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NEW *C*-NUCLEOSIDE ANALOGS BY DEHYDRATION OF 1-BENZYL-4,5,6,7-TETRAHYDRO-6,6-DIMETHYL-2-(D-*galacto*-PENTITOL-1-YL)-INDOL-4-ONE*

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ABSTRACT

The reaction between 2-(benzylamino)-2-deoxy-D-*glycero*-L-*gluco*-heptose and 5,5-dimethyl-1,3-cyclohexanedione yields 1-benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(D-*galacto*-pentitol-1-yl)-indol-4-one (**2**). Acid-catalyzed, intramolecular dehydration of **2** under kinetically controlled conditions gives 1-benzyl-4,5,6,7-tetrahydro-2-α-D-lyxofuranosyl-6,6-dimethylindol-4-one; the anomeric configuration of this compound is only suggested. When the dehydration reaction is conducted under thermodynamically controlled conditions, it produces a 1:1 mixture of the α- and β-D-lyxopyranosyl compounds. The structures of the new compounds were elucidated by chemical and physical methods.

INTRODUCTION

In studies on the preparation of *C*-nucleoside analogs, we have recently described the dehydration of some D-*galacto*-pentitol-1-yl derivatives of pyrrole and tetrahydroindol-4-one[1–3]. In that work, we had not described dehydration products having furanoid structures, and we presumed that the dehydration of these D-*galacto* compounds led exclusively to pyranoid products under conditions of kinetic or thermodynamic control. We now describe the dehydration of the new compound 1-benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(D-*galacto*-pentitol-1-yl)-indol-4-one (**2**) that yields 1-benzyl-4,5,6,7-tetrahydro-2-α-D-lyxofuranosyl-6,6-dimethylindol-4-one (**6**) under kinetically controlled conditions. If the reaction is thermodynamically controlled, it produces a 1:1 mixture of the α and β pyranoid compounds **8** and **10**.

The starting material for these syntheses was 2-(benzylamino)-2-deoxy-D-*glycero*-L-*gluco*-heptose (**1**), a compound not hitherto reported.

*Taken, in part, from the Ph. D. Thesis of M.A.A A.

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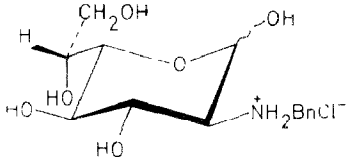
RESULTS AND DISCUSSION

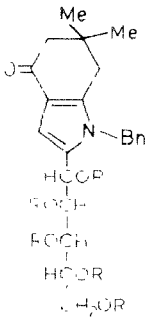
We describe the preparation of 2-(benzylamino)-2-deoxy-D-*glycero*-L-*gluco*-heptose (**1**) by the aminonitrile synthesis[4]. As previously indicated, the hydrogenation of 2-(benzylamino)-2-deoxyheptononitriles in the presence of 10% palladium-on-barium sulfate as catalyst takes place with hydrogenolysis of the benzyl group. Monitoring of the hydrogenation of 2-(benzylamino)-2-deoxy-D-*glycero*-L-*gluco*-heptononitrile by paper chromatography revealed that, after three days, the starting material had nearly all disappeared, and two new products (R_f 0.50 and 0.39) had been formed. The less-mobile product could be crystallized, and it was identified as 2-amino-2-deoxy-D-*glycero*-L-*gluco*-heptose hydrochloride[4]. The other product stayed in the mother liquor, and was identified as **1** on the basis of reactions described later. If the hydrogenation was continued for longer than three days, the 2-amino-2-deoxy-heptose was the only compound detected.

The reaction of **1** with 5,5-dimethyl-1,3-cyclohexanedione yields 1-benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(D-*galacto*-pentitol-1-yl)-indol-4-one (**2**), whose

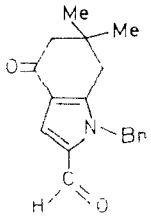


1

Bn = $PhCH_2$



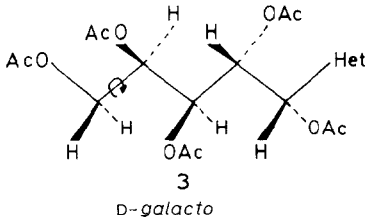
2 R = H
3 R = Ac
4 R = Bz



5

structure was 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, showing a periodate consumption of 4 mol per mol of substance. Assignment of the D-*galacto* configuration is based on the configuration of the sugar precursor of **1**, and is consistent with the Richtmyer–Hudson rules[6]. The structure of the heterocyclic ring-system was established by oxidative degradation of the polyhydroxyalkyl side-chain to give 1-benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-4-oxo-indole-2-carboxaldehyde (**5**). The structure of **2** was also proved by prepara-

tion of its pentaacetate (**3**) and pentabenzoate (**4**). The coupling constants between the chain-protons of **3** demonstrated the preponderance of the conformation having the planar, zigzag arrangement of carbon atoms 1′–5′. No unfavorable, parallel 1,3-interaction[7] of acetoxyl groups is present in this arrangement.



3

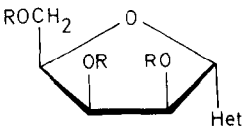
D-*galacto*

Het = heterocyclic group

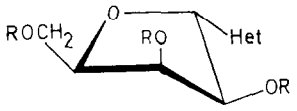
The trifluoroacetic acid-catalyzed dehydration of **2** can lead to anhydro derivatives having furanoid or pyranoid structures, depending on the reaction conditions. Thus, when the reaction mixture was made neutral with resin immediately after t.l.c. had revealed the total consumption of starting material, 1-benzyl-4,5,6,7-tetrahydro-2-α-D-lyxofuranosyl-6,6-dimethylindol-4-one (**6**) was the only product isolated. The furanoid structure of **6** was demonstrated by its p.m.r. spectrum [$(CD_3)_2SO$], which showed two doublets and one triplet, consistent with two secondary hydroxyl groups (on C-2′ and C-3′) and one primary hydroxyl group (on C-5′); in addition, compound **6** reduced 1 mol of sodium metaperiodate, indicative of two contiguous hydroxyl groups. The $J_{1',2'}$ value (8.0 Hz) did not allow assignment of the anomeric configuration. The α configuration is only tentatively assigned, on the basis of the larger steric repulsions that must be present in the β anomer, suggesting that the α anomer is the principal product, in agreement with the mechanism proposed for these reactions[2].

The preponderant conformation of the glycosyl moiety of the triacetate **7** must be E_2. The $J_{1',2'}$ value (7.6 Hz), corresponding[8,9] to a torsion angle of $\phi_{H-1',2'} = 156°$, is in agreement with this conformer. The observed values of $J_{2',3'}$ (5.0 Hz) and $J_{3',4'}$ (7.4 Hz) closely match the values calculated for this conformation.

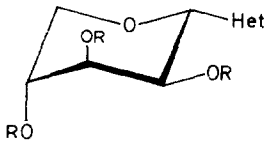
In contrast, when the reaction mixture from the dehydration of **2** is processed without neutralization of the acid, a mixture of the α- and β-pyranosyl compounds **8** and **10** was obtained in good yield (94%); this mixture was also obtained by heating an acidified, aqueous solution of **6**. Compounds **8** and **10** could be separated by

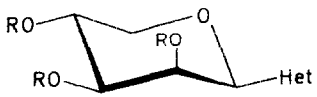


6 R = H
7 R = Ac



7-E_2





8 R=H
9 R=Ac

10 R=H
11 R=Ac

column chromatography. These products consumed two mol. equiv. of sodium metaperiodate, and showed three doublets for the hydroxyl protons in their p.m.r. spectra [$(CD_3)_2SO$], in accord with the pyranoid structures proposed. The $J_{1',2'}$ values of 9.0 and <1 Hz for **8** and **10**, respectively, indicated β and α configurations and $^4C_1$ and $^1C_4$ conformations. The p.m.r. data for their triacetates **9** and **11** are also in agreement with those assignments. On the other hand, the p.m.r. spectrum recorded for the anomeric mixture of **8** and **10** showed that these compounds are obtained in the ratio of 1:1.

These results are similar to those obtained in the acid-catalyzed dehydration of D-*gluco*- and D-*manno*-pentitol-1-ylpyrroles[1,2], and indicate that the furanoid compound **6** must be the kinetically controlled product, and the pyranoid compounds **8** and **10** must be the thermodynamically controlled products.

EXPERIMENTAL

General methods. — Solutions were evaporated *in vacuo* at temperatures below 40°. Melting points were determined with a Gallenkamp apparatus, and are uncorrected. Optical rotations were measured at 20 ±2° with a Perkin–Elmer 141 polarimeter (10-cm cell). T.l.c. was performed on silica gel GF_{254} (Merck) with 3:2 benzene–ether (solvent *A*) or 3:1 ethyl acetate–ethanol (solvent *B*), and detection with u.v. light or iodine vapor. Paper chromatography was performed on Whatman No. 1 paper with 1:1:1 1-butanol–pyridine–water as the eluant, and silver nitrate–sodium hydroxide as the indicator. Column chromatography was performed in the "flash" mode[10], with 10:1 ethyl acetate–ethanol as the eluant. I.r. spectra (KBr discs) were recorded with Beckman IR-33 and Perkin–Elmer 399 spectrophotometers, and u.v. spectra with Beckman DB-G and Pye–Unicam SP-8 250 instruments. P.m.r. spectra (90 MHz, internal Me_4Si) were recorded at 35.5° with a Perkin–Elmer R-32 spectrometer, and coupling constants were measured directly from spectra recorded at 300-Hz sweep-width. Assignments were confirmed by double-resonance experiments.

Consumption of periodate and formation of formic acid were determined as previously described[11,12].

2-(Benzylamino)-2-deoxy-D-glycero-L-gluco-*heptose hydrochloride* (**1**). — A solution of 2-(benzylamino)-2-deoxy-D-*glycero*-L-*gluco*-heptononitrile[13] (6 g, 20 mmol) in M hydrochloric acid (50 mL) was hydrogenated at atmospheric pressure and room temperature in the presence of 10% palladium-on-barium sulfate (2.5 g).

Paper chromatography showed the formation of **1** (R_F 0.50), and, after three days, the spot for the nitrile (R_F 0.83) had almost disappeared. Then, the catalyst was filtered off, and the filtrate was concentrated until crystals of ammonium chloride appeared; these were filtered off, the filtrate was evaporated, and the syrupy residue was treated with methanol (10 mL), to give crystals of 2-amino-2-deoxy-D-*glycero*-L-*gluco*-heptose hydrochloride[4] (R_F 0.39) that were collected by filtration. The filtrate was concentrated, and the residue was repeatedly evaporated with ethanol and benzene, to yield almost pure, amorphous **1** (3 g) that was used in the next step without purification.

*1-Benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(*D-galacto-*pentitol-1-yl)-indol-4-one* (**2**). — A solution of crude **1** (2.45 g) in water (15 mL) was treated with 5,5-dimethyl-1,3-cyclohexanedione (1.02 g, 7.3 mmol) in 11:4 acetone–water (15 mL). The mixture was made neutral with sodium carbonate (0.39 g, 3.6 mmol), kept for ten days at room temperature, and the acetone evaporated under diminished pressure, to give **2** as white crystals that were collected by filtration. The mother liquor yielded a second crop of crystals. Recrystallization from 1:3 acetone–water gave pure **2** (0.61 g, 21%); m.p. 179–181°, $[\alpha]_D$ +6° (*c* 0.5, pyridine); $\lambda_{max}^{^iPrOH}$ 251 and 282 nm (ε_{mM} 10.60 and 7.40); ν_{max} 3350 (OH), 1620 (C=O), and 1475 cm^{-1} (C=C aromatic); periodate consumption: 4.12 mol.

Anal. Calc. for $C_{22}H_{29}NO_6$: C, 65.50; H, 7.19; N, 3.47. Found: C, 65.72; H, 7.08; N, 3.44.

*1-Benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(penta-*O*-acetyl-*D-galacto-*pentitol-1-yl)-indol-4-one* (**3**). — A suspension of **2** (0.12 g, 0.3 mmol) in pyridine (0.9 mL) and acetic anhydride (0.5 mL) was kept for 24 h at 0°. The resulting solution was poured into a mixture of ice–water (20 mL) and sodium hydrogencarbonate (0.4 g). Compound **3** solidified on scratching, and was filtered off and successively washed on the filter with cold water and light petroleum; yield: 0.17 g (94%); m.p. 69–71°, $[\alpha]_D$ +62° (*c* 0.5, chloroform); λ_{max}^{EtOH} 248 and 277 nm (ε_{mM} 6.10 and 5.10); ν_{max} 1745 (C=O ester), 1650 (C=O ketone), and 1475 cm^{-1} (C=C aromatic); p.m.r. data ($CDCl_3$): δ 7.45–6.95 (m, 5 H, phenyl group), 6.59 (s, 1 H, H-3), 5.80 (d, 1 H, H-1', $J_{1',2'}$ 3.0 Hz), 5.41 (dd, 1 H, H-3', $J_{2',3'}$ 9.0, $J_{3',4'}$ 2.0 Hz), 5.24 (m, 2 H, CH_2-Ph), 5.22 (m, 1 H, H-4'), 4.95 (dd, 1 H, H-2'), 4.21 (dd, 1 H, H-5', $J_{4',5'}$ 6.0, $J_{5',5''}$ 12.0 Hz), 3.81 (dd, 1 H, H-5'', $J_{4',5''}$ 7.5 Hz), 2.55 (s, 2 H, H-5,5), 2.35 (s, 2 H, H-7,7), 2.01 (s, 12 H, 4 OAc), 1.92 (s, 3 H, 1 OAc), and 1.09 (s, 6 H, Me-6,6).

Anal. Calc. for $C_{32}H_{39}NO_{11}$: C, 62.63; H, 6.40; N, 2.28. Found: C, 62.46; H, 6.55; N, 2.39.

*1-Benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(penta-*O*-benzoyl-*D-galacto-*pentitol-1-yl)-indol-4-one* (**4**). — To a solution of **2** (0.1 g, 0.25 mmol) in pyridine (1 mL) at 0° was added benzoyl chloride (0.16 mL), and the mixure was kept for 24 h at 0° and poured into ice–water (100 mL) containing sodium hydrogencarbonate (0.2 g). The solid product (0.2 g, 86%) was recrystallized from acetone–water; m.p. 180–182°, $[\alpha]_D$ +50° (*c* 0.5, chloroform); λ_{max}^{EtOH} 233 and 275 nm (ε_{mM} 29.70

and 3.90); ν_{max} 1710 (C=O ester), 1650 (C=O ketone), and 1475 cm^{-1} (C=C aromatic); p.m.r. data ($CDCl_3$): δ 8.05–6.75 (m, 30 H, phenyl groups), 6.80 (1 H, H-1'), 6.50 (t, 1 H, H-3', $J_{2',3'}$ 3.0, $J_{3',4'}$ 3.0 Hz), 6.04 (m, 2 H, H-3,2'), 5.83 (m, 1 H, H-4', $J_{4',5'}$ 6.0, $J_{4',5''}$ 6.0 Hz), 5.26 (m, 2 H, CH_2-Ph), 4.44 (d, 2 H, H-5',5''), 2.28 (s, 2 H, H-5,5), 2.13 (s, 2 H, H-7,7), and 0.92 (s, 6 H, Me-6,6).

Anal. Calc. for $C_{57}H_{49}NO_{11}$: C, 74.10; H, 5.31; N, 1.52. Found: C, 73.81; H, 5.57; N, 1.69.

1-Benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-4-oxo-indole-2-carboxaldehyde (**5**). — A solution of sodium metaperiodate (0.43 g, 2.0 mmol) in water (1 mL) was added dropwise to a stirred solution of **2** (0.2 g, 0.5 mmol) in the minimal volume of 1:1 acetone–water with cooling at 0°. The product immediately began to crystallize, and the suspension was kept for 1 h in a refrigerator. The crystals (0.11 g, 78%) were collected, and recrystallized from methanol–water; m.p. 102–103°; λ_{max}^{EtOH} 235 and 298 nm (ϵ_{mM} 17.60 and 15.00); ν_{max} 1645 (C=O) and 1490 cm^{-1} (C=C aromatic); p.m.r. data ($CDCl_3$): δ 9.58 (s, 1 H, formyl group), 7.36 (s, 1 H, H-3), 7.34–6.80 (m, 5 H, phenyl group), 5.62 (m, 2 H, CH_2-Ph), 2.60 (s, 2 H, H-5,5), 2.40 (s, 2 H, H-7,7), and 1.09 (s, 6 H, Me-6,6).

Anal. Calc. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.94; H, 6.72; N, 4.66.

1-Benzyl-4,5,6,7-tetrahydro-2-α-D-lyxofuranosyl-6,6-dimethyl-indol-4-one (**6**). — A solution of **2** (0.1 g, 0.25 mmol) in 3:2 ethanol–water (5 mL) was treated with trifluoroacetic acid (0.1 mL). After 7 h at room temperature, t.l.c. (solvent *B*) revealed the absence of **2** and the formation of one more-mobile spot (R_F 0.70). The mixture was made neutral with Amberlite IR-45 (HO^-) resin, and then water was added until crystalline **6** separated; this was collected, washed with several portions of cold water (0.04 g, 42%), and recrystallized from methanol–water; m.p. 175–177°, $[\alpha]_D$ +56.5° (*c* 0.5, pyridine); λ_{max}^{EtOH} 250 and 280 nm (ϵ_{mM} 9.50 and 7.00); ν_{max} 3460 (OH), 1630 (C=O), and 1480 cm^{-1} (C=C aromatic); p.m.r. data [$(CD_3)_2SO$]: δ 7.45–6.90 (m, 5 H, phenyl group), 6.45 (s, 1 H, H-3), 5.27 (s, 2 H, CH_2-Ph), 5.09 (d, 1 OH), 4.79 (d, 1 OH), 4.57 (d, 1 H, H-1', $J_{1',2'}$ 8.0 Hz), 4.45 (t, 1 OH, OH-5'), 4.40–3.30 (m, 5 H, H-2',3',4',5',5''), 2.50 (s, 2 H, H-5,5), 2.22 (s, 2 H, H-7,7), and 0.98 (s, 6 H, Me-6,6); periodate consumption: 1.08 mol; formic acid formed: 0.00 mol.

Anal. Calc. for $C_{22}H_{27}NO_5 \cdot H_2O$: C, 65.49; H, 7.24; N, 3.47. Found: C, 65.52; H, 7.02; N, 3.64.

1-Benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(2,3,5-tri-O-acetyl-α-D-lyxofuranosyl)-indol-4-one (**7**). — A solution of **6** (0.12 g, 0.31 mmol) in pyridine (0.9 mL) and acetic anhydride (0.5 mL) was kept for 24 h at 0°, and then poured into ice–water (20 mL) containing sodium hydrogencarbonate (0.15 g). The solid **7** (0.13 g, 81%) was filtered off, washed with water, and recrystallized from methanol–water; m.p. 108–109°, $[\alpha]_D$ +45° (*c* 0.5, chloroform); λ_{max}^{EtOH} 248 and 275 nm (ϵ_{mM} 10.50 and 8.20); ν_{max} 1735 (C=O ester), 1650 (C=O ketone), and 1480 cm^{-1} (C=C aromatic); p.m.r. data ($CDCl_3$): δ 7.42–6.85 (m, 5 H, phenyl group), 6.62 (s, 1 H,

H-3), 5.64 (dd, 1 H, H-3′, $J_{2',3'}$ 5.0, $J_{3',4'}$ 7.4 Hz), 5.56 (dd, 1 H, H-2′, $J_{1',2'}$ 7.6 Hz), 5.23 (m, 2 H, CH_2-Ph), 4.97 (d, 1 H, H-1′), 4.43 (m, 1 H, H-4′), 4.19 (m, 2 H, H-5′,5″), 2.48 (s, 2 H, H-5,5), 2.33 (s, 2 H, H-7,7), 2.08 (s, 3 H, 1 OAc), 1.99 (s, 3 H, 1 OAc), 1.97 (s, 3 H, 1 OAc), and 1.04 (s, 6 H, Me-6,6).

Anal. Calc. for $C_{28}H_{33}NO_8$: C, 65.75; H, 6.46; N, 2.74. Found: C, 65.98; H, 6.72; N, 2.77.

*1-Benzyl-4,5,6,7-tetrahydro-2-α-*D*-lyxopyranosyl-6,6-dimethyl-indol-4-one* (**8**) *and 1-benzyl-4,5,6,7-tetrahydro-2-β-*D*-lyxopyranosyl-6,6-dimethyl-indol-4-one* (**10**). — *(a)* To a solution of **2** (0.1 g, 0.25 mmol) in 3:2 ethanol–water (5 mL) was added trifluoroacetic acid (0.1 mL), and the mixture was kept for 7 h at room temperature. T.l.c. (solvent *B*) then showed one only spot (R_F 0.70), corresponding to **6**. The solution was evaporated under diminished pressure to give a syrup that crystallized from 9:1 water–ethanol (0.09 g, 94%). The crystals were a mixture of **8** and **10** (R_F 0.74 and 0.63, solvent *B*), which was partitioned by column chromatography. Evaporation of the fractions containing **8** yielded this product (40%); recrystallized from acetone–water, m.p. 198–200°, $[\alpha]_D$ +15° (*c* 0.5, pyridine); λ_{max}^{EtOH} 250 and 280 nm (ϵ_{mM} 8.30 and 5.50); ν_{max} 3280 (OH), 1620 (C=O), and 1480 cm^{-1} (C=C aromatic); p.m.r. data [$(CD_3)_2SO$]: δ 7.58–6.90 (m, 5 H, phenyl group), 6.43 (s, 1 H, H-3), 5.25 (m, 2 H, CH_2-Ph), 4.87 (m, 2 OH), 4.57 (d, 1 OH), 4.38 (d, 1 H, H-1′, $J_{1',2'}$ 9.0 Hz), 4.10–3.40 (m, 5 H, H-2′,3′,4′,5′,5″), 2.50 (s, 2 H, H-5,5), 2.21 (s, 2 H, H-7,7), and 0.96 (s, 6 H, Me-6,6); periodate consumption: 2.08 mol; formic acid formed 0.98 mol.

Anal. Calc. for $C_{22}H_{27}NO_5 \cdot H_2O$: C, 65.49; H, 7.24; N, 3.47. Found: C, 65.76; H, 7.05; N, 3.57.

Further elution of the column led to **10** (37%); recrystallized from acetone–water, m.p. 169–171°, $[\alpha]_D$ −6° (*c* 0.5, pyridine); λ_{max}^{EtOH} 252 and 280 nm (ϵ_{mM} 8.70 and 6.60); ν_{max} 3300 (OH), 1615 (C=O), and 1480 cm^{-1} (C=C aromatic); p.m.r. data [$(CD_3)_2SO$]: δ 7.48–6.82 (m, 5 H, phenyl group), 6.67 (s, 1 H, H-3), 5.23 (m, 2 H, CH_2-Ph), 4.83–4.58 (m, 2 OH), 4.22 (s, 1 H, H-1′, $J_{1',2'}$ <1 Hz), 3.93–2.96 (m, 6 H, H-2′,3′,4′,5′,5″, and 1 OH), 2.52 (s, 2 H, H-5,5), 2.22 (s, 2 H, H-7,7), and 0.98 (s, 6 H, Me-6,6); periodate consumption: 2.08 mol; formic acid formed: 0.97 mol.

Anal. Calc. for $C_{22}H_{27}NO_5 \cdot 0.5\ H_2O$: C, 66.99; H, 7.16; N, 3.55. Found: C, 66.92; H, 7.26; N, 3.69.

(b) The mixture of **8** and **10** was also obtained from **6**, treated under the conditions described in *(a)*.

1-Benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(2,3,4-tri-O-*acetyl-α-*D*-lyxopyranosyl)-indol-4-one* (**9**). — Acetylation of **8** (0.1 g, 0.26 mmol) as described for **7** gave the triacetate **9** (0.09 g, 70%); m.p. 90–92°, $[\alpha]_D$ −32° (*c* 0.5, chloroform); λ_{max}^{EtOH} 248 and 275 nm (ϵ_{mM} 8.60 and 7.60); ν_{max} 1735 (C=O ester), 1645 (C=O ketone), and 1480 cm^{-1} (C=C aromatic); p.m.r. data ($CDCl_3$): δ 7.48–6.84 (m, 5 H, phenyl group), 6.69 (s, 1 H, H-3), 5.52 (dd, 1 H, H-2′, $J_{1',2'}$ 7.6, $J_{2',3'}$ 3.0 Hz), 5.45 (m, 1 H, H-3′), 5.23 (m, 2 H, CH_2-Ph), 4.92 (m, 1 H, H-4′, $J_{3',4'}$ 5.0 Hz), 4.66

(d, 1 H, H-1'), 3.78 (m, 2 H, H-5',5''), 2.49 (s, 2 H, H-5,5), 2.32 (s, 2 H, H-7,7), 2.10 (s, 3 H, 1 OAc), 2.02 (s, 3 H, 1 OAc), 1.91 (s, 3 H, 1 OAc), and 1.06 (s, 6 H, Me-6,6).

Anal. Calc. for $C_{28}H_{32}NO_8$: C, 65.75; H, 6.46; N, 2.74. Found: C, 65.53; H, 6.75; N, 2.38.

1-Benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-2-(2,3,4-tri-O-acetyl-β-D-lyxopyranosyl)-indol-4-one (**11**) — Acetylation of **10** (0.1 g, 0.26 mmol) as described for **7** gave the triacetate **11** (0.09 g, 70%); m.p. 108–110°, $[\alpha]_D$ −34° (*c* 0.5, chloroform); λ_{max}^{EtOH} 248 and 276 nm (ϵ_{mM} 8.60 and 7.20); ν_{max} 1735 (C=O ester), 1645 (C=O ketone), and 1480 cm^{-1} (C=C aromatic); p.m.r. data ($CDCl_3$): δ 7.50–6.80 (m, 5 H, phenyl group), 6.43 (s, 1 H, H-3), 5.59 (bd, 1 H, H-2', $J_{2',3'}$ 2.8, $J_{1',2'}$ <1 Hz), 5.22 (m, 1 H, H-4'), 5.17 (m, 2 H, C*H*$_2$-Ph), 4.94 (dd, 1 H, H-3', $J_{3',4'}$ 10.0 Hz), 4.32 (s, 1 H, H-1'), 4.21 (dd, 1 H, H-5', $J_{4',5'}$ 5.3 Hz), 3.21 (t, 1 H, H-5'', $J_{4',5''}$ 11.0, $J_{5',5''}$ 11.0 Hz), 2.55 (s, 2 H, H-5,5), 2.37 (s, 2 H, H-7,7), 2.17 (s, 3 H, 1 OAc), 2.04 (s, 3 H, 1 OAc), 2.01 (s, 3 H, 1 OAc), and 1.07 (s, 6 H, Me-6,6).

Anal. Calc. for $C_{28}H_{32}NO_8 \cdot H_3O^+$: C, 63.50; H, 6.66; N, 2.64. Found: C, 63.27; H, 6.41; N, 2.91.

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