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Note

New acyclic-sugar *C*-nucleoside analogs. Synthesis of 2-(alditol-1-yl)-1-alkyl-4,5,6,7-tetrahydroindol-4-ones

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The reaction between 2-amino-2-deoxyaldoses and cyclic 1,3-dicarbonyl compounds yields tetrahydro-(polyhydroxyalkyl)indol-4-ones[1,2]. These acyclic-sugar *C*-nucleoside analogs can be converted into cyclic ones by acid-catalyzed dehydration of the polyhydroxyalkyl chain[3–5]. We now report on the preparation of new 2-(alditol-1-yl)-1-alkyl-4,5,6,7-tetrahydroindol-4-ones by reaction of 5,5-dimethyl-1,3-cyclohexanedione and 1,3-cyclohexanedione with 2-(alkylamino)-2-deoxyaldoses that we have previously described[6–8].

Thus, by reaction of 2-deoxy-2-(ethylamino)-L-glucose[6] with 5,5-dimethyl-1,3-cyclohexanedione, 1-ethyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(L-*arabino*-tetritol-1-yl)indol-4-one (**1**) was obtained in good yield. The structure of **1** was demonstrated by elemental analysis and spectral data (u.v. and i.r.). Periodate oxidation of the polyhydroxyalkyl chain gave a reagent consumption of 3 mol per mol of compound, indicative of four contiguous hydroxyl groups. This oxidation yields 1-ethyl-4,5,6,7-tetrahydro-6,6-dimethyl-4-oxoindol-2-carboxaldehyde (**12**), which confirms the assigned structure of the heterocyclic ring. The presence of the tetrahydroxybutyl chain was also proved by preparing the tetra-*O*-acetyl derivative **2**. Assignment of the L-*arabino* configuration is based on the configuration of the sugar precursor of **1**, and is consistent with the positive value of its rotatory power, in agreement with generalized rules[9–11].

In the same way, the reaction of 2-deoxy-2-(ethylamino)-D-*glycero*-L-*gluco*-heptose[8] with 5,5-dimethyl-1,3-cyclohexanedione and 1,3-cyclohexanedione afforded 1-ethyl-tetrahydro-2-(D-*galacto*-pentitol-1-yl)indol-4-ones **3** and **4**, and the reaction of 2-deoxy-2-(propylamino)-D-*glycero*-L-*gluco*- or D-*glycero*-L-*manno*-heptose[8] with 5,5-dimethyl-1,3-cyclohexanedione gave tetrahydro-2-(D-*galacto*-

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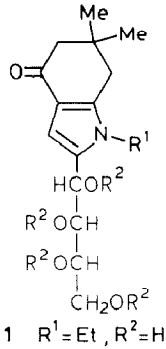
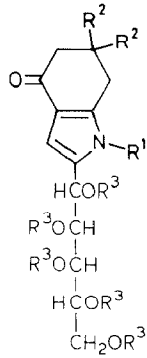
pentitol-1-yl)-1-propylindol-4-one (**5**). The structures assigned to these compounds were in agreement with their elemental analyses, spectral data (u.v. and i.r.), positive rotatory powers, and periodate oxidation of the pentahydroxypentyl chain, ~4 mol. equiv. of periodate being consumed in each case. Acetylation of these compounds gave the penta-*O*-acetyl derivatives **6–8**. The structure of the heterocyclic ring system was also confirmed by oxidative degradation of the side chain of compounds **3–5**, to give the corresponding carboxaldehydes (**12–14**).

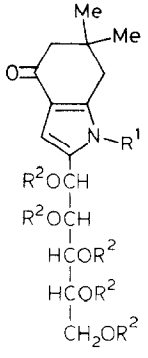
The reaction of 2-deoxy-2-(ethylamino)-D-*glycero*-D-*talo*-heptose[7] with 5,5-dimethyl-1,3-cyclohexanedione gave 1-ethyl-tetrahydro-2-(D-*manno*-pentitol-1-yl)indol-4-one (**9**), and reaction of the epimeric mixture of 2-deoxy-2-(propylamino)-D-*glycero*-D-*ido*- and D-*glycero*-D-*gulo*-heptose with the same 1,3-dicarbonyl compound led to tetrahydro-2-(D-*gluco*-pentitol-1-yl)-1-propylindol-4-one (**11**). The structures of compounds **9** and **11** were demonstrated by the methods described for compounds **3–5**.



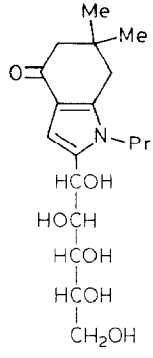
1 R^1 = Et, R^2 = H
2 R^1 = Et, R^2 = Ac



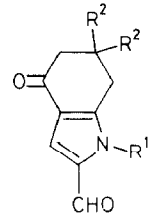
3 R^1 = Et, R^2 = Me, R^3 = H
4 R^1 = Et, R^2 = R^3 = H
5 R^1 = Pr, R^2 = Me, R^3 = H
6 R^1 = Et, R^2 = Me, R^3 = Ac
7 R^1 = Et, R^2 = H, R^3 = Ac
8 R^1 = Pr, R^2 = Me, R^3 = Ac



9 R^1 = Et, R^2 = H
10 R^1 = Et, R^2 = Ac



11



12 R^1 = Et, R^2 = Me
13 R^1 = Et, R^2 = H
14 R^1 = Pr, R^2 = Me

EXPERIMENTAL

General methods. — Solutions were evaporated *in vacuo* at temperatures below 50°. Melting points were determined with a Gallenkamp apparatus, and are uncorrected. Optical rotations were measured at 22 ±4° with a Perkin–Elmer 141 polarimeter (10-cm, 5-mL cell). I.r. spectra (KBr discs) were recorded with a Perkin–Elmer 399 spectrophotometer, and u.v. spectra with a Pye–Unicam SP8-250 instrument. Paper chromatography was performed on Whatman No. 1 paper by the ascending technique, with 1:1:1 1-butanol–pyridine–water as the eluant, and silver nitrate–sodium hydroxide or Ehrlich reagent as the indicator. T.l.c. was performed on silica gel GF_{254} (Merck) with 3:1 ethyl acetate–ethanol as the eluant, and detection with u.v. light, iodine vapor, or Ehrlich reagent for pyrroles. Consumption of periodate was determined as previously described[12]. ^{1}H-N.m.r. spectra at 90 MHz, with internal Me_4Si, were recorded with a Perkin–Elmer R-32 spectrometer, and coupling constants were measured directly from the spectra recorded at 300-Hz sweep-width (temperature of the probe, 35.5°). Assignments were confirmed by double resonance (spin-spin decoupling and spin-tickling), and overlapping signals were gradually shifted, and separated from one another, by incremental additions of $Eu(fod)_3$.

*1-Ethyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(*L-arabino-*tetritol-1-yl)indol-4-one* (**1**). — A solution of 2-deoxy-2-ethylamino-L-glucose hydrochloride[6] (4.0 g, 15.3 mmol) in water (10 mL) was treated with 5,5-dimethyl-1,3-cyclohexanedione (2.3 g, 16.4 mmol) in 2:1 acetone–water (23 mL), and sodium carbonate (0.87 g, 82 mmol) was added. The mixture was kept for 14 days at room temperature, and then the acetone was evaporated under diminished pressure. The resulting solution was washed with chloroform (2 × 15 mL), and evaporated, to yield **1**, which was filtered off, and successively washed with 1:1 ethanol–acetone, acetone, and ether (yield 3.8 g, 80%); recrystallization from acetone gave needles; m.p. 125–127°, $[\alpha]_D$ +12°, $[\alpha]_{578}$ +12.5°, $[\alpha]_{546}$ +15°, $[\alpha]_{436}$ +32°, $[\alpha]_{365}$ +75° (*c* 0.5, pyridine); λ_{max}^{EtOH} 250 and 280 nm (ε_{mM} 8.80 and 6.30); ν_{max} 3600–3000 (OH), 1635 and 1615 (C=O), 1545, and 1505 cm^{-1} (C=C pyrrole).

Anal. Calc. for $C_{16}H_{25}NO_5$: C, 61.72; H, 8.09; N, 4.50. Found: C, 61.67; H, 8.06; N, 4.64. Periodate consumption: 3.02 mol.

*1-Ethyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(tetra-*O*-acetyl-*L-arabino-*tetritol-1-yl)indol-4-one* (**2**). — A solution of **1** (0.8 g, 2.5 mmol) in pyridine (3 mL) and acetic anhydride (3.5 mL) was kept for 24 h at room temperature, and then poured into ice–water (50 mL). The solid **2** (1.1 g, 86%) was filtered off, washed with water, and dried over sodium hydroxide; m.p. 53–55°, $[\alpha]_D$ +47°, $[\alpha]_{578}$ +49°, $[\alpha]_{546}$ +55.5°, $[\alpha]_{436}$ +107°, $[\alpha]_{365}$ +201° (*c* 1.0, chloroform); ν_{max} 1725 (C=O ester), 1630 (C=O ketone), 1540, and 1500 cm^{-1} (C=C pyrrole); ^{1}H-n.m.r. data are given in Table I.

Anal. Calc. for $C_{24}H_{33}NO_9 \cdot H_2O$: C, 57.94; H, 7.09; N, 2.82. Found: C, 57.90; H, 7.17; N, 2.96.

TABLE I

^{1}H-N M R DATA[a] (90 MHz) FOR **2, 6, 7, 8,** AND **10**

Compound	*H-1'*[b]	*H-2'*	*H-3'*	*H-4'*	*H-4''*	*H-5'*	*H-5''*	*H*[c]	*CH_3*[c]	*N-Et*	*N-Pr*	*-CH_2*[c]	*OAc*
2	6.12 d[d]	5.44 dd	5.30 m	4.27 dd	4.08 dd			6.57 s	1.11 s	3.99 q (2 H)		2.61 s	2.07 s (6 H)
	$J_{1',2'}$ 4.7	$J_{2',3'}$ 6.7	$J_{3',4'}$ 3.3	$J_{4',4''}$ −12.7						1.37 t (3 H)		2.32 s	2.03 s (6 H)
			$J_{3',4''}$ 5.5										
6	5.98 d	5.30 dd	5.52 dd	5.32 m		4.28 dd	3.93 dd	6.49 s	1.10 s	3.95 q (2 H)		2.60 s	2.10 s (6 H)
	$J_{1',2'}$ 3.2	$J_{2',3'}$ 9.3	$J_{3',4'}$ 2.3	$J_{4',5'}$ 5.0		$J_{5',5''}$ −11.3				1.39 t (3 H)		2.32 s	2.04 s (6 H)
				$J_{4',5''}$ 2.6									1.95 s (3 H)
7	5.92 d	5.27 dd	5.48 dd	5.30 m		4.24 dd	3.85 dd	6.47 s		3.91 q (2 H)		2.70 m	2.03 s (6 H)
	$J_{1',2'}$ 3.3	$J_{2',3'}$ 9.3	$J_{3',4'}$ 2.0	$J_{4',5'}$ 5.3		$J_{5',5''}$ −12.0				1.36 t (3 H)		2.35 m	1.99 s (6 H)
				$J_{4',5''}$ 6.6								2.10 m	1.92 s (3 H)
8	5.97 d	5.30 dd	5.52 dd	5.32 m		4.28 dd	3.93 dd	6.50 s	1.12 s		3.82 m (2 H)	2.59 s	2.11 s (6 H)
	$J_{1',2'}$ 3.0	$J_{2',3'}$ 9.2	$J_{3',4'}$ 2.4	$J_{4',5'}$ 5.0		$J_{5',5''}$ −12.0			1.10 s		1.82 m (2 H)	2.33 s	2.05 s (6 H)
				$J_{4',5''}$ 7.5							1.01 t (3 H)		1.97 s (3 H)
10	5.82 d	5.61 dd	5.55 dd	5.10 m		4.25 dd	3.88 dd	6.67 s	1.09 s	4.10 q (2 H)		2.57 s	2.03 s (12 H)
	$J_{1',2'}$ 8.6	$J_{2',3'}$ 1.6	$J_{3',4'}$ 9.0	$J_{4',5'}$ 3.6		$J_{5',5''}$ −15.6				1.30 t (3 H)		2.30 s	1.84 s (3 H)
				$J_{4',5''}$ 7.3									

[a]Recorded for a solution in $CDCl_3$ at 35.5°; δ scale (internal Me_4Si); *J* in Hz, with assignments verified by selective proton-decoupling. [b]Single primes denote numbering of atoms on the sugar chain. Double primes are reserved for the labeling of the upfield proton (usually) of a methylene group. [c]Heterocycle. [d]Signal multiplicities. d, doublet; dd, double doublet; m, multiplet; q, quartet; s, singlet; and t, triplet.

*1-Ethyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(*D-galacto-*pentitol-1-yl)indol-4-one* (**3**). — A solution of 2-deoxy-2-ethylamino-D-*glycero*-L-*gluco*-heptose hydrochloride[8] (10.2 g, 37.3 mmol) in water (30 mL) was treated with 5,5-dimethyl-1,3-cyclohexanedione (5.2 g, 37.3 mmol) in 2:1 acetone–water (50 mL), and sodium carbonate (2.0 g, 18.7 mmol) was added. The mixture was kept for 13 days at room temperature, and then the acetone was evaporated under diminished pressure, to give **3** as white crystals that were collected by filtration (8.0 g, 63%). Recrystallized from 96% ethanol, it gave plates, m.p. 182–184°, $[\alpha]_D$ +9.5°, $[\alpha]_{578}$ +10°, $[\alpha]_{546}$ +12°, $[\alpha]_{436}$ +26°, $[\alpha]_{365}$ +64° (*c* 1.0, pyridine); λ_{max}^{EtOH} 250 and 280 nm (ε_{mM} 8.90 and 6.40); ν_{max} 3600–3100 (OH), 1620 (C=O), 1550, and 1505 cm^{-1} (C=C pyrrole).

Anal. Calc. for $C_{17}H_{27}NO_6$: C, 59.81; H, 7.97; N, 4.10. Found: C, 59.73; H, 8.15; N, 4.17. Periodate consumption: 4.16 mol.

*1-Ethyl-4,5,6,7-tetrahydro-2-(*D-galacto-*pentitol-1-yl)indol-4-one* (**4**). — A solution of 2-deoxy-2-ethylamino-D-*glycero*-L-*gluco*-heptose hydrochloride[8] (11.0 g, 40.2 mmol) in water (25 mL) was treated with 1,3-cyclohexanedione (4.5 g, 40.2 mmol) in water (20 mL), and sodium carbonate (2.1 g, 20.1 mmol) was added. The mixture was kept for 20 days at room temperature, filtered to remove some solid impurities, and the filtrate concentrated under diminished pressure until crystallization occurred. The crude product (3.5 g) was filtered off, and successively washed with cold 80% methanol and acetone. The mother liquor and washings yielded several crops of crystals (total yield: 5.3 g, 42%). Recrystallized twice from 96% ethanol, it gave plates, m.p. 163–165°, $[\alpha]_D$ +14°, $[\alpha]_{578}$ +15°, $[\alpha]_{546}$ +18°, $[\alpha]_{436}$ +36°, $[\alpha]_{365}$ +74° (*c* 0.8, pyridine); λ_{max}^{EtOH} 248 and 275 nm (ε_{mM} 9.50 and 6.80); ν_{max} 1615 (C=O), 1550, and 1505 cm^{-1} (C=C pyrrole).

Anal. Calc. for $C_{15}H_{23}NO_6$: C, 57.50; H, 7.40; N, 4.47. Found: C, 57.79; H, 7.69; N, 4.47. Periodate consumption: 3.98 mol.

*4,5,6,7-Tetrahydro-6,6-dimethyl-2-(*D-galacto-*pentitol-1-yl)-1-propylindol-4-one* (**5**). — A solution of a mixture of 2-deoxy-2-propylamino-D-*glycero*-L-*gluco*- and -D-*glycero*-L-*manno*-heptose hydrochloride[8] (1.0 g, 3.5 mmol) in water (5 mL) was treated with 5,5-dimethyl-1,3-cyclohexanedione (0.5 g, 3.5 mmol) in 2:1 acetone–water (13 mL), and sodium hydrogencarbonate (0.3 g, 3.5 mmol) was added. The mixture was kept for 13 days at room temperature, and then the acetone was evaporated under diminished pressure. The resulting solution was washed with ethyl acetate (2 × 15 mL), and then extracted with 10:1 ethyl acetate–ethanol (10 × 15 mL). The extracts were evaporated to give **5** (0.2 g, 15%). Recrystallized from abs. ethanol, it had m.p. 149–150°, $[\alpha]_D$ +6°, $[\alpha]_{578}$ +6°, $[\alpha]_{546}$ +8°, $[\alpha]_{436}$ +20°, $[\alpha]_{365}$ +54° (*c* 0.5, pyridine); λ_{max}^{EtOH} 251 and 276 nm (ε_{mM} 10.80 and 9.00); ν_{max} 1620 (C=O), 1555, and 1510 cm^{-1} (C=C pyrrole).

Anal. Calc. for $C_{18}H_{29}NO_6$: C, 60.82; H, 8.22; N, 3.93. Found: C, 60.52; H, 8.05; N, 3.87. Periodate consumption: 3.91 mol.

*1-Ethyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(penta-*O*-acetyl-*D*-galacto-pentitol-1-yl)indol-4-one* (**6**). — A suspension of **3** (0.75 g, 2.2 mmol) in pyridine (5 mL) and acetic anhydride (3.8 mL) was kept for 24 h at room temperature, and then

poured into ice–water (50 mL). The solid **6** (1.15 g, 95%) was filtered off, washed with water, and dried over sodium hydroxide; m.p. 130–132°, $[\alpha]_D$ +58°, $[\alpha]_{578}$ +61°, $[\alpha]_{546}$ +71°, $[\alpha]_{436}$ +133°, $[\alpha]_{365}$ +232° (*c* 1.0, chloroform); ν_{max} 1740 (C=O ester), 1640 (C=O ketone), 1545, and 1510 cm^{-1} (C=C pyrrole); ^{1}H-n.m.r. data are given in Table I.

Anal. Calc. for $C_{27}H_{37}NO_{11}$: C, 58.79; H, 6.76; N, 2.54. Found: C, 58.67; H, 6.98; N, 2.72.

*1-Ethyl-4,5,6,7-tetrahydro-2-(penta-*O*-acetyl-*D*-galacto-pentitol-1-yl)indol-4-one* (**7**). — A suspension of **4** (0.47 g, 1.5 mmol) in pyridine (2.5 mL) and acetic anhydride (3.8 mL) was kept for 17 h at room temperature, and then poured into ice–water (50 mL). The solid **7** (0.45 g, 57%) was filtered off, washed with cold water, and dried *in vacuo* over sodium hydroxide; m.p. 129–131°, $[\alpha]_D$ +58°, $[\alpha]_{578}$ +61°, $[\alpha]_{546}$ +70°, $[\alpha]_{436}$ +134°, $[\alpha]_{365}$ +238° (*c* 0.8, chloroform); ν_{max} 1735 (C=O ester), 1650 (C=O ketone), 1545, and 1505 cm^{-1} (C=C pyrrole); ^{1}H-n.m.r. data are given in Table I.

Anal. Calc. for $C_{25}H_{33}NO_{11}$: C, 57.35; H, 6.35; N, 2.68. Found: C, 57.34; H, 6.46; N, 2.65.

*4,5,6,7-Tetrahydro-6,6-dimethyl-2-(penta-*O*-acetyl-*D*-galacto-pentitol-1-yl)-1-propylindol-4-one* (**8**). — A suspension of **5** (0.1 g, 0.3 mmol) in pyridine (0.5 mL) and acetic anhydride (0.5 mL) was kept for 24 h at room temperature, and then poured into ice–water (30 mL). The solid **8** (0.15 g, 92%) was filtered off, washed with water, and dried over sodium hydroxide. Recrystallized from ethanol–water, it had m.p. 75–76°, $[\alpha]_D$ +47°, $[\alpha]_{578}$ +49°, $[\alpha]_{546}$ +55°, $[\alpha]_{436}$ +108.5°, $[\alpha]_{365}$ +189° (*c* 0.4, chloroform); ν_{max} 1745 (C=O ester), 1650 (C=O ketone), 1575, and 1525 cm^{-1} (C=C pyrrole); ^{1}H-n.m.r. data are given in Table I.

Anal. Calc. for $C_{28}H_{39}NO_{11} \cdot H_2O$: C, 57.62; H, 7.08; N, 2.40. Found: C, 57.87; H, 6.97; N, 2.49.

*1-Ethyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(*D*-manno-pentitol-1-yl)indol-4-one* (**9**). — A solution of 2-deoxy-2-ethylamino-D-*glycero*-D-*talo*-heptose hydrochloride[7] (5.0 g, 18.3 mmol) in water (10 mL) was treated with 5,5-dimethyl-1,3-cyclohexanedione (2.6 g, 18.3 mmol) in 2:1 acetone–water (26 mL), and sodium carbonate (0.97 g, 9.2 mmol) was added. The mixture was kept for 20 days at room temperature, and then the acetone was evaporated under diminished pressure. The resulting solution was kept for 4 days at 0°. Compound **9** was filtered off, washed successively with water, acetone, and ether, and dried over sodium hydroxide (yield 2.62 g, 42%). Recrystallized from water and then from abs. ethanol, it gave needles, m.p. 156–158°, $[\alpha]_D$ −11.5°, $[\alpha]_{578}$ −12°, $[\alpha]_{546}$ −15°, $[\alpha]_{436}$ −23°, $[\alpha]_{365}$ −34° (*c* 0.4, pyridine); λ_{max}^{EtOH} 250 and 280 nm (ε_{mM} 8.90 and 6.30); ν_{max} 3600–3000 (OH), 1610 (C=O), 1550, and 1505 cm^{-1} (C=C pyrrole).

Anal. Calc. for $C_{17}H_{27}NO_6$: C, 59.81; H, 7.97; N, 4.10. Found: C, 59.98; H, 8.26; N, 3.95. Periodate consumption: 3.97 mol.

*1-Ethyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(penta-*O*-acetyl-*D*-manno-pentitol-1-yl)indol-4-one* (**10**). — A solution of **9** (0.7 g, 2 mmol) in pyridine (3 mL) and

acetic anhydride (3.5 mL) was kept for 17 h at room temperature, and then poured into ice–water (50 mL). The solid **10** (1.0 g, 98%) was filtered off, washed with cold water, and dried over sodium hydroxide. Recrystallized from ether–light petroleum, it had m.p. 119–121°, $[\alpha]_D$ −12°, $[\alpha]_{578}$ −13°, $[\alpha]_{546}$ −15°, $[\alpha]_{436}$ −35°, $[\alpha]_{365}$ −75° (*c* 0.6, chloroform); ν_{max} 1745 (C=O ester), 1650 (C=O ketone), 1550, and 1500 cm^{-1} (C=C pyrrole); ^{1}H-n.m.r. data are given in Table I.

Anal. Calc. for $C_{27}H_{37}NO_{11}$: C, 58.79; H, 6.76; N, 2.54. Found: C, 59.02; H, 7.02; N, 2.76.

*4,5,6,7-Tetrahydro-6,6-dimethyl-2-(*D-gluco-*pentitol-1-yl)-1-propylindol-4-one* (**11**). — A solution of a mixture of 2-deoxy-2-propylamino-D-*glycero*-D-*ido*- and D-*glycero*-D-*gulo*-heptose hydrochloride[3] (1.0 g, 3.5 mmol) in water (5 mL) was treated with 5,5-dimethyl-1,3-cyclohexanedione (0.5 g, 3.5 mmol) in 2:1 acetone–water (13 mL), and sodium hydrogencarbonate (0.3 g, 3.5 mmol) was added. The mixture was kept for 13 days at room temperature, and then the acetone was evaporated under diminished pressure. The resulting solution was washed with chloroform (2 × 15 mL), and then extracted with 10:1 ethyl acetate–ethanol (10 × 15 mL). These extracts were evaporated to give **11** (0.15 g, 12%). Recrystallized from acetone, it had m.p. 117–118°, $[\alpha]_D$ +1°, $[\alpha]_{578}$ +2°, $[\alpha]_{546}$ +2°, $[\alpha]_{436}$ +12°, $[\alpha]_{365}$ +43° (*c* 1.0, pyridine); λ_{max}^{EtOH} 252 and 280 nm (ε_{mM} 10.00 and 7.90); ν_{max} 1630 (C=O), 1560, and 1510 cm^{-1} (C=C pyrrole).

Anal. Calc. for $C_{18}H_{29}NO_6$: C, 60.82; H, 8.22; N, 3.93. Found: C, 60.75; H, 8.40; N, 4.12. Periodate consumption: 4.00 mol.

1-Alkyl-4,5,6,7-tetrahydro-4-oxoindol-2-carboxaldehydes (general method). — An ice-cold suspension of the 2-(alditol-1-yl)-1-alkyl-4,5,6,7-tetrahydroindol-4-one (3 mmol) in water (10 mL) was treated with a cold, aqueous solution (14 mL) of sodium periodate (12 mmol) under continuous stirring. After a few minutes, the compound crystallized, and it was recrystallized from ethanol.

TABLE II

^{1}H-N M R DATA[a] (90 MHz) FOR **12**, **13**, AND **14**

Compound	*CHO*	*H (heterocycle)*	*N-Et*	*N-Pr*	*CH_2 (heterocycle)*	*CH_3 (heterocycle)*
12	9.56 s[b]	7.29 s	4.37 q 1.33 t *J* 7.0		2.71 s (2 H) 2.40 s (2 H)	1.16 s (6 H)
13	9.56 s	7.29 s	4.36 q 1.35 t *J* 7.0		2.86 t (2 H) 2.52 m (2 H) 2.23 m (2 H)	
14	9.53 s	7.31 s		4.25 t 1.73 m 0.93 t	2.71 s (2 H) 2.40 s (2 H)	1.20 s (6 H)

[a]Recorded for a solution in $CDCl_3$ at 35.5°; δ scale (internal Me_4Si), *J* in Hz. [b]Signal multiplicities: m, multiplet; q, quartet; s, singlet; t, triplet.

1-Ethyl-4,5,6,7-tetrahydro-6,6-dimethyl-4-oxoindol-2-carboxaldehyde (**12**). — This was prepared from **1, 3,** or **9** by the method just described; yield, 72%; m.p. 113–115°; λ_{max}^{EtOH} 230, 254, and 294 nm (ε_{mM} 19.60, 9.10, and 18.80); ν_{max} 1640 (C=O), 1515, and 1480 cm^{-1} (C=C pyrrole); ^{1}H-n.m.r. data are given in Table II.

Anal. Calc. for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 70.99; H, 7.93; N, 6.45.

1-Ethyl-4,5,6,7-tetrahydro-4-oxoindol-2-carboxaldehyde (**13**). — This was prepared from **4** by the general method; yield, 82%; m.p. 140–142°; λ_{max}^{EtOH} 230, 254, and 294 nm (ε_{mM} 19.80, 8.90, and 18.60); ν_{max} 1640 (C=O), 1520, and 1485 cm^{-1} (C=C pyrrole); ^{1}H-n.m.r. data are given in Table II.

Anal. Calc. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.86; H, 7.05; N, 7.32.

4,5,6,7-Tetrahydro-6,6-dimethyl-4-oxo-1-propylindol-2-carboxaldehyde (**14**). — This was prepared from **5** or **11** by the general method; yield, 86%; m.p. 110–111°; λ_{max}^{EtOH} 298 nm (ε_{mM} 5.30); ν_{max} 1665 and 1650 (C=O), 1555, and 1515 cm^{-1} (C=C pyrrole); ^{1}H-n.m.r. data are given in Table II.

Anal. Calc. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.32; H, 8.54; N, 5.72.

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