## Note

# Acyclic-sugar pyrrole C-nucleoside-analogs derived from 2-(alkylamino)-2deoxyaldoses

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The reaction of 2-amino-2-deoxyaldoses with 1,3-dicarbonyl compounds yields (alditol-1-yl)pyrroles<sup>1,2</sup> which can be considered to be acyclic *C*-nucleosideanalogs. These compounds can become cyclic by acid-catalyzed, intramolecular dehydration of the polyhydroxyalkyl chain<sup>3-5</sup>. We now report on the preparation of new 1-alkyl-(tetritol-1-yl)- and -(pentitol-1-yl)-pyrroles from 2-(alkylamino)-2deoxyhexoses and 2-(alkylamino)-2-deoxyheptoses, respectively.

The reaction of 2-deoxy-2-(ethylamino)-L-glucose<sup>6</sup> with 2,4-pentanedione or ethyl 3-oxobutanoate yields the 1-ethyl-5-(L-*arabino*-tetritol-1-yl)pyrroles 1 or 2, whose structures were demonstrated by elemental analyses and spectral data (u.v. and i.r.). The presence of the tetrahydroxybutyl chain was proved by periodate oxidation, showing a periodate consumption of 3 mol per mol of compound. This oxidation produces the pyrrolecarboxaldehydes 17 and 19, which confirm the structures of the heterocyclic ring-systems. Furthermore, the polyhydroxyl chain was proved by preparing the tetra-O-acetyl derivatives 3 and 4.

In a similar way, by reaction of 2,4-pentanedione or ethyl 3-oxobutanoate with 2-deoxy-2-(ethylamino)-D-glycero-L-gluco-heptopyranose<sup>7</sup>, the 1-ethyl-5-(D-galacto-pentitol-1-yl)pyrroles 5 or 6 were respectively obtained; the reaction of the epimeric mixture of 2-deoxy-2-(propylamino)-D-glycero-L-gluco- and -D-glycero-L-manno-heptose<sup>8</sup> with 2,4-pentanedione yielded 3-acetyl-2-methyl-5-(D-galacto-pentitol-1-yl)-1-propylpyrrole (7), as the chirality of C-2 is lost in the course of these reactions. The structures of these compounds were proved as indicated for 1 and 2; they showed a periodate consumption of 4 mol per mol of compound, indicative of five contiguous hydroxyl groups, and yielded in these oxidations the corresponding pyrrolecarboxaldehyde (17, 18, or 19). In addition, conventional treatment with acetic anhydride in pyridine gave the penta-O-acetyl derivatives 8, 9, and 10.

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Equally, the reaction of the epimeric mixture of 2-deoxy-2-(ethylamino)-Dglycero-D-ido- and -D-glycero-D-gulo-heptopyranose<sup>7</sup> with 2,4-pentanedione or ethyl 3-oxobutanoate gave the 1-ethyl-5-(D-gluco-pentitol-1-yl)pyrroles 11 and 12, and the reaction of the mixture of 2-deoxy-2-(propylamino)-D-glycero-D-ido- and -D-glycero-D-gulo-heptopyranose<sup>8</sup> with 2,4-pentanedione led to 3-acetyl-2-methyl-5-(D-gluco-pentitol-1-yl)-1-propylpyrrole (13). The 1-alkyl-(D-manno-pentitol-1yl)pyrroles 14–16 were also obtained from 2-deoxy-2-(ethylamino)-D-glycero-Dtalo-heptose<sup>7</sup> and from the epimeric mixture of 2-deoxy-2-(propylamino)-D-glycero-Dero-D-talo- and -D-glycero-D-galacto-heptose<sup>8</sup> by reaction with the 1,3-dicarbonyl compounds mentioned. The structures of these compounds (11–16) were also demonstrated by the conventional methods described for 1 and 2.



#### 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  $22 \pm 4^{\circ}$  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. 90-MHz, <sup>1</sup>H-n.m.r. spectra, with internal Me<sub>4</sub>Si or sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS), were recorded with a Perkin–Elmer R-32 spectrometer, and coupling constants were measured directly from spectra recorded at 300-Hz sweepwidth (temperature of the probe, 35.5°). Assignments were confirmed by double-resonance (spin–spin decoupling), and overlapping signals were gradually shifted, and separated from one another, by incremental addition of Eu(fod)<sub>3</sub>.

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<sup>9</sup>.

3-Acetyl-1-ethyl-2-methyl-5-(L-arabino-tetritol-1-yl)pyrrole (1). — A solution of 2-deoxy-2-(ethylamino)-L-glucose hydrochloride<sup>6</sup> (4.0 g, 15.3 mmol) in water (10 mL) was treated with sodium hydrogencarbonate (1.4 g, 16.6 mmol), and 2,4-pentanedione (5.0 mL, 50 mmol) in ethanol (15 mL) was added. The mixture was kept for 10 days in the dark at room temperature and then concentrated under diminished pressure until crystallization occurred. Compound 1 was filtered off, and washed with cold abs. ethanol. The mother liquor yielded a second crop of crystals (overall yield 2.7 g, 64%). Recrystallized from abs. ethanol, it gave needles; m.p. 128–130°,  $[\alpha]_{D}$  +11°,  $[\alpha]_{578}$  +11°,  $[\alpha]_{546}$  +12°,  $[\alpha]_{436}$  +22°,  $[\alpha]_{365}$  +41.5° (c 0.5, pyridine);  $\lambda_{max}^{EtOH}$  248 and 281 nm ( $\varepsilon_{mM}$  8.80 and 6.10);  $\nu_{max}$  3600–3000 (OH), 1650 (C=O), 1540, and 1500 cm<sup>-1</sup> (C=C pyrrole).

*Anal.* Calc. for C<sub>13</sub>H<sub>21</sub>NO<sub>5</sub>: C, 57.55; H, 7.80; N, 5.16. Found: C, 57.80; H, 7.50; N, 5.05. Periodate consumption: 2.96 mol.

3-(Ethoxycarbonyl)-1-ethyl-2-methyl-5-(L-arabino-tetritol-1-yl)pyrrole (2). — This was prepared from 2-deoxy-2-(ethylamino)-L-glucose hydrochloride<sup>6</sup> (4.0 g, 15.3 mmol) and ethyl 3-oxobutanoate (7.5 mL, 58.8 mmol) as described for 1. After 8 days, the mixture was concentrated under diminished pressure until crystallization began. Water (12 mL) and ether (10 mL) were then added and the mixture was kept overnight at 0°. Crude 2 (1.74 g, 38%) was filtered off, and successively washed with cold 96% ethanol and ether. Recrystallized from abs. ethanol, it gave needles; m.p. 144–145°,  $[\alpha]_D$  +7°,  $[\alpha]_{578}$  +8°,  $[\alpha]_{546}$  +9°,  $[\alpha]_{436}$  +16°,  $[\alpha]_{365}$  +27° (c 0.5, pyridine);  $\lambda_{max}^{\rm EtOH}$  228 and 256 nm ( $\varepsilon_{\rm mM}$  8.80 and 6.20);  $\nu_{max}$  3600–3100 (OH), 1680 (C=O), 1550, and 1505 cm<sup>-1</sup> (C=C pyrrole).

N.M.R. DATA <sup>a</sup>	(90 MHz) FOF	₹3, 4, 8, 9, A	ND 10								
Compound No.	<sub>q</sub> ,1-H	Н-2'	Н-3'	H-4'	H-4"	Н-5'	Н-5"	Н-4	CH <sub>3</sub> (heterocyc	N-R <sup>c</sup> COI	rd OAc
3	6.16d J <sub>1<sup>,</sup>2<sup>,</sup>6.0</sub>	5.56 dd J <sub>2',3'</sub> 5.7	5.21 m J <sub>3',4'</sub> 3.3 J <sub>3',4"</sub> 5.6	4.30 dd J <sub>4',4</sub> " –12.6	4.03 d			6.63s	2.53 s	4.02 q (2H) 2.38 1.32 t (3 H)	s 2.08 s (3H) 2.05 s (3H) 2.03 s (3H) 2.02 s (3H)
4	6.12 d J <sub>1<sup>',2'</sup> 5.7</sub>	5.49 t J <sub>2',3'</sub> 5.7	5.23 m J <sub>3',4'</sub> 3.3 J <sub>3',4"</sub> 5.7	4.40–3	.80 m			6.62 s	2.51 s	4.40–3.80 m (4 ] 1.32–1.30 m (6F	<ul> <li>1) 2.05 s (3H)</li> <li>1) 2.04 s (6H)</li> <li>2.01 s (3H)</li> </ul>
æ	6.03 d ▲ J <sub>1',2'</sub> 4.0		- 5.50–5.20 n	n $I_{4',5'}$ 5.0 $I_{4',5''}$ 7.0		$4.27  \mathrm{dd}$ $J_{5',5'} - 11.$	3.88 dd 5	6.48 s	2.52 s	3.98 q (2H) 2.35 1.33 t (3H)	s 2.08s(3H) 2.04s(6H) 2.01s(6H)
a	5.97 d		- 5.55-5.15 n	$n \to J_{4',5'} 5.2$ $J_{4',5'} 7.1$		4.4 J <sub>5',5"</sub> -11.3	0–3.70 m 8	6.49 s	2.48 s	4.22–3.90 m (4 1.31–1.27 m (6	<ul> <li>H) 2.03 s (6H)</li> <li>H) 2.02 s (3H)</li> <li>2.00 s (3H)</li> <li>1.98 s (3H)</li> </ul>
10	6.04 d • J <sub>1<sup>',2'</sup> 4.0</sub>		- 5.60-5.20 п	$n \to J_{4, 5', 5.0}$ $J_{4', 5', 7.5}$		4.25 dd J <sub>S<sup>, S<sup>r</sup></sup></sub> -12.	3.88 dd 0	6.49 s	2.53 s	3.85 m (2H) 2.37 1.90 m (2H) 1.00 t (3H)	s 2.07 s (3H) 2.05 s (6H) 2.02 s (6H)
"Recorded in	CDCl <sub>3</sub> at 35.	.5°; 8 scale (i	internal Me <sub>4</sub> 5	Si); J in Hz, <sup>1</sup>	with assign	ments verifie	d by selectiv	e proton-de	scoupling. <sup>b</sup> Si	ngle primes denote r	umbering of atoms

on the sugar-chain atoms. Double primes are reserved for labeling of the upfield proton (usually) of a methylene group.  ${}^{c}R = Et$  in 3, 4, 8, and 9. R = Pr in 10.  ${}^{d}R' = Me$  in 3, 8, and 10. R' = OEt in 4, and 9. R in the sugar-chain atom.  ${}^{c}R = OEt$  in 4, and 9. R in 10.  ${}^{d}R'$ 

156

TABLEI

Anal. Calc. for  $C_{14}H_{23}NO_6$ : C, 55.80; H, 7.69; N, 4.65. Found: C, 55.89; H, 7.56; N, 4.67. Periodate consumption: 3.00 mol.

3-Acetyl-1-ethyl-2-methyl-5-(tetra-O-acetyl-L-arabino-tetritol-1-yl)pyrrole (3). — To a suspension of 1 (0.68 g, 2.5 mmol) in pyridine (2 mL) was added acetic anhydride (4 mL) at ~25°. After 24 h, the mixture was poured over ice. The resulting precipitate was filtered off, washed on the filter with cold water (yield 0.92 g, 84%), and recrystallized from light petroleum (b.p. 100–140°); m.p. 130–132°,  $[\alpha]_D$ +54°,  $[\alpha]_{578}$  +58°,  $[\alpha]_{546}$  +67°,  $[\alpha]_{436}$  +134°,  $[\alpha]_{365}$  +259° (c 1.0, chloroform);  $\nu_{max}$  1735 (C=O ester), 1645 (C=O ketone), 1550, and 1505 cm<sup>-1</sup> (C=C pyrrole); <sup>1</sup>H-n.m.r. data are given in Table I.

Anal. Calc. for  $C_{21}H_{29}NO_9$ : C, 57.40; H, 6.65; N, 3.19. Found: C, 57.50; H, 6.91; N, 3.20.

3-(Ethoxycarbonyl)-1-ethyl-2-methyl-5-(tetra-O-acetyl-L-arabino-tetritol-1yl)-pyrrole (4). — Acetylation of 2 (0.6 g, 2 mmol) as described for 3 gave the tetraacetate 4 (0.87 g, 93%). Recrystallized from ether-hexane, it gave needles; m.p. 92–94°,  $[\alpha]_D$  +41°,  $[\alpha]_{578}$  +43°,  $[\alpha]_{546}$  +51°,  $[\alpha]_{436}$  +100°,  $[\alpha]_{365}$  +191° (c 1.0, chloroform);  $\nu_{max}$  1735 and 1690 (C=O, ester), 1560, and 1515 cm<sup>-1</sup> (C=C pyrrole); <sup>1</sup>H-n.m.r. data are given in Table I.

*Anal.* Calc. for C<sub>22</sub>H<sub>31</sub>NO<sub>10</sub>: C, 56.28; H, 6.66; N, 2.98. Found: C, 56.39; H, 6.90; N, 3.01.

3-Acetyl-1-ethyl-2-methyl-5-(D-galacto-pentitol-1-yl)pyrrole (5). — This was prepared from 2-deoxy-2-(ethylamino)-D-glycero-L-gluco-heptopyranose hydro-chloride<sup>7</sup> (11.1 g, 40.6 mmol) and 2,4-pentanedione (8.1 mL, 81.3 mmol) as described for 1. The mixture was kept for 20 days at room temperature, and then evaporated under diminished pressure. The resulting, thick syrup was treated with water (20 mL), and the solution was extracted with ether to remove the excess of dicarbonyl compound. The aqueous layer was concentrated to half-volume and cooled, to give **5** as white crystals that were collected by filtration. The mother liquor yielded a second crop of crystals (overall yield 2.8 g, 23%). Recrystallized twice from abs. ethanol, it gave needles; m.p. 163–165°,  $[\alpha]_D$  +3.5°,  $[\alpha]_{578}$  +3°,  $[\alpha]_{546}$  +4°,  $[\alpha]_{436}$  +10°,  $[\alpha]_{365}$  +27° (c 1.0, pyridine);  $\lambda_{max}^{EtOH}$  249 and 284 nm ( $\varepsilon_{mM}$  8.50 and 5.60);  $\nu_{max}$  3600–3000 (OH), 1640 (C=O), 1540, and 1500 cm<sup>-1</sup> (C=C pyrrole).

*Anal.* Calc. for C<sub>14</sub>H<sub>23</sub>NO<sub>6</sub>: C, 55.80; H, 7.69; N, 4.65. Found: C, 55.49; H, 8.00; N, 4.84. Periodate consumption: 3.97 mol.

3-(Ethoxycarbonyl)-1-ethyl-2-methyl-5-(D-galacto-pentitol-1-yl)pyrrole (6). — This was synthesized from 2-deoxy-2-(ethylamino)-D-glycero-L-gluco-heptopyranose hydrochloride<sup>7</sup> (4.4 g, 16.1 mmol) and ethyl 3-oxobutanoate (8.2 mL, 64.4 mmol) as described for 5. The aqueous solution remaining after extraction was concentrated until crystallization occurred. After 24 h at 0°, compound 6 was filtered off, and successively washed with cold abs. ethanol, acetone, and ether. The mother liquor yielded a second crop of crystals (overall yield 0.99 g, 19%). Recrystallized from abs. ethanol, it had m.p. 145-147°,  $[\alpha]_{D} = +6^{\circ}$ ,  $[\alpha]_{578} = +6^{\circ}$ ,  $[\alpha]_{546}$  +7°,  $[\alpha]_{436}$  +13°,  $[\alpha]_{365}$  +24° (c 0.5, pyridine);  $\lambda_{max}^{EtOH}$  228 and 256 nm ( $\varepsilon_{mM}$  8.90 and 6.30);  $\nu_{max}$  3600–3000 (OH), 1650 (C=O), 1560, and 1505 cm<sup>-1</sup> (C=C pyr-role).

*Anal.* Calc. for C<sub>15</sub>H<sub>25</sub>NO<sub>7</sub>: C, 54.37; H, 7.60; N, 4.23. Found: C, 54.30; H, 7.90; N, 3.95. Periodate consumption: 3.97 mol.

3-Acetyl-2-methyl-5-(D-galacto-pentitol-1-yl)-1-propylpyrrole (7). — Compound 7 was prepared from the epimeric mixture of 2-deoxy-2-(propylamino)-D-glycero-L-gluco- and D-glycero-L-manno-heptose hydrochloride<sup>8</sup> (1.0 g, 3.5 mmol) and 2,4-pentanedione (1.8 mL, 17.7 mmol) as described for 5. After 5 days, the mixture was processed, to give crystalline product (0.36 g, 33%) which was recrystallized from ethanol; m.p. 181–182°,  $[\alpha]_D + 2^\circ$ ,  $[\alpha]_{578} + 2^\circ$ ,  $[\alpha]_{546} + 3^\circ$ ,  $[\alpha]_{436} + 8^\circ$ ,  $[\alpha]_{365} + 24^\circ$  (c 0.5, pyridine);  $\lambda_{max}^{\text{EtOH}}$  252 and 279 nm ( $\varepsilon_{mM}$  10.30 and 8.20);  $\nu_{max}$  3600–3200 (OH), 1650 (C=O), 1560, and 1515 cm<sup>-1</sup> (C=C pyrrole).

*Anal.* Calc. for C<sub>15</sub>H<sub>25</sub>NO<sub>6</sub>: C, 57.12; H, 7.99; N, 4.44. Found: C, 57.42; H, 8.15; N, 4.40. Periodate consumption: 3.95 mol.

3-Acetyl-1-ethyl-2-methyl-5-(penta-O-acetyl-D-galacto-pentitol-1-yl)pyrrole (8). — Acetylation of 5 (0.3 g, 1.0 mmol), as described for 3, afforded the pentaacetate 8 (0.49 g, 96%). Recrystallized from 96% ethanol, it gave needles; m.p. 145–147°,  $[\alpha]_D$  +71°,  $[\alpha]_{578}$  +74°,  $[\alpha]_{546}$  +86°,  $[\alpha]_{436}$  +159°,  $[\alpha]_{365}$  +280° (c 0.7, chloroform);  $\nu_{max}$  1640 (C=O ester), 1635 (C=O ketone), 1545, and 1500 cm<sup>-1</sup> (C=C pyrrole); <sup>1</sup>H-n.m.r. data are given in Table I.

*Anal.* Calc. for C<sub>24</sub>H<sub>33</sub>NO<sub>4</sub>: C, 56.35; H, 6.50; N, 2.74. Found: C, 56.67; H, 6.69; N, 2.79.

3-(Ethoxycarbonyl)-1-ethyl-2-methyl-5-(penta-O-acetyl-D-galacto-pentitol-1yl)pyrrole (9). — Conventional treatment of 6 (0.33 g, 1.0 mmol), as described for the preparation of 3, gave the pentaacetate 9 (0.54 g, 99%); m.p. 99–101°,  $[\alpha]_D$ +59.5°,  $[\alpha]_{578}$  +63°,  $[\alpha]_{546}$  +72.5°,  $[\alpha]_{436}$  +137°,  $[\alpha]_{365}$  +244° (c 1.0, chloroform);  $\nu_{max}$  1735 and 1690 (C=O ester), 1560 and 1515 cm<sup>-1</sup> (C=C pyrrole); <sup>1</sup>H-n.m.r. data are given in Table I.

*Anal.* Calc. for C<sub>25</sub>H<sub>35</sub>NO<sub>12</sub>: C, 55.45; H, 6.51; N, 2.59. Found: C, 55.01; H, 6.67; N, 2.49.

3-Acetyl-2-methyl-5-(penta-O-acetyl-D-galacto-pentitol-1-yl)-1-propylpyrole (10). — Acetylation of 7 (0.06 g, 0.2 mmol), as described for 3, gave 10 (0.09 g, 94%). Recrystallized from ethanol, it had m.p. 118–120°,  $[\alpha]_D$  +58°,  $[\alpha]_{578}$  +61°,  $[\alpha]_{546}$  +71°,  $[\alpha]_{436}$  +136°,  $[\alpha]_{365}$  +251° (c 0.5, chloroform);  $\nu_{max}$  1760–1730 (C=O ester), 1650 (C=O ketone), 1555, and 1510 cm<sup>-1</sup> (C=C pyrrole); <sup>1</sup>H-n.m.r. data are given in Table I.

*Anal.* Calc. for C<sub>25</sub>H<sub>35</sub>NO<sub>11</sub>: C, 57.13; H, 6.71; N, 2.67. Found: C, 57.28; H, 6.81; N, 2.90.

3-Acetyl-1-ethyl-2-methyl-5-(D-gluco-pentitol-1-yl)pyrrole (11). — Compound 11 was prepared from the epimeric mixture of 2-deoxy-2-(ethylamino)-Dglycero-D-ido- and -D-glycero-D-gulo-heptopyranose hydrochloride<sup>7</sup> (11.2 g, 41 mmol) and 2,4-pentanedione (10.0 mL, 100 mmol) as described for 1. The mixture was kept for 10 days at room temperature and then evaporated under diminished pressure. The resulting syrup was treated with water (15 mL) and extracted with (a) 4:1 (4 × 25 mL) and (b) 10:1 ethyl acetate–ethanol (3 × 20 mL). The extracts were combined, dried (MgSO<sub>4</sub>), and evaporated. The resulting syrup crystallized from abs. ethanol–ether (yield 1.54 g, 13%). Recrystallized from abs. ethanol and then from 96% ethanol, it gave needles; m.p. 150–152°,  $[\alpha]_{D} -9°$ ,  $[\alpha]_{578} -9.5°$ ,  $[\alpha]_{546} -11°$ ,  $[\alpha]_{436} -15°$ ,  $[\alpha]_{365} -17°$  (c 0.5, pyridine);  $\lambda_{max}^{EtOH}$  249 and 282 nm ( $\varepsilon_{mM}$  8.30 and 5.80);  $\nu_{max}$  3600–3100 (OH), 1625 (C=O), 1555, and 1505 cm<sup>-1</sup> (C=C pyrrole).

Anal. Calc. for  $C_{14}H_{23}NO_6$ : C, 55.80; H, 7.69; N, 4.65. Found: C, 55.73; H, 7.83; N, 4.74. Periodate consumption: 3.90 mol.

3-(Ethoxycarbonyl)-1-ethyl-2-methyl-5-(D-gluco-pentitol-1-yl)pyrrole (12). — Compound 12 was prepared from the epimeric mixture of 2-deoxy-2-(ethylamino)-D-glycero-D-ido- and -D-glycero-D-gulo-heptopyranose hydrochloride<sup>8</sup> (9.7 g, 35.5 mmol) and ethyl 3-oxobutanoate (18.1 mL, 142 mmol) as described for 1. After 5 days, the mixture was processed as described for 11, to give a syrup that crystallized on dissolving in hot abs. ethanol and then adding ether to incipient crystallization (yield 1.48 g, 12%). Recrystallized from ethyl acetate, it had m.p. 79–81°,  $[\alpha]_D$  –2°,  $[\alpha]_{578}$  –2°,  $[\alpha]_{546}$  –2°,  $[\alpha]_{436}$  –2°,  $[\alpha]_{365}$  +2° (c 0.5, pyridine);  $\lambda_{max}^{EtOH}$  228 and 256 nm ( $\varepsilon_{mM}$  8.10 and 5.90);  $\nu_{max}$  3600–3100 (OH), 1695 (C=O), 1555, and 1505 cm<sup>-1</sup> (C=C pyrrole).

*Anal.* Calc. for C<sub>15</sub>H<sub>25</sub>NO<sub>7</sub>: C, 54.37; H, 7.60; N, 4.23. Found: C, 54.44; H, 7.67; N, 4.18. Periodate consumption: 3.83 mol.

3-Acetyl-2-methyl-5-(D-gluco-pentitol-1-yl)-1-propylpyrrole (13). — This was prepared from a mixture of 2-deoxy-2-(propylamino)-D-glycero-D-ido- and -D-glycero-D-gluo-heptopyranose hydrochloride<sup>7</sup> (7.0 g, 24.3 mmol) and 2,4-pentanedione (12.6 mL, 126 mmol) as described for 1. After 5 days, the mixture was processed as described for 11, to give crystalline 13 (2.52 g, 33%). Recrystallized from ethanol, it had m.p. 119–120°,  $[\alpha]_{D}$  = 5.5°,  $[\alpha]_{578}$  = 5°,  $[\alpha]_{546}$  = 7°,  $[\alpha]_{436}$  = 12°,  $[\alpha]_{365}$  = 19° (c 0.4, pyridine);  $\lambda_{max}^{EtOH}$  252 and 287 nm ( $\varepsilon_{mM}$  9.00 and 5.80);  $\nu_{max}$  3600–3000 (OH), 1625 (C=O), 1540, and 1500 cm<sup>-1</sup> (C=C pyrrole).

Anal. Calc. for  $C_{15}H_{25}NO_6$ : C, 57.12; H, 7.99; N, 4.46. Found: C, 57.30; H, 8.01; N, 4.37. Periodate consumption: 4.13 mol.

3-Acetyl-1-ethyl-2-methyl-5-(D-manno-pentitol-1-yl)pyrrole (14). — This was prepared from 2-deoxy-2-(ethylamino)-D-glycero-D-talo-heptopyranose hydro-chloride<sup>7</sup> (5.0 g, 18.3 mmol) and 2,4-pentanedione (3.7 mL, 37.0 mmol) as described for **5**. The remaining aqueous solution was concentrated until onset of incipient crystallization. After 12 h at 0°, compound 14 was filtered off and successively washed with cold abs. ethanol, acetone, and ether (yield 1.57 g, 29%). Recrystallized twice from 80% ethanol, it had m.p. 197–199°,  $[\alpha]_D = -16^\circ$ ,  $[\alpha]_{578} = -16^\circ$ ,  $[\alpha]_{546} = -18^\circ$ ,  $[\alpha]_{436} = -25^\circ$ ,  $[\alpha]_{365} = -13^\circ$  (c 0.5, pyridine);  $\lambda_{max}^{E1OH}$  249 and 284 nm ( $\varepsilon_{mM}$  8.50 and 5.50);  $\nu_{max}$  3600–3000 (OH), 1620 (C=O), 1550, and 1510 cm<sup>-1</sup> (C=C pyrrole).

Anal. Calc. for  $C_{14}H_{23}NO_6$ : C, 55.80; H, 7.69; N, 4.65. Found: C, 55.66; H, 8.03; N, 4.61. Periodate consumption: 3.92 mol.

3-(Ethoxycarbonyl)-1-ethyl-2-methyl-5-(D-manno-pentitol-1-yl)pyrrole (15). — This was prepared from 2-deoxy-2-(ethylamino)-D-glycero-D-talo-heptopyranose hydrochloride<sup>7</sup> (5.0 g, 18.3 mmol) and ethyl 3-oxobutanoate (9.3 mL, 73 mmol) as described for 11. After concentrating the organic layer, the resulting yellow solid was triturated with the aid of ethyl acetate. After 24 h at 0°, the solid was filtered off and washed with ethyl acetate (yield 0.71 g, 12%). Recrystallized from acetone, it gave needles; m.p. 143–145°,  $[\alpha]_D - 10^\circ$ ,  $[\alpha]_{578} - 10^\circ$ ,  $[\alpha]_{546} - 11^\circ$ ,  $[\alpha]_{436} - 16^\circ$ ,  $[\alpha]_{365} - 13^\circ$  (c 0.5, pyridine);  $\lambda_{max}^{EtOH}$  228 and 256 nm ( $\varepsilon_{mM}$  8.60 and 6.00);  $\nu_{max}$  3600–3100 (OH), 1670 (C=O), 1555, and 1505 cm<sup>-1</sup> (C=C pyrrole).

*Anal.* Calc. for C<sub>15</sub>H<sub>25</sub>NO<sub>7</sub>: C, 54.37; H, 7.60; N, 4.23. Found: C, 54.61; H, 7.86; N, 4.12. Periodate consumption: 4.00 mol.

3-Acetyl-2-methyl-5-(D-manno-pentitol-1-yl)-1-propylpyrrole (16). — Compound 16 was prepared from a mixture of 2-deoxy-2-(propylamino)-D-glycero-D-talo- and D-glycero-D-galacto-heptopyranose hydrochloride<sup>8</sup> (2.5 g, 8.7 mmol) and 2,4-pentanedione (4.5 mL, 44.2 mmol) as described for 11. The organic layer was evaporated *in vacuo* to give a thick syrup that crystallized from ethanol (yield 0.5 g, 18%). Recrystallized from abs. ethanol, it had m.p. 161–162°,  $[\alpha]_D = -15^\circ$ ,  $[\alpha]_{578} = -17^\circ$ ,  $[\alpha]_{546} = -18^\circ$ ,  $[\alpha]_{436} = -26^\circ$ ,  $[\alpha]_{365} = -18^\circ$  (c 0.4, pyridine);  $\lambda_{max}^{\text{EtOH}}$  252 and 287 nm ( $\varepsilon_{\text{mM}}$  9.00 and 5.80);  $\nu_{\text{max}}$  3600–3050 (OH), 1620 (C=O), 1555, and 1510 cm<sup>-1</sup> (C=C pyrrole).

*Anal.* Calc. for C<sub>15</sub>H<sub>25</sub>NO<sub>6</sub>: C, 57.12; H, 7.99; N, 4.46. Found: C, 56.89; H, 8.34; N, 4.27. Periodate consumption: 4.09 mol.

3-Acetyl-1-ethyl-2-methylpyrrole-5-carboxaldehyde (17). — An ice-cold solution of 1, 5, 11, or 14 (1.3 g, 4.3 mmol) in water (10 mL) was treated with a cold, aqueous solution (20 mL) of sodium periodate (3.7 g, 13.3 mmol) under continuous stirring. The product (19) began to crystallize after a few minutes, and the suspension was left for 2 h in a refrigerator. The crystals (~75% yield) were collected, and recrystallized from abs. ethanol; m.p. 131–133° (lit.<sup>10</sup> m.p. 114–115°);  $\lambda_{max}^{EtOH}$  232 and 292 nm ( $\varepsilon_{mM}$  19.50 and 18.90);  $\nu_{max}$  1640 (C=O), 1525, and 1475 cm<sup>-1</sup> (C=C pyrrole); <sup>1</sup>H-n.m.r. data (CDCl<sub>3</sub>):  $\delta$  9.51 (s, 1 H, CHO), 7.28 (s, 1 H, CH pyrrole), 4.42 (q, 2 H, CH<sub>2</sub>), 2.63 (s, 3 H, CH<sub>3</sub>), 2.46 (s, 3 H, COCH<sub>3</sub>), and 1.32 (t, 3 H, CH<sub>2</sub>CH<sub>3</sub>).

Anal. Calc. for C<sub>10</sub>H<sub>13</sub>NO<sub>2</sub>: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.09; H, 7.37; N, 7.61.

3-Acetyl-2-methyl-1-propylpyrrole-5-carboxaldehyde (18). — Compound 18 was prepared from 7, 13, or 16 as described for 17. The crystals (~95% yield) were collected, and recrystallized from abs. ethanol; m.p. 62–63°;  $\lambda_{max}^{EtOH}$  296 nm ( $\varepsilon_{mM}$  15.40);  $\nu_{max}$  1645 (C=O), 1560, and 1520 cm<sup>-1</sup> (C=C pyrrole); <sup>1</sup>H-n.m.r. data (CDCl<sub>3</sub>):  $\delta$  9.44 (s, 1 H, CHO), 7.22 (s, 1 H, CH pyrrole), 4.32 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.60 (s, 3 H, CH<sub>3</sub>), 2.44 (s, 3 H, COCH<sub>3</sub>), 1.70 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), and 0.92 (t, 3 H, CH<sub>2</sub>CH<sub>3</sub>CH<sub>3</sub>).

*Anal.* Calc. for C<sub>11</sub>H<sub>15</sub>NO<sub>2</sub>: C, 68.34; H, 7.82; N, 7.27. Found: C, 68.50; H, 7.96; N, 7.56.

3-(Ethoxycarbonyl)-1-ethyl-2-methylpyrrole-5-carboxaldehyde (19). — An ice-cold solution of 2, 6, 12, or 15 in 20% ethanol was treated as described for 17. The crystals (~95% yield) were collected, and recrystallized from abs. ethanol; m.p. 49–51°. This product was identified by its i.r. spectrum and m.p. with the product already described<sup>10</sup>.

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