5,6,7), 4.00 (dd, 1 H, H-5′), 4.24 (dd, 1 H, $J_{5',5''}$ 12.0 Hz, H-5″), 5.15 (m, 1 H, $J_{4',5'}$ 5.0, $J_{4',5''}$ 3.0 Hz, H-4′), 5.25 (dd, 1 H, $J_{3',4'}$ 8.0 Hz, H-3′), 5.64 (dd, 1 H, $J_{2',3'}$ 2.5 Hz, H-2′), 5.80 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 6.56 (d, 1 H, $J_{1,3}$ 2.0 Hz, H-3), and 9.67 (m, 1 H, H-1).

Anal. Calc. for $C_{23}H_{29}NO_{11}$: C, 55.75; H, 5.86; N, 2.83. Found: C, 56.03; H, 5.98; N, 2.68.

2-(D-manno-*Pentitol-1-yl*)*-4,5,6,7-tetrahydroindol-4-one* (**5c**). — A solution of 2-amino-2-deoxy-D-*glycero*-D-*talo*-heptose hydrochloride[5] (7.4 g, 30.1 mmol) in water (40 ml) was treated with cyclohexane-1,3-dione (3.37 g, 30.1 mmol). The mixture was neutralized with sodium carbonate (1.6 g, 15.0 mmol), kept at room temperature for 10 days, concentrated to small volume, and extracted with acetone (5 × 25 ml). The acetonic layer was concentrated under diminished pressure to half-volume and kept in a refrigerator. After 7–10 days, crystalline **5c** (1.3 g, 15%) was filtered off; m.p. 153–155° (from 80% ethanol), $[\alpha]_D$ −17.8°, $[\alpha]_{578}$ −18.4°, $[\alpha]_{546}$ −21.0°, $[\alpha]_{436}$ −36.4°, $[\alpha]_{365}$ −57.4° (*c* 0.5, water); $\lambda_{max}^{H_2O}$ 212, 246, and 286 nm (ε 13,300, 6,750, and 5,700); ν_{max} 3530–3240 (NH, OH), 1630 (C=O), 1620 and 1475 cm^{-1} (C=C pyrrole).

Anal. Calc. for $C_{13}H_{19}NO_6$: C, 54.74; H, 6.66; N, 4.91. Found: C, 54.57; H, 6.72; N, 4.81. Periodate consumption: 7.94 equivalents.

2-(*Penta-*O*-acetyl-*D-manno-*pentitol-1-yl*)*-4,5,6,7-tetrahydroindol-4-one* (**9c**). — Acetylation of compound **5c** (0.1 g, 0.35 mmol), as described for **8a**, afforded its penta-*O*-acetyl derivative **9c** (110 mg, 64%), m.p. 168–170° (from water–ethanol, 3:1), $[\alpha]_D$ −19.6°, $[\alpha]_{578}$ −20.2°, $[\alpha]_{546}$ −23.8°, $[\alpha]_{436}$ −45.6°, $[\alpha]_{365}$ −80.4° (*c* 0.5, pyridine); λ_{max}^{EtOH} 237 and 274 nm (ε 18,400 and 18,900); ν_{max} 3260 (NH), 1740 (C=O ester), 1625 (C=O ketone), 1605 and 1475 cm^{-1} (C=C pyrrole); p.m.r. data: ($CDCl_3$); δ 2.01, 2.09, 2.12 (3 s, 15 H, 5 OAc), 2.44, 2.80 (2 t, 6 H, CH_2-5,6,7), 4.08 (dd, 1 H, H-5′), 4.18 (dd, 1 H, $J_{5',5''}$ 12.0 Hz, H-5″), 5.14 (m, 1 H, $J_{4',5'}$ 5.0, $J_{4',5''}$ 3.5 Hz, H-4′), 5.57 (dd, 1 H, $J_{3',4'}$ 9.0 Hz, H-3′), 5.65 (dd, 1 H, $J_{2',3'}$ 1.5 Hz, H-2′), 5.83 (d, 1 H, $J_{1',2'}$ 9.0 Hz, H-1′), 6.45 (d, 1 H, $J_{1,3}$ 2.0 Hz, H-3), and 9.35 (m, 1 H, H-1).

Anal. Calc. for $C_{23}H_{29}NO_{11}$: C, 55.75; H, 5.86; N, 2.83. Found: C, 55.49; H, 6.16; N, 2.83.

4-Oxo-4,5,6,7-tetrahydroindole-2-carbaldehyde[4] (**7**). — Periodate oxidation of

compounds **5a–c**, as described for the preparation of **6**, afforded the aldehyde **7** (70–78%), m.p. 205–207° (from 50% ethanol). This product was identified by i.r. spectrum and mixture m.p. with the product already described[4].

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