FISCHER INDOLE SYNTHESIS WITH SELECTED 2,3-DIDEOXY-D-*glycero*-ALDOPENTOSE DERIVATIVES. CONVERSION OF D-XYLOSE TO (2*S*)-3-(INDOL-3-YL)PROPANE-1,2-DIOL

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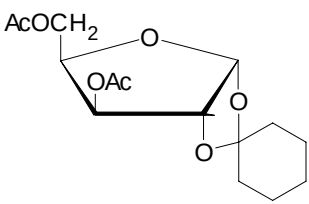
Two independent routes towards (2*S*)-3-(indol-3-yl)propane-1,2-diol (**11**) were achieved starting from 3,5-di-*O*-acetyl-1,2-*O*-cyclohexylidene-α-D-xylofuranose (**1**). Ethanethiolysis of **1** afforded acyclic diethyl dithioacetal **2** which was further *O*-deacetylated to give **3**. Selective benzoylation of **3** gave 5-*O*-benzoyl derivative **4.** Treatment of **4** with *N*-bromosuccinimide in methanol gave methyl furanoside **5** which was further desulfurized over Raney nickel to afford **6**. An acid hydrolysis of **6** gave hemiacetal **7** which upon treatment with phenylhydrazine, according to standard Fischer indolization procedure, yielded a mixture of chiral indoles **10**. *O*-Debenzoylation of **10** gave the crystalline diol **11**. A more efficient route towards the chiral indole **11** included the initial dethioacetalation of **2** into dimethyl acetal **8** which was further desulfurized over Raney nickel to give the corresponding 2,3-dideoxy derivative **9**. Direct Fischer indolization of **9** with phenylhydrazine, followed by *O*-deacetylation of intermediate **12**, afforded the expected indole **11** in good yield.
Key words: Ethanethiolysis; Dethioacetalation; Fischer indol synthesis; D-Xylose.

Various indole derivatives have often been prepared by the well known Fischer indole synthesis[1], that includes an acid catalyzed cyclization of a phenylhydrazine and aldehyde or ketone. In connection with our recent studies on the synthesis of optically pure non-carbohydrate molecules by chirality transfer from monosaccharides[2], the Fischer indolization of phenylhydrazine and 2,3-dideoxy-D-*glycero*-pentose derivatives **7** and **9** was examined, in order to prepare 3-substituted indoles bearing (2*S*)-propane-1,2-diol residue as a chiral segment.

Both **7** and **9** were prepared starting from 3,5-di-*O*-acetyl-1,2-*O*-cyclohexylidene-α-D-xylofuranose (**1**) which is readily available from D-xylose in three synthetic steps[3]. Ethanethiolysis of **1** under the conditions similar to those already reported[4], afforded 84% yield of the 4,5-di-*O*-acetyl-2,3-di-*S*-ethyl-2,3-dithio-D-ribose diethyl dithioacetal (**2**). The structure of product **2** was elucidated by NMR spectra as well as on the basis

of our earlier findings that similar ethanethiolysis of certain 1,2-*O*-isopropylidene-α-D-glucofuranose derivatives gave the corresponding 2,3-di-*S*-ethyl-2,3-dithio-D-allose diethyl dithioacetals in excellent yields[4]. Treatment of **2** with sodium methoxide in methanol gave the corresponding diol **3** which was further selectively benzoylated to give 5-*O*-benzoyl derivative **4** (85% from **2**).

Reaction of diethyl dithioacetal **4** with *N*-bromosuccinimide in dry methanol afforded methyl β-furanoside **5** as the only reaction product in a yield of 90%. This transformation is analogous to the reported method for cleavage of dithioacetals by iodine–methanol reagent system[5]. The characteristic singlet in ^{1}H NMR spectrum of **5** at δ 3.31 (3 H) together with the corresponding signal in ^{13}C NMR spectrum (δ 54.62) indicated the presence of OCH_3 group at C-1. The low-field signal in proton NMR spectrum at δ 5.0 ppm (brs, 1 H, $J(1,2) < 1$ Hz) together with the corresponding one in the ^{13}C NMR spectrum (δ 108.72 d, ^1J = 177 Hz) unambiguously proved β-configura-



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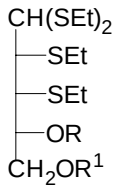
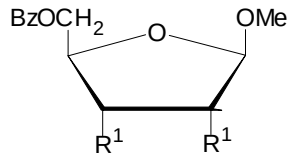


2, R = R^1= Ac

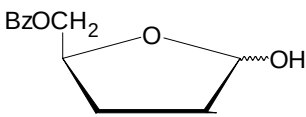
3, R = R^1= H

4, R = H; R^1= Bz

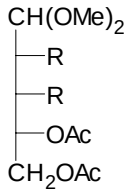


5, R^1 = SEt

6, R^1 = H

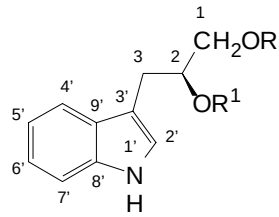


7



8, R = SEt

9, R = H



10, R, R^1= Bz, H

11, R = R^1= H

12, R = R^1= Ac

tion of the anomeric centre. Raney nickel desulfurization of **5** in boiling dioxane–ethanol afforded the known[6] methyl 5-*O*-benzoyl-2,3-dideoxy-β-D-*glycero*-pentofuranoside (**6**) in a yield of 84%. Compound **6** upon hydrolysis with diluted sulfuric acid in aqueous dioxane gave the corresponding hemiacetal **7** in a yield of 88%.

Treatment of **7** with phenylhydrazine hydrochloride and sodium acetate in presence of sulfuric acid as a catalyst afforded the desired indole derivative **10** as a mixture of regio-isomers, i.e. 1-*O*-benzoyl and 2-*O*-benzoyl derivatives, in a combined yield of 75%. Obviously the Fischer indolization of **6** was followed by successive migration of benzoyl group. *O*-Debenzoylation of crude mixture **10** gave crystalline (2*S*)-3-(indol-3-yl)-propane-1,2-diol (**11**) as the only reaction product in a yield of 80%. Both ^{1}H and ^{13}C spectral data for the synthesized product were consistent with the expected structure **11**. An NOE experiment performed on the product **11** was crucial in assigning the protons from indole ring. Namely, irradiation of the low-field signal at δ 8.14 (bs, 1 H, N-H) resulted in enhancement of both signals at δ 7.02 (bs, 1 H, H-2′) and δ 7.35 (dd, 1 H, J = 7.9 Hz, H-7′). All of the remaining protons of **11** have unambiguously been assigned by homo-decoupling experiments that enabled further assignment of the corresponding C-atoms in ^{13}C NMR spectrum by using an additional 2D XHCORR experiment.

Compound **11** was also efficiently prepared by an independent route via acyclic intermediates **8** and **9**. *N*-Bromosuccinimide dethioacetalation[7] of compound **2** afforded acyclic dimethyl acetal derivative **8** in a yield of 89%. Raney nickel desulfurization of compound **8** gave 4,5-di-*O*-acetyl-2,3-dideoxy-D-*glycero*-pentose dimethyl acetal **9** in 68% yield. Compound **9** upon treatment with phenylhydrazine, according to standard Fischer indolization procedure, afforded a mixture of indoles **11** and **12** as the major reaction products. The crude mixture was further treated with sodium methoxide in methanol whereupon the expected diol **11** was obtained in a yield of 65%. Treatment of compound **11** with acetic anhydride in pyridine gave the corresponding 1,2-di-*O*-acetyl derivative **12** in a yield of 73%.

It is expected that synthesized diol **11** could serve as a suitable intermediate in planned enantiospecific syntheses of some biologically active 3-substituted indole derivatives from D-xylose, including both D- and L-tryptophan, as well as (*S*)-indole-3-lactic acid.

EXPERIMENTAL

Melting points were determined on Büchi SMP 20 apparatus and were not corrected. Optical rotations were measured on automatic polarimeter Polamat A (Zeiss, Jena) at 23 °C in chloroform solutions. NMR spectra (^{1}H at 250 MHz and ^{13}C at 62.5 MHz) were recorded on a Bruker AC 250 E instrument in deuteriochloroform with tetramethylsilane as an internal standard. Chemical shifts are given in ppm (δ-scale) and coupling constants (J) in Hz. Thin-layer chromatography (TLC) was performed on DC Alufolien Kieselgel 60 F_{254} (Merck). Short column chromatography was carried out on Kieselgel 60 (under 0.063 mm). Typical sample/adsorbent ratio was 1 : 30 (w/w). The extracts were dried with anhydrous sodium sulfate.

4,5-Di-*O*-acetyl-2,3-di-*S*-ethyl-2,3-dithio-D-ribose Diethyl Dithioacetal (**2**)

To a cooled (0 °C) and stirred solution of 3,5-di-*O*-acetyl-1,2-*O*-cyclohexylidene-α-D-xylofuranose[3] (**1**; 3.1 g, 10 mmol) in ethane thiol (10 ml, 132 mmol) was added pre-cooled concentrated hydrochloric acid (10 ml). The reaction mixture was stirred at 0 °C for 3 h and then at room temperature for additional 20 h. After neutralization with $PbCO_3$ the precipitate was filtered off and the clear solution extracted with ethyl acetate. The extract was washed with brine, dried and evaporated to give the crude product **2** (4 g). After chromatographic purification on a column of silica gel (30 g; hexane–ethyl acetate, 6 : 1), the pure **2** was obtained (3.8 g, 82%) as a colourless syrup, $[\alpha]_D$ +18.44° (*c* 1.0). ^{1}H NMR spectrum: 1.16 m, 12 H (4 × CH_3 from SEt); 2.06 2 s, 2 × 3 H (2 × CH_3CO); 2.88 m, 8 H (4 × CH_2 from SEt); 3.0 t, 1 H (H-2); 3.55 t, 1 H (H-3); 4.35–4.45 two overlapped dd, 2 H (H-5a and H-5b); 4.48 d, 1 H (H-1); 5.62 m, 1 H (H-4). ^{13}C NMR spectrum: 14.27, 14.44, 14.55 and 14.77 (4 × $SCH_2\mathbf{C}H_3$), 20.75 and 21.97 (2 × CH_3CO), 25.53, 26.23, 28.18 and 29.99 (4 × $S\mathbf{C}H_2CH_3$), 50.3 (C-3), 56.33 (C-2), 57.3 (C-1), 63.57 (C-5), 73.35 (C-4), 169.55 and 170.54 (2 × C=O).

2,3-Di-*S*-ethyl-2,3-dithio-D-ribose Diethyl Dithioacetal (**3**)

To a solution of compound **2** (3.5 g, 8.2 mmol) in methanol (30 ml) was added a solution of sodium methoxide in methanol (*c* 1 mol l^{-1}; 10 ml). The mixture was stirred for 24 h at room temperature and then neutralized (Dowex-50 (H^+); 10 g), filtered and evaporated. The syrupy residue (2.8 g) was chromatographed on a column of silica gel (hexane–ethyl acetate, 5 : 1) whereupon the pure **3** was obtained (2.5 g, 90%) as a colourless oil, $[\alpha]_D$ +30.45° (*c* 1.02). ^{1}H NMR spectrum: 1.19–1.3 m, 12 H (4 × $SCH_2C\mathbf{H}_3$); 2.03 s, 1 H (OH); 2.56–2.89 m, 8 H (4 × $SC\mathbf{H}_2CH_3$); 3.1 dd, 1 H, *J*(1,2) = 5.3, *J*(2,3) = 7 (H-2); 3.29 t, 1 H, *J*(3,4) = 7.2 (H-3); 3.72 dd, 1 H, *J*(5a,5b) = 11.4, *J*(4,5a) = 6.8 (H-5a); 3.78 bs, 1 H (OH); 3.86 dd, 1 H, *J*(4,5b) = 3.2 (H-5b); 4.14 dt, 1 H (H-4); 4.58 d, 1 H (H-1). ^{13}C NMR spectrum: 14.31, 14.60, 14.66 and 15.05 (4 $SCH_2\mathbf{C}H_3$), 25.88, 26.31, 28.32 and 30.08 (4 $S\mathbf{C}H_2CH_3$), 53.00 (C-3), 56.97 (C-2), 57.39 (C-1), 64.59 (C-5), 73.23 (C-4).

5-*O*-Benzoyl-2,3-di-*S*-ethyl-2,3-dithio-D-ribose Diethyl Dithioacetal (**4**)

To a cooled (–10 °C) and stirred solution of compound **3** (2.5 g, 7.3 mmol) in pyridine (30 ml) was added benzoyl chloride (0.95 ml, 8.8 mmol) and the resulting solution left at –10 °C for 48 h. The reaction mixture was poured onto ice, acidified with aqueous hydrochloric acid (*c* 5 mol l^{-1}) to pH 2 and extracted with ethyl acetate (3 × 30 ml). The extract was washed with brine, saturated $NaHCO_3$ solution, dried and evaporated. The oily residue was purified on a column of silica gel (cyclohexane–ethyl acetate, 6 : 1) to yield the pure **4** (3.2 g, 98%). ^{1}H NMR spectrum: 1.10–1.33 m, 12 H (4 × $SCH_2C\mathbf{H}_3$); 2.47–3.00 m, 8 H (4 × $SC\mathbf{H}_2CH_3$); 3.10 bs, 1 H (OH); 3.15 t, 1 H, *J*(1,2) = *J*(2,3) = 6.5 (H-2); 3.50 t, 1 H, *J*(3,4) = 7.3 (H-3); 4.47 m, 1 H, *J*(4,5a) = 5, *J*(4,5b) = 3 (H-4); 4.53–4.67 m, 3 H (H-1 and 2 H-5); 7.36–8.10 m, 5 H (Bz). ^{13}C NMR spectrum: 14.35, 14.59, 14.63 and 15.12 (4 × $SCH_2\mathbf{C}H_3$), 25.72, 26.29, 28.41 and 30.2 (4 × $S\mathbf{C}H_2CH_3$), 52.78 (C-3), 57.07 (C-2), 57.81 (C-1), 67.46 (C-5), 71.74 (C-4), 128.44, 129.54, 129.78, 129.84 and 133.22 (ArC), 166.89 (C=O).

Methyl 5-*O*-Benzoyl-2,3-di-*S*-ethyl-2,3-dithio-β-D-ribofuranoside (**5**)

N-Bromosuccinimide (2.5 g, 14 mmol) was added in portions to a stirred and cooled (0 °C) solution of compound **4** (2.5 g, 5.6 mmol) in methanol (30 ml). The mixture was stirred at 0 °C for 10 min and then poured into cold solution of $Na_2S_2O_3$. 5 H_2O (2.5 g) and $NaHCO_3$ (3 g) in water (100 ml). The resulting suspension was stirred for 20 min and extracted with ethyl acetate. The extract was washed with brine, dried and concentrated to an oil. After chromatographic purification on a column of silica gel (hexane–ethyl acetate, 5 : 1) the pure product **5** was obtained (1.8 g, 90%) as a colour-

less oil. ^{1}H NMR spectrum: 1.29 m, 6 H (2 × $SCH_2C\mathbf{H}_3$); 2.63 m, 4 H (2 × $SC\mathbf{H}_2CH_3$); 3.31 s, 3 H (OCH_3); 3.45 d, 1 H (H-2); 3.78 dd, 1 H (H-3); 4.28 m, 1 H (H-4); 4.4 dd, 1 H (H-5a); 3.31 s, 3 H (OCH_3); 3.45 d, 1 H (H-2); 3.78 dd, 1 H (H-3); 4.28 m, 1 H (H-4); 4.4 dd, 1 H (H-5a); 4.65 dd, 1 H (H-5b); 5.0 s, 1 H (H-1); 7.32–8.16 m, 5 H (Bz). ^{13}C NMR spectrum: 14.28 and 14.63 (2 × $SCH_2\mathbf{C}H_3$), 26.2 and 26.77 (2 × $S\mathbf{C}H_2CH_3$), 47.15 and 54.35 (C-2 and C-3), 64.58 (C-5), 82.03 (C-4), 108.72 (C-1), 128.2, 129.52, 129.82 and 132.9 (ArC), 166.06 (C=O).

Methyl 5-*O*-Benzoyl-2,3-dideoxy-β-D-*glycero*-pentofuranoside (**6**)

A suspension of Raney nickel (20 ml) in ethanol (40 ml) was added to a solution of compound **5** (1.8 g, 5 mmol) in a mixture of dioxane (25 ml) and ethanol (25 ml). The mixture was vigorously stirred at reflux temperature for 2 h. The suspension was filtered through a Celite pad and the catalyst was washed with a mixture of dioxane–ethanol (1 : 1), the filtrate and washings were combined and evaporated in vacuo. Silica gel column chromatography (hexane–ethyl acetate, 5 : 1) of the residue afforded pure **6** (1 g, 84%) as a colourless syrup, $[\alpha]_D$ –72.6° (*c* 1.71); literature[6] gives $[\alpha]_D$ –73° (*c* 1.8).

5-*O*-Benzoyl-2,3-dideoxy-D-*glycero*-pentofuranose (**7**)

To a solution of compound **6** (1 g, 4.2 mmol) in dioxane (15 ml) was added aqueous H_2SO_4 (*c* 2 mol l^{-1}; 5 ml) and the resulting mixture was stirred at 100 °C for 5 h. The reaction mixture was neutralized by stirring with an excess of $CaCO_3$, filtered and concentrated to give chromatographically homogeneous hemiacetal **7** (0.8 g, 88%) as a colourless oil (1 : 1 mixture of α- and β-anomers). ^{1}H NMR spectrum: 1.20–2.36 m, 4 H (2 H-2 and 2 H-3); 3.94–4.52 m, 4 H (H-4, 2 H-5 and OH); 5.61 m, 1 H (H-1α and H-1β); 7.36–8.12 m, 5 H (ArH). ^{13}C NMR spectrum: 25.52 and 25.73 (C-3), 32.57 and 33.38 (C-2), 66.55 and 68.0 (C-5), 75.85 and 77.9 (C-4), 98.72 and 98.9 (C-1), 128.27, 129.62, 129.84, 129.9 and 132.96 (ArC), 166.42 and 166.53 (C=O).

4,5-Di-*O*-acetyl-2,3-di-*S*-ethyl-2,3-dithio-D-ribose Dimethyl Acetal (**8**)

To a stirred and cooled (0 °C) solution of compound **2** (3.26, 7.61 mmol) in methanol (30 ml) was added *N*-bromosuccinimide (3.26 g, 18.2 mmol) in portions. The mixture was stirred at 0 °C for 10 min, then poured into cold water (200 ml) containing $NaHCO_3$ (5 g) and $Na_2S_2O_3$ (5 g) and extracted with ethyl acetate (3 × 100 ml). The combined extracts were washed with brine, dried and concentrated, to afford chromatographically pure **8** (2.3 g, 89%) as a colourless oil, $[\alpha]_D$ +38.1° (*c* 1.2). ^{1}H NMR spectrum: 1.25 t, 6 H (2 × $SCH_2C\mathbf{H}_3$ from 2 SEt); 2.08 2 s, 6 H (2 × CH_3COO); 2.71 m, 4 H (2 × $SC\mathbf{H}_2CH_3$); 3.18 m, 1 H (H-2); 3.30 m, 1 H (H-3); 3.41 2 s, 6 H (2 × OCH_3); 4.35 m, 1 H (H-5a); 4.53 d, 1 H (H-1); 4.63 m, 1 H (H-5b); 5.2 m, 1 H (H-4). ^{13}C NMR spectrum: 14.62 and 14.72 (2 × $SCH_2\mathbf{C}H_3$), 20.8 and 21.11 (2 × $\mathbf{C}H_3COO$), 27.76 and 28.23 (2 × $S\mathbf{C}H_2CH_3$), 48.54 (C-3), 51.96 (C-2), 55.79 and 56.21 (2 × CH_3O), 63.32 (C-4), 108.12 (C-1), 169.52 and 170.56 (2 × C=O).

4,5-Di-*O*-acetyl-D-*glycero*-pentose Dimethyl Acetal (**9**)

To a solution of compound **8** (1.0 g, 2.67 mmol) in dioxane was added a suspension of Raney nickel (23 g) in ethanol (20 ml). The mixture was refluxed for 2 h, then filtered through Celite pad. The catalyst was washed with hot ethanol and the combined filtrates and washings were concentrated in vacuo. Silica gel column chromatography (cyclohexane–ethyl acetate, 3 : 1) of the residue afforded pure **9** (0.5 g, 68%) as a colourless oil, $[\alpha]_D$ –1.73° (*c* 1.16). ^{1}H NMR spectrum: 1.3 m, 4 H (2 H-2 and 2 H-3); 2.1 d, 6 H (2 × CH_3COO); 3.35 s, 6 H (2 × OCH_3); 4.2 m, 2 H (2 H-5); 4.35 m, 1 H (H-1); 5.05 m, 1 H (H-4).

(2*S*)-3-(Indol-3-yl)propane-1,2-diol (**11**)

A) The solution of phenylhydrazine hydrochloride (1 g, 6.92 mmol) and sodium acetate (1 g, 12.19 mmol) in ethanol (30 ml) was stirred under nitrogen for 30 min. The solution of hemiacetal **7** (0.8 g, 3.6 mmol), mixture of anomers in ethanol (10 ml) was then added and the resulting mixture stirred at room temperature for 1 h. The solution was acidified with aqueous H_2SO_4 (*c* 1 mol l^{-1}; 10 ml) and refluxed while stirring for the additional 2 h. The reaction mixture was neutralized with an excess of $CaCO_3$ and filtered. The solvents were removed by co-distillation with toluene to give an oily residue which was chromatographed on a column of silica gel (cyclohexane–ethyl acetate, 4 : 1) to afford an inseparable mixture of 1- and 2-*O*-benzoyl derivatives **10** (0.8 g, 75%), as an oil. ^{1}H NMR spectrum (selected signals): 2-*O*-benzoyl derivative: 2.25 bs, 1 H (OH); 3.21 m, 2 H (2 H-3); 3.8 m, 2 H (2 H-1); 5.45 m, 1 H (H-2); 1-*O*-benzoyl derivative: 3.02 m, 2 H (2 H-3); 4.4 m, 3 H (2 H-1) and H-2). ^{13}C NMR spectrum (selected signals): 2-*O*-benzoyl derivative: 26.33 (C-3), 63.9 (C-1), 76.16 (C-2); 1-*O*-benzoyl derivative: 29.72 (C-3), 68.32 (C-1), 76.16 (C-2). To a solution of 1- and 2-*O*-benzoyl derivatives **10** (0.6 g, 2.03 mmol) in methanol (10 ml) was added a solution of sodium methoxide in methanol (*c* 0.43 mol l^{-1}; 10 ml). The mixture was stirred at room temperature for 16 h and then neutralized (Dowex-50 (H^+); 5 g) filtered and evaporated. The crude residue (0.5 g) was chromatographed on a column of silica gel (dichloromethane–acetone, 1 : 1) to give pure **11** (0.31 g, 80%), m.p. 60–62 °C, $[\alpha]_D$ –21.9° (*c* 1.0).

B) To a stirred solution of compound **9** (0.5 g, 2 mmol) and phenylhydrazine hydrochloride (0.5 g, 3.47 mmol) in ethanol (20 ml) was added concentrated H_2SO_4 (0.5 ml) in portions. The reaction mixture was refluxed for 2 h and then poured into ice and water (150 ml) and ectracted with ethyl acetate (3 × 50 ml). The combined extracts were washed with brine (to pH 7), dried and evaporated. The crude mixture was treated with sodium methoxide in methanol as described above (procedure *A*) to give pure **11** (0.25, 65%) as colourless crystals, m.p. 61–62 °C, $[\alpha]_D$ –21.87° (*c* 0.96). ^{1}H NMR spectrum: 2.7 bs, 2 H (2 × OH); 2.81–3.01 m, 2 H, *J*(3a,3b) = 14.6, *J*(2,3a) = 7.8, *J*(2.3b) = 5.5 (H-3a and H-3b); 3.54 dd, 1 H, *J*(1a,1b) = 11.2, *J*(1a,2) = 6.9 (H-1a); 3.71 dd, 1 H, *J*(1b,2) = 3.2 (H-1b); 4.02 m, 1 H (H-2); 7.02 s, 1 H (H-2′); 7.14 dt, 1 H, *J*(4′,5′) = 7.5, *J*(5′,6′) = 6.9, *J*(5′,7′) = 1.3 (H-5′); 7.22 dt, 1 H, *J*(6′,7′) = 7.9, *J*(4′,6′) = 1.2 (H-6′); 7.35 d, 1 H (H-7′); 7.61 d, 1 H (H-4′); 8.14 bs, 1 H (NH). ^{13}C NMR spectrum: 29.28 (C-3), 66.28 (C-1), 72.03 (C-2), 111.33 (C-7′), 111.44 (C-3′), 118.87 (C-4′), 119.61 (C-5′), 122.28 (C-6′), 123.01 (C-2′), 127.52 (C-8′), 136.4 (C-9′). For $C_{11}H_{13}NO_2$ (191.1) calculated: 69.07% C, 6.86% H, 7.33% N; found: 68.82% C, 6.92% H, 7.00% N.

(2*S*)-3-(Indol-3-yl)propane-1,2-diol Diacetate (**12**)

A solution of compound **11** (0.19 g, 1.0 mmol) and acetic anhydride (1 ml, 10.6 mmol) in pyridine (5 ml) was stored at room temperature for 16 h. The reaction mixture was poured onto ice acidified with diluted hydrochloric acid (*c* 2 mol l^{-1}) to pH 2 and extracted with ethyl acetate. The extract was washed with brine, dried and evaporated to give a chromatographically homogeneous di-*O*-acetyl derivative **12** (0.2 g, 73%) as a colourless oil, $[\alpha]_D$ –80.5° (*c* 1.23). ^{1}H NMR spectrum: 2.07 and 2.08 2 s, 6 H (2 × CH_3COO); 3.04 dd, 1 H *J*(3a,3b) = 13.8, *J*(2,3a) = 7.6 (H-3a); 3.14 dd, 1 H, *J*(2,3b) = 5.8 (H-3b); 4.09 dd, 1 H, *J*(1a,1b) = 11.9, *J*(1a,2) = 6.4 (H-1a); 4.26 dd, 1 H, *J*(1b,2) = 3.3 (H-1b); 5.37 m, 1 H (H-2); 7.06 s, 1 H *J*(NH,2′) = 2.2 (H-2′); 7.18 m, 2 H (H-5′ and H-6′); 7.38 dd, 1 H, *J*(6′,7′) = 7.4, *J*(5′,7′) = 1.5 (H-7′); 7.70 d, 1 H, *J*(4′,5′) = 7.45 (H-4′); 8.16 bs, 1 H (NH). ^{13}C NMR spectrum: 20.82 and 21.2 (2 × **C**H_3COO), 29.69 (C-3), 64.47 (C-1), 71.8 (C-2), 110.63 (C-3′), 111.13 (C-7′), 118.9 (C-4′), 119.62 (C-5′), 122.23 (C-6′), 122.61 (C-2′), 136.13 (C-9′), 170.55 and 170.8 (2 × C=O).

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