Investigations on the Reactivity of Fascaplysin

Part II

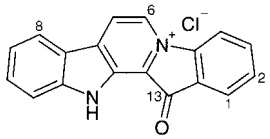
General Stability Considerations and Products Formed with Nucleophiles

by **Heinz Fretz***[a]), **Katharina Ucci-Stoll**[a]), **Paul Hug**[b]), **Joseph Schoepfer**[a]), and **Marc Lang**[a])

[a]) Oncology Research and
[b]) Core Technologies Area, *Novartis Pharma AG*, CH-4002 Basel

Reversible deprotonation of fascaplysin (**1**) was achieved with non-nucleophilic bases (*Scheme 1*). Under basic aqueous conditions, opening of ring D of **1** occurred, yielding zwitter-ionic reticulatine **2a**, whereas, in a methoxide-containing MeOH solution, an unexpected addition of three molecules of MeOH to the pyridinium ring produced an isomer mixture **3** of a trimethoxy-substituted compound (*Scheme 2*). Transformation of the keto group of **1** to the oxime **4A** took place in the presence of pyridine as base (*Scheme 3*). *Grignard* and alkyllithium reagents added as expected to the keto group of **1**, providing tertiary alcohols **5** and **6** (*Scheme 4*).

1. Introduction. – The red pigment fascaplysin (**1**) was isolated in 1988 from the Fijian sponge *Fascaplysinopsis* BERGQUIST sp. [1], and more recently from its relative *Fascaplysinopsis reticulata* as a complex with dehydroluffariellolide diacid monoanion [2]. Antibiotic and antiproliferative properties of this natural product have been reported [1][3]. Recently, it has been demonstrated that fascaplysin interferes with elements of the cell cycle machinery by inhibiting cyclin-dependent kinase 4 (Cdk4) [4a][1]) and by interacting with DNA [5].



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Such extraordinary biological properties render fascaplysin an attractive target for synthetic chemists, and there have been several successful total syntheses [6–9]. In our preceding study, we examined the reactivity of this unique molecule with regard to aromatic electrophilic substitutions [10], whereas, herein, we report on general stability aspects of fascaplysin in the presence of bases and nucleophiles.

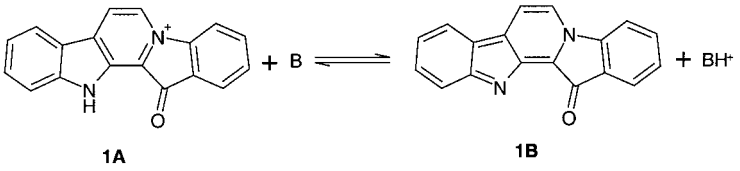
Results and Discussion. – Synthetic fascaplysin (**1**) was used throughout the experiments described in this work. The material was obtained in a five-step synthesis by the procedure of *Radchenko* and co-workers [6]. The main spectral characteristics

[1]) Parts of the results were presented at the annual meeting of the American Association of Cancer Research, April 1–5, 2000, in San Francisco, CA [4b]

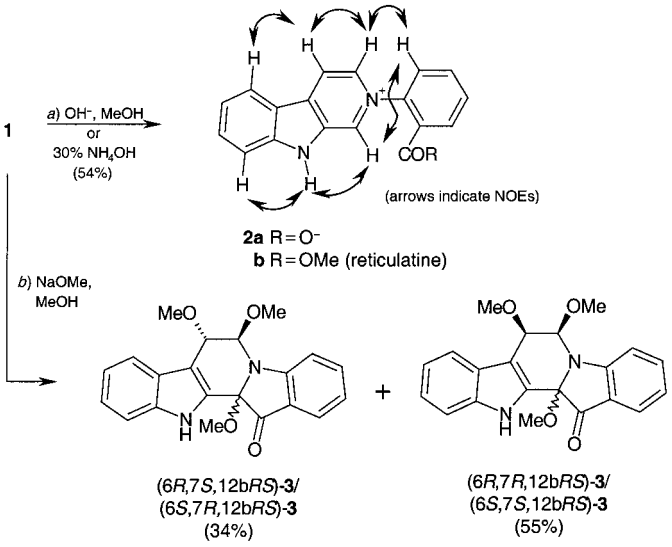
(IR, UV, MS, and ^{1}H- and ^{13}C-NMR) of synthesized **1** were identical to those published for the natural product [1].

Fascaplysin (**1**) preferentially exists in its stable acidic form **1A**, which we assumed to be part of an acid-base equilibrium (*Scheme 1*). The conjugate anhydronium base **1B** was thought to be formed in the presence of alkali, similarly to the behavior of cryptolepine, a *N*-methylquinoloindole alkaloid [11]. However, already *Roll* and co-workers [1] mentioned the occurrence of irreversible alterations in the UV spectrum of the natural product when recorded in a MeOH solution containing OH^- [1]. From this observation, we concluded that fascaplysin is transformed into a new product under alkaline conditions. Since no further characterization of the newly formed compound was given, we decided to treat samples of fascaplysin with 1M NaOH or 30% aqueous NH_4OH solution. Under both conditions, zwitter-ionic β-carboline **2a** was obtained (*Scheme 2*, *Path a*). Its structure was elucidated by 1D-NOE, ^{1}H,^{1}H-COSY, and direct ^{1}H,^{13}C-HSQC correlations. A precedent for this compound class has been described earlier with the natural product reticulatine **2b**, the methyl ester of **2a**. Reticulatine was isolated as a salt with accompanying sesterpene dehydroluffariellolide diacide anion from *Fascaplysinopsis reticulata* [2].

Scheme 1



Scheme 2



Since the ring system of fascaplysin was found to be unstable in the presence of OH^-, non-nucleophilic bases such as Et_3N, *N,N*-diisopropylethylamine ($^iPrEt_2N$), or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were used to reversibly produce the deprotonated form **1B**. A titration experiment was performed, in which aliquots of these bases were added to MeOH solutions of **1**. A change of the deep red color of the pigment to green was observed, indicating an acid-base reaction. The spectral changes were monitored by UV/VIS spectroscopy (*Fig.*). After addition of *ca.* 2 equiv. of base, the spectrum remained unchanged, indicating deprotonation. Addition of 4M HCl in dioxane to this final solution gave a UV/VIS spectrum identical to the spectrum of **1**. Unchanged **1** was recovered as could be demonstrated by HPLC and MS analysis, indicating reversibility of this deprotonation procedure. An additional titration experiment was performed and monitored by ^{1}H-NMR spectroscopy. Addition of 0.5 equiv. of DBU revealed instant disappearance of the NH proton at 13.5 ppm, accompanied by an extreme line broadening. In the presence of >1 equiv. of DBU, a highfield shift (0.3 ppm) of the aromatic-proton signals was observed, the line broadening became less pronounced, and the line splitting was visible again. Conclusively, the display of spectroscopic characteristics different from **1A** indicated that **1B** can be generated reversibly with non-nucleophilic bases.

In the following, the reactivity of **1** is demonstrated when exposed to nucleophiles. Nucleophilic attack was primarily expected to occur at the carbonyl C(13) atom. As we already learned, attack of OH^- leads to opening of ring D. Therefore, reaction of **1** with methoxide (*Scheme 2*, *Path b*) was expected to give reticulatine (**2b**). However, the ^{1}H-NMR spectrum of the crude product revealed a complex compound mixture, all compounds displaying identical mass spectra with *m/z* 365. Separation by flash chromatography furnished two mixtures of stereoisomers, the earlier eluate containing (6*R*,7*S*,12b*RS*)-**3** and (6*S*,7*R*,12b*RS*)-**3** with the MeO groups at C(6) and C(7) *trans*-configured, and the later consisting of (6*R*,7*R*,12b*RS*)-**3** and (6*S*,7*S*,12b*RS*)-**3** with *cis*-configured MeO–C(6) and MeO–C(7). No further separation of the stereoisomers could be achieved. This unprecedented product formation can be attributed to the reactivity of the unique 12*H*-pyrido[1,2-*a*:3,4-*b*′]diindole ring system.

Transformation of the keto group of **1** was achieved with hydroxylamine in the presence of pyridine as base, furnishing oxime **4A** in its deprotonated form as dark green crystals (*Scheme 3*). In DMSO solution, the compound predominantly exists in its tautomeric nitroso form **4B**, as could be verified by IR spectroscopy, as well as on the basis of ^{1}H,^{1}H–COSY, direct ^{1}H,^{13}C-HSQC, and long-range ^{1}H,^{13}C-HMBC correlations. In a 1D-NOE experiment, irradiation of the D_2O exchangeable proton at δ 12.5 showed an enhancement of H–C(8) resonating at δ 7.87. Treatment with HCl in MeOH caused a change of the dark green color to red, which could be attributed to protonated oxime **4C**. It should be noted, that no oxime was formed in the presence of NaOAc as base.

No methenylation of the keto group to the exocyclic C=C bond was detectable after treatment of **1** with *Wittig* or *Tebbe* reagents under various conditions. This was assumed to be due to the bulkiness of the reagents and the poor reactivity of the aromatic keto group.

Organometallic reagents were studied as examples for the addition of C-nucleophiles to the keto group of the pentacyclic ring system (*Scheme 4*). For example, 2 equiv. of *Grignard* reagent MeMgBr were required to produce **5**. After completion of

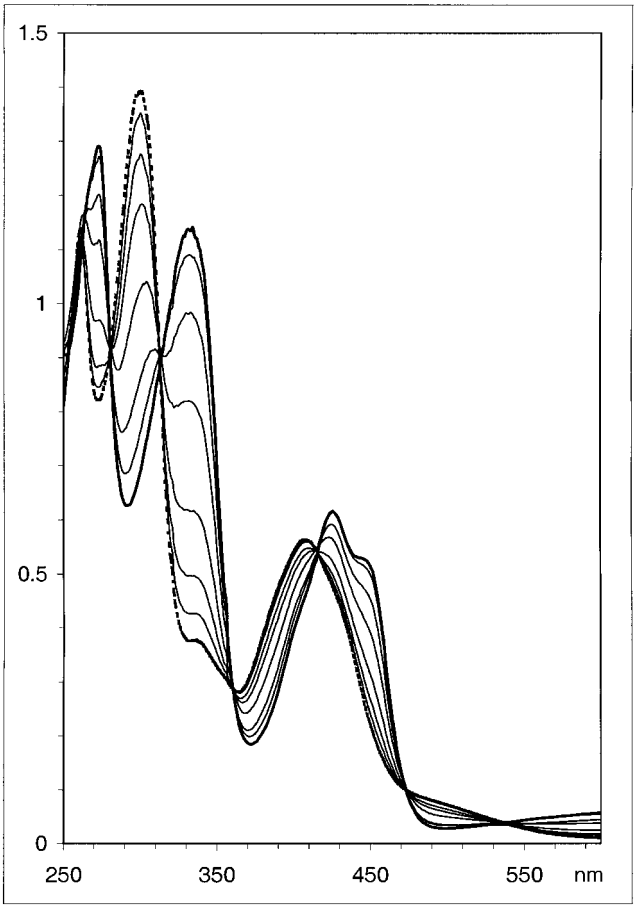
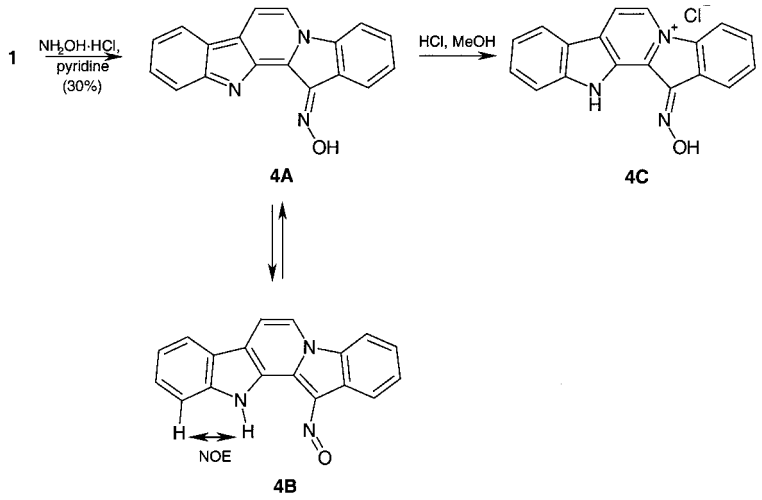


Figure. *UV/VIS Spectra of fascaplysin in its protonated form* **1A** (dashed, bold line) *and after addition of 2 mol-equiv. of DBU in its deprotonated form* **1B** (bold line). The base/drug ratio was increased as follows: 0, 0.1, 0.25, 0.5, 1.0, 1.25, 1.5, 2. Spectra are not corrected.

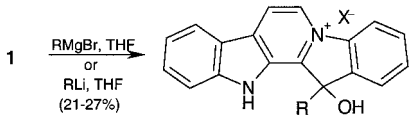
the reaction, hydrolysis gave the racemate of expected tertiary alcohol **5** in its protonated form. In a 1D-NOE experiment, irradiation of the Me protons resonating at δ 2.1 showed an enhancement of the aromatic H–C(1) resonating at δ 7.96 and the NH proton resonating at δ 13.22, respectively. Direct $^{1}H,^{13}C$ connectivities were obtained by HSQC correlations, whereas 2D-COSY and long-range $^{1}H,^{13}C$ correlations from HMBC experiments provided further connectivity information, all consistent with the structure of alcohol **5**. Similar results were obtained by reacting **1** with alkyllithium reagents. Again, 2 equiv. of MeLi or BuLi were necessary for the formation of tertiary alcohols **5** and **6**, respectively. The first equiv. of reagent was shown to be consumed for the deprotonation of **1**, producing **1B** (*Scheme 1*).

Conclusions. – In this report, reversible deprotonation of fascaplysin (**1**) was shown to be effective with non-nucleophilic bases, whereas fast destruction of the pentacyclic

Scheme 3



Scheme 4



5 R = Me, X = CF_3COO
6 R = Bu, X = CF_3COO

ring system occurred under aqueous basic conditions. An unexpected mixture of isomeric trimethoxy adducts was obtained in high yield after treating fascaplysin with methoxide. Apart from these unforeseen results, the carbonyl group of deprotonated fascaplysin displayed a reactivity comparable to aromatic ketones. Oxime formation and addition of organometallic reagents such as *Grignard* and alkyllithium reagents to the carbonyl group occurred as expected, the latter providing the respective tertiary alcohols. Taken together, all information on chemical stability and reactivity of **1** is of importance for ongoing studies on this biologically interesting compound class.

The authors thank *Stephan Kläusler* for expert technical assistance, and *Serge Moss* for IR measurements.

Experimental Part

1. *General*. All reagents were commercially available and used without further purification. The reactions were monitored, and the products were analyzed by TLC and reversed-phase HPLC. TLC: silica gel *60 F254* plates (*Merck*, Darmstadt, FRG). Reversed-phase HPLC: *Merck-Hitachi* system, consisting of an autosampler *AS-2000*, intelligent pump *L-6200A*, diode-array detector *L-4500*, and interface *D-6000*; *Nucleosil-C_{18}* column (125 × 3.0 mm, 3 μm, 100 Å; *Macherey-Nagel*, Düren, FRG); linear gradient of 0.09% CF_3COOH/MeCN (*A*) and 0.1% CF_3COOH/ H_2O (*B*) from 2 to 100% *B* within 15 min; flow rate 0.7 ml/min; detection at 215 nm; t_R in min. Flash chromatography (FC): silica gel *60* (230–400 mesh; *Merck*, Darmstadt, FRG). Reversed-phase MPLC: [10]. IR Spectra: KBr micro plates; *Bruker IFS-88-FT-IR* spectrophotometer; in cm^{-1}. UV/VIS Spectra: *Beckmann-DU-400* spectrophotometer; λ_{max} in nm. NMR Spectra (^1H, ^{13}C, 1D-NOE, COSY, HMBC, HSQC):

Bruker DPX-400 or *Bruker Avance-500* spectrometer; at 300 K, (D_6)DMSO soln.; δ in ppm downfield from $SiMe_4$ rel. to the residual solvent signal (δ(H) 2.49 and δ(C) 39.5 for (D_6)DMSO) as an internal standard; coupling constants *J* in Hz. Electrospray (ESI) MS: *Fisons Instruments VG Platform II*; *m/z*.

2. *Titration of* **1** *with DBU.* UV/VIS (**1** in MeOH): 261, 300, 345 (sh.), 409. ^{1}H-NMR (**1**, 400 MHz, (D_6)DMSO, red soln.): 13.52 (*s*, NH, exchange with D_2O); 9.65 (br. *s*, 1 H); 9.16 (br. *s*, 1 H); 8.60–8.45 (*m*, 2 H); 8.10–7.90 (*m*, 2 H); 7.90–7.70 (*m*, 3 H); 7.51 (br. *s*, 1 H). UV/VIS (**1** + 2 equiv. of DBU in MeOH): 273, 334, 425, 621. ^{1}H-NMR (**1** + 1 equiv. of DBU, 400 MHz, (D_6)DMSO, green soln.): 9.32 (br. *d*, 1 H); 8.93 (br. *d*, 1 H); 8.46 (*d*, 1 H); 8.31 (*d*, 1 H); 8.04 (*d*, 1 H); 7.97 (*dd*, 1 H); 7.89 (*dd*, 1 H); 7.82 (*dd*, 1 H); 7.74 (*dd*, 1 H); 7.53 (*dd*, 1 H).

3. *3-(2-Carboxyphenyl)-9*H*-pyrido[3,4-*b*]indol-3-ium Inner Salt* (**2a**). A suspension of **1** (76.5 mg, 0.15 mmol) in dioxane (10 ml) was treated with 1M NaOH (1 ml, 1 mmol) for 3 h at r.t. The mixture was evaporated and the residue submitted to FC (silica gel, CH_2Cl_2/MeOH 4:1): **2a** (39 mg, 54%). Pale red crystals. M.p. 145° (dec.). R_f (CH_2Cl_2/MeOH 4:1) 0.17. t_R 7.05 (98%). UV (MeOH): 206, 234, 260, 313, 383. IR (KBr): 3061, 2924, 2853, 2765, 2649, 1643, 1607, 1568, 1518, 1474, 1449, 1367, 1339, 1258, 1204, 1144, 1116, 1099, 1046, 1005, 920, 869, 830, 770, 752, 728, 667, 664, 636. ^{1}H-NMR (400 MHz, (D_6)DMSO): 13.5 (*s*, H-N(9), exchange with D_2O); 9.43 (*d*, *J* = 1, H–C(1)); 8.70 (*d*, *J* = 6.3, H–C(4)); 8.67 (*d*, *J* = 6.3, H–C(3)); 8.30 (*d*, *J* = 7.8, H–C(5)); 7.86 (*d*, *J* = 7.4, H–C(6′)); 7.68 (*dd*, *J* = 8.6, 7.4, H–C(7)); 7.64 (*d*, *J* = 7.8, H–C(3′)); 7.63 (*dd*, *J* = 7.4, 7.8, H–C(5′)); 7.56 (*dd*, *J* = 7.8, H–C(4′)); 7.53 (*d*, *J* = 8.6, H–C(8)); 7.31 (*dd*, *J* = 7.8, 7.4, H–C(6)). 1D-NOE (400 MHz, (D_6)DMSO): irrad. at 13.5 → NOE at 9.43 and 7.53; irrad. at 9.43 → NOE at 13.5 and 7.64; irrad. at 8.70 → NOE at 8.30; irrad. at 8.67 → NOE at 7.64; irrad. at 7.64 → NOE at 9.43 and 8.67. ^{13}C-NMR (100 MHz, (D_6)DMSO): 166.6 (COOH); 144.4; 141.5; 138.9; 134.3; 133.4 (C(3)); 132.0; 131.5 (C(7)); 131.2 (C(1)); 130.0 (C(5′), C(6′)); 128.5 (C(4′)); 125.8 (C(3′)); 123.2 (C(5)); 121.0 (C(6)); 118.9; 116.2 (C(4)); 112.8 (C(8)). ESI-MS (pos. mode): 289 (M^+).

4. *6,7,12,12b-Tetrahydro-6,7,12b-trimethoxy-13*H*-pyrido[1,2-*a*;3,4-*b′*]diindol-13-one* (**3**). To a cooled soln. of **1** (76.5 mg, 0.25 mmol) in MeOH (7 ml), 5.4M NaOMe/MeOH (46.5 µl, 0.25 mmol) was added. The mixture was stirred at r.t. for 16 h and then evaporated. The residue was submitted to FC (silica gel, hexane/AcOEt 2:1): mixture of isomeric (6*R*,7*S*,12b*RS*)-**3** and (6*S*,7*R*,12b*RS*)-**3** (34 mg, 34%). Yellow crystals. ^{1}H-NMR (500 MHz, (D_6)DMSO): 11.41 (*s*, H–N(12), exchange with D_2O); 7.68 (*d*, H–C(4)); 7.65 (*dd*, H–C(3)); 7.57 (*d*, H–C(1)); 7.50 (*d*, H–C(8)); 7.35 (*d*, H–C(11)); 7.11 (*dd*, H–C(10)); 6.98 (*dd*, H–C(2)); 6.96 (*dd*, H–C(9)); 4.77 (*d*, H–C(6)); 4.66 (*d*, H–C(7)); 3.71 (*s*, MeO–C(6)); 3.62 (*s*, MeO–C(7)); 3.33 (*s*, MeO–C(12b)). 1D-NOE (500 MHz, (D_6)DMSO): irrad. at 4.77 → no NOE at 4.66 and *vice versa*. ^{13}C-NMR (125.75 MHz, (D_6)DMSO): 195.3 (C(13)); 157.9 (C(4a)); 138.6 (C(3)); 137.6 (C(11a)); 128.5 (C(12a)); 124.6 (C(1)); 124.3 (C(7b)); 122.7 (C(10)); 121.6 (C(13a)); 120.9 (C(2)); 120.2 (C(8)); 119.3 (C(9)); 115.1 (C(4)); 112.5 (C(7a)); 91.2 (C(6)); 91.1 (C(12b)); 74.8 (C(7)); 57.8 (*Me*O–C(7)); 56.5 (*Me*O–C(6)); 52.2 (*Me*O–C(12b)). ESI-MS (pos. mode): 365 ($[M+H]^+$).

Further elution furnished a mixture of isomeric (6*R*,7*R*,12b*RS*)-**3** and (6*S*,7*S*,12b*RS*)-**3** (55 mg, 55%). Yellow crystals. ^{1}H-NMR (500 MHz, (D_6)DMSO): 11.58 (*s*, H–N(12), exchange with D_2O); 7.66 (*d*, H–C(3)); 7.61 (*dd*, H–C(4)); 7.59 (*d*, H–C(8)); 7.53 (*d*, H–C(1)); 7.45 (*d*, H–C(11)); 7.15 (*dd*, H–C(10)); 7.04 (*dd*, H–C(9)); 6.93 (*dd*, H–C(2)); 5.68 (*d*, H–C(6)); 4.72 (*d*, H–C(7)); 3.49 (*s*, MeO–C(6)); 3.23 (*s*, MeO–C(7)); 3.20 (*s*, MeO–C(12b)). 1D-NOE (500 MHz, (D_6)DMSO): irrad. at 4.72 → NOE at 5.68; irrad. at 5.68 → NOE at 4.72. ^{13}C-NMR (125.75 MHz, (D_6)DMSO): 196.0 (C(13)); 161.8 (C(4a)); 138.4 (C(3)); 136.8 (C(11a)); 127.5 (C(12a)); 125.7 (C(7b)); 124.1 (C(1)); 122.5 (C(10)); 120.2 (C(2)); 119.4 (C(9)); 119.3 (C(13a)); 118.6 (C(8); 113.3 (C(4)); 109.2 (C(7a)); 86.8 (C(6)); 85.9 (C(12b)); 73.4 (C(7)); 54.3 (*Me*O–C(7)); 55.7 (*Me*O–C(6)); 50.9 (*Me*O–C(12b)). ESI-MS (pos. mode): 365 ($[M+H]^+$).

5. *13*H*-Pyrido[1,2-*a*;3,4-*b′*]diindol-13-one Oxime* (**4A**). A mixture containing **1** (123 mg, 0.4 mmol) and $NH_2OH \times HCl$ (139 mg, 0.8 mmol) in pyridine (7 ml) was stirred at 80° for 24 h. The product was filtered off and submitted to FC (silica gel, CH_2Cl_2/MeOH 6:1): **4A** (34 mg, 30%). Dark green crystals. M.p. < 35° (dec.). R_f (CH_2Cl_2/MeOH 4:1) 0.59. t_R 8.33 (single peak). IR (KBr): 3050, 1645, 1619, 1585, 1540, 1518, 1468, 1452, 1436, 1397, 1333, 1318, 1282, 1200, 1142, 1110, 1060, 1008, 984, 923, 875, 789, 743. ^{1}H-NMR (400 MHz, (D_6)DMSO): 12.50 (*s*, 1 H); 9.18 (*d*, H–C(6)); 8.50 (*d*, H–C(1)); 8.44 (*d*, H–C(4)); 8.39 (*d*, H–C(8)); 8.30 (*d*, H–C(7)); 7.87 (*d*, H–C(11)); 7.61 (*m*, H–C(2)); H–C(3)); H–C(10), H–C); 7.38 (*dd*, H–C(9)). 1D-NOE (400 MHz, (D_6)DMSO): irrad. at 12.5 → NOE at 7.87; irrad. at 9.18 → NOE at 8.44 and at 8.30, irrad. at 8.30 → NOE at 9.18 and 8.39. ^{13}C-NMR (100 MHz, (D_6)DMSO): 149.8 (C(13)); 142.7 (C(11a)); 135.7 (C(12b)); 134.0 (C(4a)); 129.3 (C(2)); 127.6 (C(12a)); 126.1 (C(3)); 123.9 (C(7a)); 121.7 (C(8)); 121.3 (C(1)); 121.2 (C(7b)); 120.9 (C(9)); 128.2 (C(10)); 119.8 (C(6)); 115.5 (C(13a)); 113.5 (C(11)); 112.3 (C(4)); 110.1 (C(7)). ESI-MS (pos. mode): 286 ($[M+H]^+$).

6. *12,13-Dihydro-13-hydroxy-13-methylpyrido[1,2-*a*;3,4-*b*′]diindol-5-ium Trifluoroacetate* (**5**). At 0°, 3M MeMgBr in Et_2O (400 µl, 1.2 mmol) was added to a stirred suspension of **1** (152 mg, 0.5 mmol) in THF (3 ml). The green mixture was stirred for 16 h at 0°, then quenched with 1M HCl (4 ml, 4 mmol), and evaporated. The residue was purified by MPLC: **5** (30 mg, 21%). Pale brown amorphous solid. R_f (CH_2Cl_2/MeOH 4 : 1) 0.31. t_R 7.61 (single peak, 100%). ^{1}H-NMR (400 MHz, (D_6)DMSO): 13.22 (*s*, H–N(12), exchange with D_2O); 9.55 (*d*, H–C(6)); 9.03 (*d*, H–C(7)); 8.59 (*d*, H–C(8)); 8.45 (d, H–C(4)); 7.96 (*d*, H–C(1)); 7.87 (*dd*, H–C(10)); 7.87 (*d*, H–C(11)); 7.78 (*dd*, H–C(3)); 7.71 (*dd*, H–C(2)); 7.53 (dd, H–C(9)); 6.8 (br *s*, OH, exchange with D_2O); 2.09 (s, Me–C(13)). 1D-NOE (400 MHz, (D_6)DMSO): irrad. at 9.55 → NOE at 9.03 and 8.45; irrad. at 9.03 → NOE at 8.59; irrad. at 2.1 → NOE at 13.22 and 7.96. ^{13}C-NMR (100 MHz, (D_6)DMSO): 145.0 (C(11a)); 143.9 (C(12b)); 139.8 (C(4a)); 139.1 (C(13a)); 134.4 (C(7a)); 132.5 (C(10)); 130.5 (C(2), C(3)); 130.4 (C(12a)); 124.7 (C(1)); 124.0 (C(6)); 123.6 (C(8)); 122.0 (C(9)); 119.7 (C(7b)); 117.7 (C(7)); 114.6 (C(4)); 113.2 (C(11)); 77.8 (C(13)); 23.9 (*Me*–C(13)). ESI-MS (pos. mode): 287 (M^+).

7. *13-Butyl-12,13-dihydro-13-hydroxypyrido[1,2-*a*;3,4-*b*′]diindol-5-ium Trifluoroacetate* (**6**). At –78°, 1.6M BuLi in hexane (140 µl, 0.22 mmol) was added to a stirred suspension of **1** (30.7 mg, 0.1 mmol) in THF (0.5 ml). The green reaction mixture was stirred at –78° for 1 h, then at r.t. for 2 h. The reaction was quenched with 20% AcOH in THF (0.5 ml) and the mixture evaporated. The product was isolated by MPLC: **6** (12 mg, 27%). Yellow foam. t_R 9.67 (single peak, 100%). ^{1}H-NMR (400 MHz, (D_6)DMSO): 13.21 (*s*, H–N(12), exchange with D_2O); 9.58 (*d*, H–C(6)); 9.06 (*d*, H–C(7)); 8.61 (*d*, H–C(8)); 8.46 (*d*, H–C(4)); 7.92 (*d*, H–C(1)); 7.88 (*dd*, H–C(10)); 7.88 (*d*, H–C(11)); 7.80 (*dd*, H–C(3)); 7.72 (*dd*, H–C(2)); 7.53 (*dd*, H–C(9)); 6.97 (*s*, OH, exchange with D_2O), 2.60 (*t*, $MeCH_2CH_2CH_2$); 0.87, 0.74 (*m*, $MeCH_2CH_2CH_2$); 1.13 (*m*, $MeCH_2CH_2CH_2$); 0.67 (*t*, $MeCH_2CH_2CH_2$)). ^{13}C-NMR (100 MHz, (D_6)DMSO): 145.1 (C(11a)); 143.3 (C(12b)); 140.3 (C(4a)); 137.7 (C(13a)); 134.4 (C(7a)); 132.6 (C(10)); 130.6 (C(2); 130.5 (C(12a), C(3)); 125.1 (C(1)); 124.3 (C(6)); 123.7 (C(8)); 122.1 (C(9)); 119.7 (C(7b)); 117.8 (C(7)); 114.7 (C(4)); 113.3 (C(11)); 81.1 (C(13)); 36.9 (C(1′)); 24.9 (C(2′)); 21.9 (C(3′)); 13.4 (C(4′)). ESI-MS (pos. mode): 329 (M^+).

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