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Received August 31, 1998

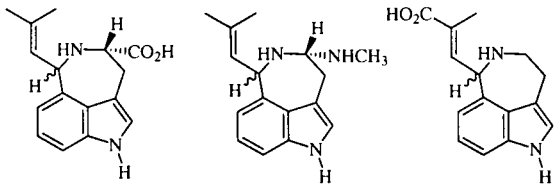
Dedicated to Professor W. Wiegrebe on the occasion of his retirement

3-Amino-4-(3-indolyl)pyrrolin-2,5-diones are condensed with various aldehydes and ketones to the corresponding imines. Under Pictet-Spengler conditions, the latter do not cyclize to pyrrolo-β-carbolines, but readily yield pyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-diones.

J. Heterocyclic Chem., **37**, 1177 (2000).

Due to their manifold biological activities, azepino-[5,4,3-*cd*]indoles have been synthesized and investigated by various groups [1,2]. These compounds show affinity to α_2- and $5HT_1$-receptors [1] and were tested for central nervous and cardiovascular activity [1]. Moreover, the skeleton of these molecules is derived from natural products related to the ergot alkaloids, clavicipitic acid (**1**), chanoclavine (**2**) and aurantioclavine (**3**), *e.g.* [3-9]

Figure 1



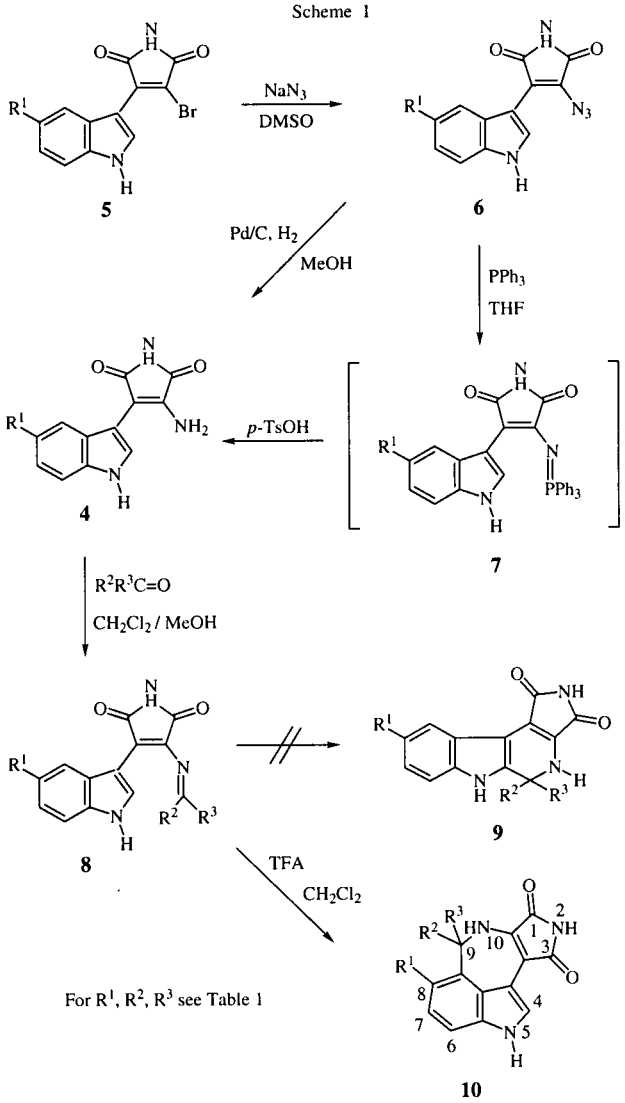
1 **2** **3**

Derivatives of azepino[5,4,3-*cd*]indole are starting materials for the synthesis of biologically active substances [6,10]. Azepino[5,4,3-*cd*]indoles with anellated maleimide moieties, however, are not known.

The maleimide of 3-amino-4-(3-indolyl)pyrroline-2,5-diones **4** is derived from the corresponding bromo derivatives **5** [11,12] *via* the azides **6**, which in turn can be hydrogenated. These azides, however, decompose easily due to their sensitivity to oxygen, especially when being dry. Thus, an alternative route was developed: the moist azides **6** were dissolved in tetrahydrofurane, and treatment with triphenylphosphine led to the iminophosphoranes [13] **7**, which were directly hydrolyzed to the amino-maleinimides **4** with *p*-toluenesulfonic acid as a catalyst. In this manner, the amino-maleinimides **4** can be obtained in gram quantities (Scheme 1).

We intended to react amines **4** with aldehydes and ketones according to Pictet-Spengler [14,15] in order to obtain the 3,4-dihydro-β-carbolines **9** *via* the imines **8**. The formation of these imines progressed well in dichloromethane with 15% of methanol, and their solubility increased relative to the amine **4**. Non-reacted **4** was separated by filtration, the solvent was removed, and the crude imines **8** were treated with trifluoroacetic acid in dichloromethane at -78°C.

Scheme 1



5 **6** **4** **7** **8** **9** **10**

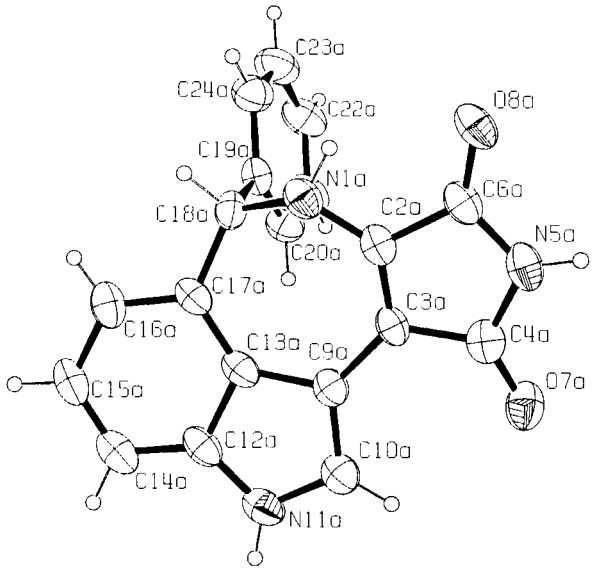


Figure 2. X-Ray structure of **10a** showing crystallographic numbering scheme (thermal ellipsoids for 30% probability [17]).

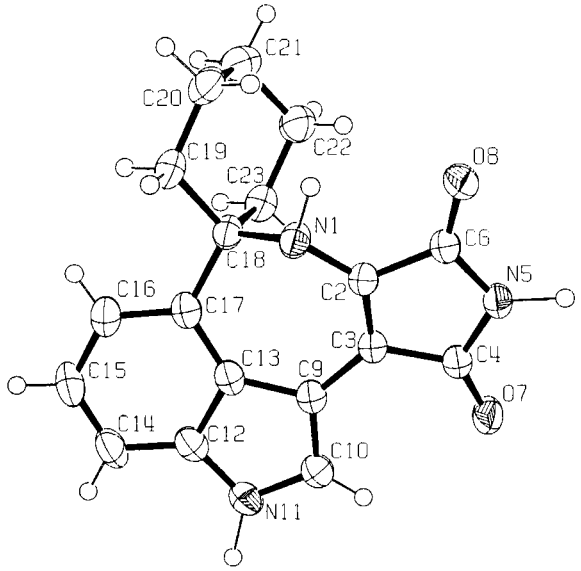


Figure 3. X-Ray structure of **10dd** showing crystallographic numbering scheme (thermal ellipsoids for 50% probability [17]).

Instead of the expected β-carbolines **9** we obtained red, nicely crystallized compounds in 9 - 45% yields. The ^{1}H-NMR spectra exhibit a characteristic vicinal coupling of the NH-proton with one proton at the C-2 of the basic

Table 1

Compound	R^1	R^2	R^3	Yield %
10a	H	Ph	H	45
10b	H	4-CN-Ph	H	35
10c	H	3,4,5-tri-MeO-Ph	H	25
10d	H	4-*tert*-BuO-Ph	H	26
10e	H	4-EtO-Ph	H	30
10f	H	4-MeO-Ph	H	20
10g	H	4-OH-Ph	H	23
10h	H	4-Me-Ph	H	37
10i	H	4-F-Ph	H	30
10j	H	3,5-di-MeO-Ph	H	35
10k	H	CH_2-Ph	H	30
10l	H	2-OH-3-MeO-Ph	H	33
10m	H	2-MeO-Ph	H	40
10n	H	2-Me-Ph	H	32
10o	H	3-MeO-Ph	H	29
10p	H	3-Me-Ph	H	25
10q	H	3-OH-4-MeO-Ph	H	22
10r	H	*N*-Boc-2-pyrrolidinyl	H	30
10s	H	2-pyrrolidinyl	H	36
10t	H	2,4-di-MeO-Ph	H	32
10u	H	3,4-di-MeO-Ph	H	35
10v	H	2,4,6-tri-MeO-Ph	H	18
10w	H	4-OH-3-MeO-Ph	H	22
10x	H	4-OH-3,5-di-MeO-Ph	H	20
10y	OCH_3	Ph	H	21
10z	OCH_3	3,4-di-MeO-Ph	H	9
10aa	OCH_3	3,4,5-tri-MeO-Ph	H	9
10bb	OCH_3	4-OH-3,5-di-MeO-Ph	H	9
10cc	H	$-(CH_2)_4-$		17
10dd	H	$-(CH_2)_5-$		23
10ee	H	$-(CH_2)_6-$		19
10ff	H	$-(CH_2)_2$-CHPh-$(CH_2)_2-$		20
10gg	H	$-(CH_2)_2$-CH(*tert*-Bu)-$(CH_2)_2-$		23

Table 2

Crystallographic Analysis of Compounds **10a** and **10dd**

Crystal Parameters	Compound **10a**	Compound **10dd**
Formula	$C_{19}H_{13}N_3O_2$ * 1/3 H_2O	$C_{18}H_{17}N_3O_2$
Crystal dimensions (mm)	0.032 x 0.256 x 0.256	0.352 x 0.512 x 0.832
Formula weight ($gmol^{-1}$)	315.33	307.34
Space group	P 2_1/c (monoclinic)	P -1 (triclinic)
a (A)	8.152(6)	6.9151(5)
b (Å)	17.465(3)	8.3951(8)
c (Å)	32.44(2)	13.1643(12)
α (degree)		86.602(8)
β (degree)	97.10(3)	79.394(7)
γ (degree)		79.680(7)
V ($Å^3$)	4584(4)	738.7(1)
Z	12	2
D_c (gcm^{-3})	1.397	1.382
μ (mm^{-1})	0.77	0.75
F (000)	2008	324
RadiationCu-K_α graphite monochromatized	λ = 1.5418 Å	
Diffractometer	CAD4 (Enraf-Nonius)	
T (K)	298	298
Scan method	ω / 2θ	
Data collection range	$1.5° \le \theta \le 75.0°$	
No. unique reflections	9424	3048
No. of observed reflections	3193	2970
Correction	Lorentz- and polarization correction variation of standard reflections corrected with a cubic spline function	
Solution	Program: SHELXS-86 (direct methods)	
Refinement	Program: SHELXL-97 [16] (full-matrix least-squares)	
wR2 for unique reflections [a]	0.3892	0.1268
R1 for observed reflections [b]	0.1075	0.0454
Largest positive peak ($eÅ^{-3}$)	0.70	0.36
Largest negative peak ($eÅ^{-3}$)	- 0.31	- 0.22

[a] $wR1 = [\Sigma[w(F_o^2 - F_c^2)^2]\Sigma[w(F_o^2)^2]]^{1/2}$.

[b] $R1 = [s \| F_o \| - \| F_c \| / \Sigma \| F_o \|]$. Weighting scheme: $w = 1/[s^2(F_o^2) + (0.0601*P)^2 + 0.32*P]$ with $P = (Max(F_o^2,0) + 2*F_c^2)/3$

Table 3

Positional Parameters and Equivalent Displacement Parameters $(Å)^2$ of **10a** with Estimated Standard Deviations in Parenthesis $U_{eq} = (1/3) * \Sigma\Sigma U_{ij} a_i^+ a_j^+ a_i a_j$

Atom	X	Y	Z	U_{eq}
N1a	0.7510(6)	0.7724(3)	0.1709(2)	0.063(2)
C2a	0.8403(7)	0.7360(4)	0.2033(2)	0.057(2)
C3a	0.8008(7)	0.6791(4)	0.2280(2)	0.054(2)
C4a	0.9445(9)	0.6686(4)	0.2596(2)	0.066(3)
N5a	1.0637(7)	0.7211(3)	0.2519(2)	0.070(2)
C6a	1.0106(8)	0.7633(4)	0.2174(2)	0.061(2)
O7a	0.9610(6)	0.6226(3)	0.2875(2)	0.080(2)
O8a	1.0876(5)	0.8125(3)	0.2019(2)	0.075(2)
C9a	0.6468(7)	0.6398(4)	0.2268(2)	0.055(2)
C10a	0.5914(8)	0.5914(4)	0.2560(2)	0.064(3)
N11a	0.4306(7)	0.5732(3)	0.2433(2)	0.069(2)
C12a	0.3761(8)	0.6090(4)	0.2068(2)	0.062(3)
C13a	0.5079(7)	0.6523(3)	0.1946(2)	0.057(2)
C14a	0.2215(9)	0.6099(4)	0.1839(3)	0.074(3)
C15a	0.2008(8)	0.6524(4)	0.1490(3)	0.074(3)
C16a	0.3332(8)	0.6947(4)	0.1368(2)	0.070(3)
C17a	0.4890(7)	0.6944(4)	0.1588(2)	0.057(2)
C18a	0.6272(7)	0.7337(4)	0.1408(2)	0.057(2)
C19a	0.7152(7)	0.6821(4)	0.1125(2)	0.056(2)
C20a	0.7347(8)	0.6045(4)	0.1192(2)	0.065(3)
C21a	0.8186(9)	0.5598(4)	0.0945(2)	0.078(3)
C22a	0.8854(10)	0.5899(5)	0.0620(3)	0.085(3)
C23a	0.8670(10)	0.6677(6)	0.0544(2)	0.090(4)
C24a	0.7826 (9)	0.7132(4)	0.0793(2)	0.075(3)

Bond Length (Å) of **10a**

O7a-C4a	1.207(9)	C9a-C10a	1.385(9)
O8a-C6a	1.210(8)	C12a-C13a	1.410(9)
N1a-C2a	1.360(8)	C12a-C14a	1.383(10)
N1a-C18a	1.479(8)	C13a-C17a	1.370(9)
N5a-C4a	1.381(9)	C14a-C15a	1.346(12)
N5a-C6a	1.366(9)	C15a-C16a	1.405(10)
N11a-C10a	1.363(9)	C16a-C17a	1.378(9)
N11a-C12a	1.363(10)	C17a-C18a	1.496(9)
C2a-C3a	1.340(9)	C18a-C19a	1.528(9)
C2a-C6a	1.485(9)	C19a-C20a	1.378(9)
C3a-C4a	1.469(9)	C20a-C21a	1.362(10)
C3a-C9a	1.428(8)	C21a-C22a	1.353(11)
C9a-C13a	1.458(9)	C22a-C23a	1.387(13)

Bond Angles (°) of **10a**

C2a-N1a-C18a	123.59(45)	C13a-C12a-C14a	121.19(56)
C4a-N5a-C6a	110.31(54)	C9a-C13a-C12a	105.67(51)
C10a-N11a-C12a	110.66(53)	C9a-C13a-C17a	133.17(49)
N1a-C2a-C3a	131.53(49)	C12a-C13a-C17a	121.16(52)
N1a-C2a-C6a	118.56(49)	C12a-C14a-C15a	118.08(62)
C3a-C2a-C6a	109.81(51)	C14a-C15a-C16a	120.43(61)
C2a-C3a-C4a	106.24(53)	C15a-C16a-C17a	122.88(56)
C2a-C3a-C9a	128.00(50)	C13a-C17a-C16a	116.19(54)
C4a-C3a-C9a	125.58(49)	C13a-C17a-C18a	124.48(49)
O7a-C4a-C3a	127.80(55)	C16a-C17a-C18a	119.13(50)
O7a-C4a-N5a	124.14(57)	N11a-C12a-C13a	108.18(54)
N5a-C4a-C3a	108.04(43)	N11a-C12a-C14a	130.57(57)
O8a-C6a-N5a	126.62(53)	C17a-C18a-C19a	113.31(46)
O8a-C6a-C2a	127.84(51)	N1a-C18a-C17a	115.90(45)
N5a-C6a-C2a	105.55(52)	N1a-C18a-C19a	109.55(44)
C3a-C9a-C13a	123.39(48)	C18a-C19a-C20a	122.56(50)
C10a-C9a-C13a	106.89(52)	C19a-C20a-C21a	121.77(56)
C3a-C9a-C10a	129.38(50)	C20a-C21a-C22a	121.09(63)
N11a-C10a-C9a	108.60(53)	C21a-C22a-C23a	118.32(69)

Table 4

Positional Parameters and Equivalent Displacement Parameters $(Å)^2$ of **10dd** with Estimated Standard Deviations in Parenthesis $U_{eq} = (1/3) * \Sigma\Sigma U_{ij} a_i^+ a_j^+ a_i a_j$

Atom	X	Y	Z	U_{eq}
N1	0.1452(2)	0.1458(2)	0.2950(1)	0.0344(4)
C2	0.2600(2)	0.2211(2)	0.3436(1)	0.0310(4)
C3	0.4448(2)	0.1695(2)	0.3652(1)	0.0312(4)
C4	0.4938(2)	0.2980(2)	0.4229(1)	0.0337(5)
N5	0.3313(2)	0.4238(2)	0.4328(1)	0.0373(4)
C6	0.1862(2)	0.3884(2)	0.3844(1)	0.0329(4)
O7	0.6456(2)	0.2981(1)	0.4567(1)	0.0474(4)
O8	0.0299(2)	0.4746(1)	0.3745(1)	0.0445(4)
C9	0.5646(2)	0.0127(2)	0.3445(1)	0.0323(4)
C10	0.7278(2)	-0.0597(2)	0.3858(1)	0.0367(5)
N11	0.7854(2)	-0.2150(2)	0.3533(1)	0.0397(4)
C12	0.6584(2)	-0.2470(2)	0.2912(1)	0.0378(5)
C13	0.5170(2)	-0.1061(2)	0.2823(1)	0.0337(4)
C14	0.6570(3)	-0.3909(2)	0.2433(1)	0.0470(6)
C15	0.5091(3)	-0.3889(2)	0.1871(2)	0.0532(7)
C16	0.3684(3)	-0.2492(2)	0.1757(2)	0.0471(6)
C17	0.3686(2)	-0.1040(2)	0.2212(1)	0.0357(5)
C18	0.2298(2)	0.0533(2)	0.1987(1)	0.0328(4)
C19	0.0522(2)	0.0215(2)	0.1528(1)	0.0387(5)
C20	-0.0762(3)	0.1742(2)	0.1182(2)	0.0480(6)
C21	0.0470(3)	0.2752(3)	0.0423(2)	0.0587(7)
C22	0.2211(3)	0.3139(2)	0.0874(2)	0.0470(6)
C23	0.3504(2)	0.1597(2)	0.1206(1)	0.0378(5)

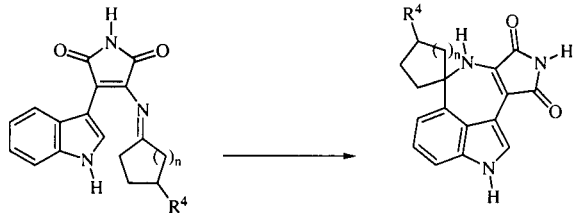
Bond Length (Å) of **10dd**

O7-C4	1.213(2)	C12-C13	1.408(2)
O8-C6	1.212(2)	C12-C14	1.398(2)
N1-C2	1.361(2)	C13-C17	1.413(2)
N1-C18	1.494(2)	C14-C15	1.365(2)
N5-C4	1.390(2)	C15-C16	1.403(3)
N5-C6	1.366(2)	C16-C17	1.390(2)
N11-C10	1.363(2)	C17-C18	1.535(2)
N11-C12	1.374(2)	C18-C23	1.547(2)
C2-C3	1.350(2)	C18-C19	1.535(2)
C2-C6	1.501(2)	C19-C20	1.520(3)
C3-C4	1.476(2)	C20-C21	1.513(3)
C9-C10	1.371(2)		

Bond Angles (°) of **10dd**

C2-N1-C18	121.91(11)	C13-C12-C14	122.52(13)
C4-N5-C6	110.53(12)	C9-C13-C12	105.76(12)
C10-N11-C12	109.19(12)	C9-C13-C17	133.76(11)
N1-C2-C3	130.42(12)	C12-C13-C17	120.48(12)
N1-C2-C6	121.27(11)	C12-C14-C15	116.46(15)
C3-C2-C6	108.31(12)	C14-C15-C16	122.08(16)
C2-C3-C4	107.44(12)	C15-C16-C17	122.52(12)
C2-C3-C9	126.36(12)	C13-C17-C16	115.89(13)
C4-C3-C9	125.97(11)	C13-C17-C18	121.53(12)
O7-C4-C3	127.87(12)	C16-C17-C18	122.33(13)
O7-C4-N5	124.78(12)	N1-C18-C23	108.94(11)
N5-C4-C3	107.35(12)	C17-C18-C19	112.22(11)
O8-C6-N5	127.39(12)	N1-C18-C17	111.31(11)
O8-C6-C2	126.30(12)	N1-C18-C19	106.92(11)
N5-C6-C2	106.30(11)	C17-C18-C23	108.85(11)
C3-C9-C13	124.16(11)	C19-C18-C23	108.51(12)
C10-C9-C13	107.11(12)	C18-C19-C20	113.94(13)
C3-C9-C10	128.42(12)	C19-C20-C21	111.45(14)
N11-C10-C9	109.59(12)	C20-C21-C22	110.83(15)
N11-C12-C13	108.34(12)	C21-C22-C23	111.26(14)
N11-C12-C14	129.14(13)	C18-C23-C22	112.70(12)

Scheme 2



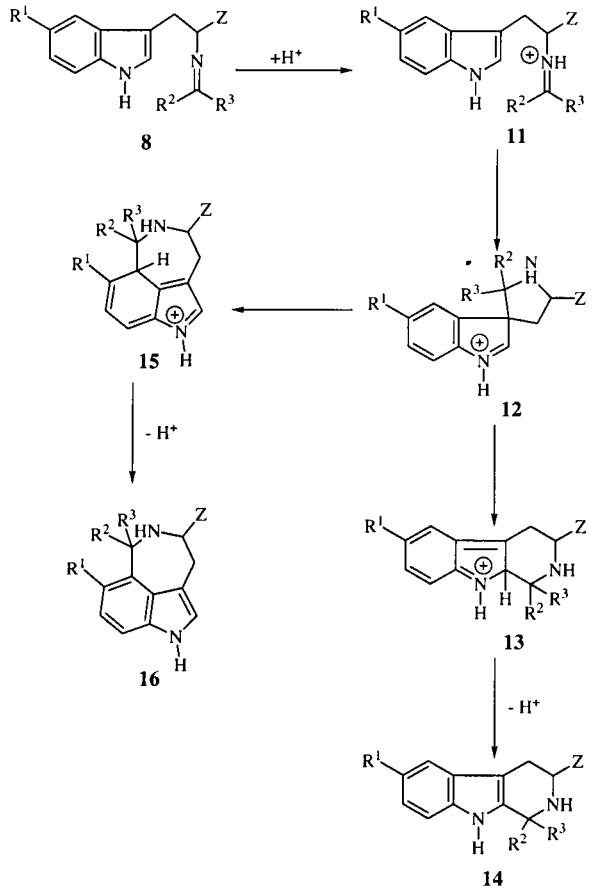
8 **10t, 10y - 10bb**

(n = 1-3, R^4 = H, Ph, *tert*-Bu)

indole moiety, thus excluding the formation of a 3,4-dihydro-β-carboline moiety. Moreover, if the 5-position of the indole moiety is substituted by methoxy, (compounds **10y - 10bb**, Table 1), the reaction product shows an AB system of 6-H and 7-H (J = 8.8 Hz) of the indole moiety (numbering of indole), but no additional *m*-coupling. Taken together, these data indicate a pyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione **10** structure (Scheme 1). Table 1 shows the variety of substituents R^1 - R^3 for **10** and its precursors.

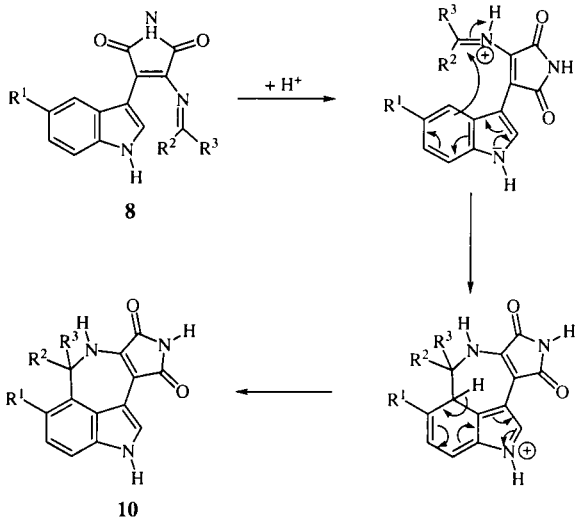
The X-ray structure analyses [18] of compounds **10a** and **10dd** confirm the pyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione structure (Figures 2 and 3).

Scheme 3



8 **11** **12** **13** **14** **15** **16**

Scheme 4



8 **10**

2-, 3-, and 4-nitrobenzaldehyde, *N,N*-dimethyl-4-amino-benzaldehyde, pyridine-4-carbaldehyde, indole-3-carbaldehyde and *N*-methyl-4-piperidone did not yield pyrrolo[3,4-*b*]azepino[5,4,3-*cd*]indole-1,3-diones because no imines **8** are formed.

There are only a few examples of this abnormal Pictet-Spengler reaction of tryptamine-imines leading to indoloazepines [19,20] instead of β-carbolines.

According to Kowalski *et al.* [15] and Novák *et al.* [20] a Pictet-Spengler reaction of compound **8** after protonation should afford the 3,3-spiroindolenine **12**, which rearranges according to Wagner-Meerwein leading to the 3,4-dihydro-β-carboline **14** (Scheme 3). According to Bergman *et al.* [19] an abnormal rearrangement affording an azepino[5,4,3-*cd*]indole is favoured by electron withdrawing groups Z (cf. Scheme 3). The results obtained with amine **4** are in accord with Bergman's [19] rules of regiochemistry and can be rationalized as shown in Scheme 4.

EXPERIMENTAL

All reactions were carried out in flame-dried glassware under nitrogen, that had been dried over self-indicating silica gel, concentrated sulphuric acid, and potassium hydroxide. Solvents and commercially available reagents were dried and purified according to standard procedures. Column chromatography was performed using Merck silica gel 60 (70-230 mesh). Recrystallizations were carried out from dichloromethane, unless stated otherwise. Melting points were recorded on a Reichert Thermovar 300419 microscope heating stage and are not corrected. ^{1}H nmr spectra were recorded on a Bruker AC250 (250 MHz) spectrometer. FT-IR spectroscopy was performed on a Nicolet 510 FT-IR spectrometer. Mass spectra were recorded on a Varian MAT 112 S/SS (70 eV). Microanalyses were performed by Analytical Lab. Univ. Regensburg.

3-Azido-4-(3-indolyl)pyrroline-2,5-dione (**6a**).

Sodium azide (0.25 g, 3.85 mmol) was suspended in dry dimethyl sulfoxide (3 mL). 3-bromo-4-(3-indolyl)pyrroline-2,5-

dione (**5a**) (0.20 g, 0.68 mmol) was added and the reaction mixture was stirred at ambient temperature. After 4 hours the solvent was removed *in vacuo*, water (15 mL) and dichloromethane (15 mL) were added. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 x 20 mL). The combined organic extracts were washed with water (10 mL), then dried over sodium sulfate. Removal of the solvent *in vacuo* and purification by chromatography (column 1 cm x 10 cm, silica gel, dichloromethane / ethyl acetate 10:1) yielded 0.67 g (69%) of orange-red crystals: mp 257°C (diethyl ether); ir (potassium bromide): (ν cm^{-1}) 3355, 3055 (CH), 2115 (N_3),1765, 1705 (C=O), 1615, 1495, 1460 (C=C).; ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ 7.00 - 7.21 (5 H, m), 11.31 (1 H (exch.), s), 12.21 (1 H (exch.), br s).

Anal. Calcd. for $C_{12}H_7N_5O_2$: C, 56.91; H, 2.79; N, 27.66. Found: C, 57.19; H, 2.87; N, 26.35.

3-Amino-4-(3-indolyl)pyrroline-2,5-dione (**4a**).

Method a): **6a** (30 mg, 0.12 mmol) and 40 mg 5% palladium on charcoal were stirred in dry methanol (2 mL) under hydrogen (balloon) for 4 hours. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography (column 1 cm x 10 cm, silica gel, dichloromethane/ethyl acetate 10:1): orange crystals, yield 16 mg (61%): mp 256°C (ref. [21]: not cited) ir (potassium bromide): (ν cm^{-1}) 3410, 3300, 3210 (NH); 3135 - 3055 (CH); 1765, 1720 (C=O); 1635, 1615, 1535, 1460 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 6.63 (2 H (exch.), br s), 6.97 - 7.13 (2 H, m), 7.36 - 7.43 (2 H, m), 7.42 (1 H, d, J = 2.5 Hz), 10.19 (1 H (exch.), br s), 11.31 (1 H (exch.), br s).

Method b): 3-Bromo-4-(3-indolyl)pyrroline-2,5-dione (**5a**) (5.00 g, 17.18 mmol) and sodium azide (1.23 g, 18.89 mmol) were stirred for 1 hour in dry dimethyl sulfoxide (50 mL) at ambient temperature. The red precipitate resulting on addition of water (500 mL) was collected and washed with ice-water. The humid red solid was dissolved in tetrahydrofurane (100 mL) and triphenylphosphine (4.51 g, 17.18 mmol), immediately followed by the addition of *p*-toluenesulfonic acid (6.54 g, 34.36 mmol). After 1 hour of stirring at ambient temperature the solvent was removed *in vacuo,* and the crude product was recrystallized: orange crystals, yield 2.83 g (73%). - Analytical data method a).

3-Amino-4-(5-methoxy-3-indolyl)pyrroline-2,5-dione (**4b**).

Preparation analogous to **4a**, method b): orange crystals, yield 2.56 g (70%): mp 240°C (ethanol); ir (potassium bromide): (ν cm^{-1}) 3440, 3335, 3195 (NH), 1765, 1660 (C=O); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.73 (3 H, s), 6.59 (2 H (exch.), br s), 6.76 (1 H, dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 7.08 (1 H, d, J = 2.4 Hz), 7.28 (1 H, d, J = 8.8 Hz), 7.38 (1 H, d, J = 2.6 Hz), 10.17 (1 H (exch.), s), 11.17 (1 H (exch.), d, J = 1.4 Hz); MS (EI) m/z (rel. intensity) = 257 (M^+, base), 242 (M - CH_3, 18), 224 (242 - CO, 19).

Anal. Calcd. for $C_{13}H_{11}N_3O_3$: C, 60.70; H, 4.31; N, 16.33. Found: C, 60.63; H, 4.59; N, 16.04.

6-Phenyl-2,6,7,8,9,10-hexahydro-pyrrolo[3',4':2,3]azepino-[4,5,6-*cd*]indole-8,10-dione (**10a**).

4a (75 mg, 0.33 mmol) and benzaldehyde (0.035 mL, 0.35 mmol) were dissolved in dry dichloromethane (7 mL) and dry methanol (1 mL) and stirred for 4 hours at 25°. The solvents were removed *in vacuo*, dry dichloromethane (7 mL) was added and the solution of the imine cooled to -78°C. Trifluoroacetic acid (0.055 mL, 0.71 mmol) was added dropwise. After 1 hour the mixture was allowed to warm to ambient temperature. The resulting solution was poured onto ice-water, alkalized with 2N aqueous sodium carbonate solution, and the organic layer was separated. The aqueous phase was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were washed with water (20 mL), dried over sodium sulphate, and the solvent was removed *in vacuo*. The residue was purified by chromatography (column 1 cm x 7 cm, silica gel, dichloromethane/ethyl acetate 5:1): red crystals, yield 47 mg (45%): mp 227°; ir (potassium bromide): (ν cm^{-1}) 3385, 3350, 3285 (NH), 3060 (CH), 1760, 1700 (C=O), 1610, 1545, 1490, 1455 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 5.83 (1 H, d, J = 4.6 Hz), 6.98 - 7.78 (9 H, m), 7.38 (1 H (exch.), d, J = 5.9 Hz), 10.27 (1 H (exch.), s), 11.48 (1 H (exch.), br s); MS: m/z (rel. intensity): 315 (100) (M^+, base), 238 (M - C_6H_5, 69).

Anal. Calcd. for $C_{19}H_{13}N_3O_2$: C, 72.37; H, 4.16; N, 13.33. Found: C, 71.95; H, 4.10; N, 13.28.

Compounds **10b - 10gg** were prepared analogously. They were obtained as red crystals.

6-(4-Cyanophenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10b**).

Yield 39 mg (35%): mp 185°C; ir (potassium bromide): (ν cm^{-1}) 3330 (NH), 3050 - 2870 (CH), 2230 (CN), 1760, 1705 (C=O), 1615, 1540 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 5.98 (1 H, d, J = 4.8 Hz), 7.06 - 7.84 (4 H, m), 7.22; 7.68 (4 H, AA'BB', J = 8.4 Hz), 7.94 (1 H (exch.), d, J = 4.8 Hz), 10.35 (1 H (exch.), s), 11.59 (1 H (exch.), br s; NH); MS (EI): m/z (rel. intensity): 340 (M^+, base), 238 (M - C_6H_4CN, 71).

Anal. Calcd. for $C_{20}H_{12}N_4O_2$: C, 70.58; H, 3.55; N, 16.46. Found: C, 70.62; H, 3.60; N, 16.51.

6-(3,4,5-Trimethoxyphenyl)-2,6,7,8,9,10-hexahydro-pyrrolo-[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10c**).

Yield 33 mg (25%): mp 193°C; ir (potassium bromide): (ν cm^{-1}) 3295 (NH), 3060 - 2960 (CH), 1760, 1705 (C=O), 1595, 1540, 1495, 1465 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.53 (6 H, s), 3.55 (3 H, s), 5.74 (1 H, d, J = 4.6 Hz), 6.39 (2 H, s), 6.99 - 7.79 (4 H, m), 7.68 (1 H (exch.), d, J = 4.6 Hz), 10.29 (1 H (exch.), s), 11.49 (1 H (exch.), d, J = 2.4 Hz); MS (EI): m/z (rel. intensity): 405 (M^+), 238 (M - $C_6H_2(OCH_3)_3$, 49).

Anal. Calcd. for $C_{22}H_{19}N_3O_5$: C, 65.18; H, 4.72; N, 10.36. Found: C, 65.13; H, 4.77; N, 10.31.

6-(4-*tert*-Butyloxyphenyl)-2,6,7,8,9,10-hexahydropyrrolo-[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10d**).

Yield 33 mg (26%): mp 226°C; ir (potassium bromide): (ν cm^{-1}) 3415 (NH), 3050 - 2900 (CH), 1760, 1700 (C=O), 1670, 1560, 1540 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 1.20 (9 H, s), 5.79 (1 H, d, J = 4.7 Hz), 6.78; 6.96 (4 H, AA'BB', J = 8.5 Hz), 6.98 - 7.77 (4 H, m), 7.75 (1 H (exch.), d, J = 4.5 Hz), 10.28 (1 H (exch.), s), 11.47

(1 H (exch.), d, J = 2.3 Hz); MS (EI): m/z (rel. intensity): 387 (M^+, 33), 72 (M - CH_3, 4), 331 (M - C_4H_8, base), 238 (M - C_6H_4-O-C_4H_9, 44), 56 (C_4H_8, 24), 41 (C_4H_8 - CH_3, 55).

Anal. Calcd. for $C_{23}H_{21}N_3O_3$: C, 71.30; H, 5.46; N, 10.85. Found: C, 71.25; H, 5.40; N, 10.91.

6-(4-Ethoxyphenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10e**).

Yield 36 mg (30%): mp 196°C; ir (potassium bromide): (ν cm^{-1}) 3369 (NH), 3095 - 2986 (CH), 1753, 1698 (C=O), 1611, 1541, 1512 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 1.23 (3 H, t, J = 7.0 Hz), 3.88 (2 H, q, J = 7.0 Hz), 5.76 (1 H, d, J = 4.8 Hz), 6.72; 6.91 (4 H, AB, J = 8.6 Hz), 7.07 - 7.76 (4 H, m), 7.71 (1 H (exch.), d, J = 4.7 Hz), 10.26 (1 H (exch.), s), 11.47 (1 H (exch.), d, J = 2.3 Hz); MS (EI): m/z (rel. intensity): 359 (M^+, base), 238 (M - C_6H_4-O-C_2H_5, 57).

Anal. Calcd. for $C_{21}H_{17}N_3O_3$: C, 70.18; H, 4.77; N 11.69. Found: C, 69.93; H, 4.70; N, 11.72.

6-(4-Methoxyphenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10f**).

Yield 23 mg (20%): mp 187°C; ir (potassium bromide): (ν cm^{-1}) 3340 (NH), 3095 - 2995 (CH), 1760, 1705 (C=O), 1610, 1540, 1510, 1460 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.63 (3 H, s), 5.77 (1 H, d, J = 4.8 Hz), 6.73; 6.93 (4 H, AA'BB', J = 8.8 Hz), 6.93 - 7.76 (4 H, m), 7.72 (1 H (exch.), d, J = 4.8 Hz), 10.26 (1 H (exch.), s), 11.46 (1 H (exch.), d, J = 2.5 Hz); MS (EI): m/z (rel. intensity): 345 (M^+, base), 238 (M - C_6H_4O-CH_3, 41).

Anal. Calcd. for $C_{20}H_{15}N_3O_3$: C, 69.56; H, 4.38; N, 12.17. Found: C, 69.51; H, 4.32; N, 12.22.

6-(4-Hydroxyphenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10g**).

Yield 25 mg (23%): mp 211°C; ir (potassium bromide): (ν cm^{-1}) 3400, 3325 (NH, OH), 3100 - 2950 (CH), 1760, 1700 (C=O), 1600, 1540, 1510, 1440 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 5.72 (1 H, d, J = 4.7 Hz), 6.55; 6.82 (4 H, AA'BB', J = 8.6 Hz), 6.88 - 7.79 (4 H, m), 7.65 (1 H (exch.), d, J = 4.7 Hz), 9.26 (1 H (exch.), br s), 10.25 (1 H (exch.), s), 11.44 (1 H (exch.), d, J = 2.3 Hz); MS (EI): m/z (rel. intensity): 331 (M^+, base), 238 (M - C_6H_4OH, 44), 93 (C_6H_4OH, 50).

Anal. Calcd. for $C_{19}H_{13}N_3O_3$: C, 68.88; H, 3.95; N, 12.68. Found: C, 68.93; H, 3.92; N, 12.61.

6-(4-Methylphenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10h**).

Yield 40 mg (37%): mp 220°C; ir (potassium bromide): (ν cm^{-1}) 3355 (NH), 3180 - 2950 (CH), 1760, 1700 (C=O), 1615, 1540, 1510, 1460 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 2.15 (3 H, s), 5.78 (1 H, d, J = 4.7 Hz), 6.89 - 7.76 (4 H, m), 7.05; 7.36 (4 H, AA'BB', J = 8.0 Hz), 7.74 (1 H (exch.), d, J = 4.8 Hz), 10.26 (1 H (exch.), s), 11.47 (1 H (exch.), d, J = 2.0 Hz); MS: m/z (rel. intensity): 329 (100) [$M^{+\bullet}$], 238 (53) [M - $^\bullet C_7H_7$]$^+$, 91 (18) [C_7H_7]$^+$.

Anal. Calcd. for $C_{20}H_{15}N_3O_2$: C, 72.96; H, 4.59; N, 12.76. Found: C, 73.00; H, 4.52; N, 12.83.

6-(4-Fluorophenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10i**).

Yield 38 mg (30%): mp 190°C; ir (potassium bromide): (ν cm^{-1}) 3340 (NH), 3050 - 2970 (CH), 1760, 1705 (C=O), 1615, 1540, 1505 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 5.84 (1 H, d, J = 4.8 Hz), 6.98 - 7.78 (8 H, m;), 7.80 (1 H (exch.), d, J = 4.8 Hz), 10.29 (1 H (exch.), s), 11.51 (1 H (exch.), d, J = 1.9 Hz); MS (EI): m/z (rel. intensity): 333 (M^+, base), 238 (M - C_6H_6F, 55).

Anal. Calcd. for $C_{19}H_{12}N_3O_2F$: C, 68.47; H, 3.63; N, 12.61. Found: C, 68.40; H, 3.60; N, 12.55.

6-(3,5-Dimethoxyphenyl)-2,6,7,8,9,10-hexahydropyrrolo-[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10j**).

Yield 43 mg (35%): mp 178°C; ir (potassium bromide): (ν cm^{-1}) 3410, 3330 (NH), 3050 - 2935 (CH), 1770, 1715 (C=O), 1645, 1600, 1520, 1460 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.58 (6 H, s), 5.68 (1 H, d, J = 4.7 Hz), 6.19 - 7.77 (7 H, m), 7.75 (1 H (exch.), d, J = 4.7 Hz), 10.29 (1 H (exch.), s), 11.49 (1 H (exch.), d, J = 2.0 Hz); MS (EI): m/z (rel. intensity): 375 (M^+, base), 238 (M - $C_6H_3OCH_3)_2$, 62).

Anal. Calcd. for $C_{21}H_{17}N_3O_4$: C, 67.19; H, 4.56; N, 11.19. Found: C, 67.11; H, 4.50; N, 11.25.

6-Benzyl-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]azepino-[4,5,6-*cd*]indole-8,10-dione (**10k**).

Yield 33 mg (30%): mp 212°C; ir (potassium bromide): (ν cm^{-1}) 3415, 3380 (NH), 3060 - 2920 (CH), 1760, 1710 (C=O), 1605, 1540, 1495 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 4.80 (1 H, br t, J = 7.6 Hz), 4.94 (2 H, d, J = 7.9 Hz), 7.10 - 7.37 (10 H, m), 7.68 (1 H, d, J = 2.4 Hz), 10.24 (1 H (exch.), s), 11.35 (1 H (exch.), d, J = 2.7 Hz); MS (EI): m/z (rel. intensity): 329 (M^+, 2), 238 (M - CH_2Ph, 19), 91 (C_7H_7, base).

Anal. Calcd. for $C_{20}H_{15}N_3O_2$: C, 72.94; H, 4.59; N, 12.76. Found: C, 73.22; H, 4.13; N, 12.44.

6-(2-Hydroxy-3-methoxyphenyl)-2,6,7,8,9,10-hexahydro-pyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10l**).

Yield 39 mg (33%): mp 197°C; ir (potassium bromide): (ν cm^{-1}) 3525, 3440, 3375, 3350 (NH, OH), 3050 - 2975 (CH), 1750, 1700 (C=O), 1600, 1540, 1510, 1480 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.77 (3 H, s), 5.97 - 7.80 (9 H, m), 6.28 (1 H, d, J = 4.4 Hz), 9.15 (1 H (exch.), s), 10.28 (1 H (exch.), s), 11.50 (1 H (exch.), d, J = 2.6 Hz); MS (EI): m/z (rel. intensity): 361 (M^+, base), 238 (M - $C_6H_3(OH)(OCH_3)$, 44).

Anal. Calcd. for $C_{20}H_{15}N_3O_4$: C, 66.48; H, 4.18; N, 11.60. Found: C, 66.43; H, 4.12; N, 11.55.

6-(2-Methoxyphenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10m**).

Yield 46 mg (40%): mp 183°C; ir (potassium bromide): (ν cm^{-1}) 3435 (NH), 3050 - 2995 (CH), 1760, 1690 (C=O), 1630, 1535, 1500, 1435 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.92 (3 H, s), 6.27 (1 H, d, J = 4.5 Hz), 6.42 - 7.81 (8 H, m), 7.15 (1 H (exch.), d, J = 4.6

Hz), 10.28 (1 H (exch.), s), 11.52 (1 H (exch.), d, J = 2.2 Hz); MS (EI): m/z (rel. intensity): 345 (M^+, base), 238 (M - $C_6H_4OCH_3$, 93).

Anal. Calcd. for $C_{20}H_{15}N_3O_3$: C, 69.56; H, 4.38; N, 12.17. Found: C, 69.63; H, 4.33; N, 12.12.

6-(2-Methylphenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10n**).

Yield 34 mg (32%): mp 210°C; ir (potassium bromide): (ν cm^{-1}) 3410 (NH), 3050 - 2970 (CH), 1760, 1690 (C=O), 1540 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 2.63 (3 H, s), 6.06 (1 H, d, J = 4.2 Hz), 6.63 - 7.64 (8 H, m), 7.85 (1 H (exch.), d, J = 4.6 Hz), 10.30 (1 H (exch.), s), 11.54 (1 H (exch.), d, J = 1.9 Hz); MS (EI): m/z (rel. intensity): 329 (M^+, base), 238 (M - C_7H_7, 74).

Anal. Calcd. for $C_{20}H_{15}N_3O_2$: C, 72.96; H, 4.59; N, 12.76. Found: C, 72.91; H, 4.63; N, 12.72.

6-(3-Methoxyphenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10o**).

Yield 33 mg (29%): mp 216°C; ir (potassium bromide): (ν cm^{-1}) 3355 (NH); 3050 - 2970 (CH), 1750, 1700 (C=O), 1605, 1540, 1485 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.61 (3 H, s), 5.78 (1 H, d, J = 4.8 Hz), 6.56 - 7.79 (9 H, m), 10.28 (1 H (exch.), s), 11.50 (1 H (exch.), d, 2.0 Hz); MS (EI): m/z (rel. intensity): 345 (M^+, base), 238 (M - C_6H_4O-CH_3, 78).

Anal. Calcd. for $C_{20}H_{15}N_3O_3$: C, 69.56; H, 4.38; N, 12.17. Found: C, 69.49; H, 4.33; N, 12.13.

6-(3-Methylphenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10p**).

Yield 27 mg (25%): mp 188°C; ir (potassium bromide): (ν cm^{-1}) 3350 (NH), 3060 - 2970 (CH), 1765, 1710 (C=O), 1645, 1605, 1590 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 2.40 (3 H, s), 5.71 (1 H, d, J = 4.3 Hz), 6.77 - 7.72 (9 H, m), 10.27 (1 H (exch.), s), 11.40 (1 H (exch.), br s); MS (EI): m/z (rel. intensity): 329 (M^+, base), 238 (M - C_7H_7, 76), 91 (C_7H_7, 15).

Anal. Calcd. for $C_{20}H_{15}N_3O_2$: C, 72.96; H, 4.59; N, 12.76. Found: C, 72.99; H, 4.55; N, 12.70.

6-(3-Hydroxy-4-methoxyphenyl)-2,6,7,8,9,10-hexahydro-pyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10q**).

Yield 26 mg (22%): mp 191°C; ir (potassium bromide): (ν cm^{-1}) 3435, 3315 (NH, OH), 3050 - 2980 (CH), 1760, 1790 (C=O), 1615, 1595, 1545 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.64 (3 H, s), 5.68 (1 H, d, J = 4.7 Hz), 6.42 - 7.75 (8 H, m), 7.65 (1 H (exch.), d, J = 4.7 Hz), 8.79 (1 H (exch.), br s), 10.26 (1 H (exch.), s), 11.44 (1 H (exch.), d, J = 2.6 Hz); MS (EI): m/z (rel. intensity): 361 (M^+, base), 238 (M - $C_6H_3(OH)(OCH_3)$, 54).

Anal. Calcd. for $C_{20}H_{15}N_3O_4$: C, 66.48; H, 4.18; N, 11.60. Found: C, 66.42; H, 4.22; N, 11.65.

6-(1-*tert*-Butyloxycarbonyl-2-pyrrolidinyl)-2,6,7,8,9,10-hexa-hydropyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10r**).

Yield 40 mg (30%): mp 235°C; ir (potassium bromide): (ν cm^{-1}) 3310 (NH); 3050 - 2975 (CH); 1760, 1710 (C=O); 1615, 1545, 1480 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 1.05 - 3.17 (6 H, m), 1.42 (9 H, s), 4.16 (1 H, m), 4.81 (1 H, m), 6.73 - 7.68 (4 H, m), 7.59 (1 H (exch.), br s), 10.15 (1 H (exch.), s), 11.32 (1 H (exch.), br s); MS (EI): m/z (rel. intensity): 408 (M^+, 6), 238 (M - C_4H_7N-Boc, 54).

Anal. Calcd. for $C_{22}H_{24}N_4O_4$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.73; H, 5.98; N, 13.77.

2,6,7,8,9,10-Hexahydro-6-(2-pyrrolidinyl)-pyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10s**).

Yield 37 mg (36%): mp 162°C; ir (potassium bromide): (ν cm^{-1}) 3330 (NH); 3050 - 2945 (CH); 1755, 1705 (C=O); 1615, 1535 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 1.02 - 3.24 (6 H, m), 4.24 - 4.30 (2 H, m; CH), 6.90 - 7.65 (5 H, m), 10.21 (1 H (exch.), br s), 11.32 (1 H (exch.), br s); MS (EI): m/z (rel. intensity): 308 (M^+, 3), 239 (M - C_4H_7N, 21), 238 (M - C_4H_8N, 20).

Anal. Calcd. for $C_{17}H_{16}N_4O_2$: C, 66.22; H, 5.23; N, 18.17. Found: C, 66.18; H, 5.19; N, 18.10.

6-(2,4-Dimethoxyphenyl)-2,6,7,8,9,10-hexahydro-pyrrolo-[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-diones (**10t**).

Yield 40 mg (32%): mp 238°C; ir (potassium bromide): (ν cm^{-1}) 3355 (NH), 3050 - 2970 (CH), 1750, 1700 (C=O), 1605, 1540, 1485 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.67 (3 H, s), 3.90 (3 H, s), 5.98 - 8.08 (10 H, m), 10.34 (1 H (exch.), s), 11.51 (1 H (exch.), br s); MS (EI): m/z (rel. intensity): 375 (M^+, base), 238 (M - $C_6H_3(OCH_3)_2$, 49).

Anal. Calcd. for $C_{21}H_{17}N_3O_4$: C, 67.19; H, 4.56; N, 11.19. Found: C, 67.25; H, 4.52; N, 11.23.

6-(3,4-Dimethoxyphenyl)-2,6,7,8,9,10-hexahydropyrrolo-[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10u**).

Yield 43 mg (35%): mp 257°C; ir (potassium bromide): (ν cm^{-1}) 3355 (NH), 3050 - 2970 (CH), 1750, 1700 (C=O), 1605, 1540, 1485 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ 3.60 (3 H, s), 3.61 (3 H, s), 5.75 (1 H, d, J = 4.7 Hz), 6.27 - 7.76 (7 H, m), 7.68 (1 H (exch.), d, J = 4.7 Hz), 10.25 (1 H (exch.), s), 11.46 (1 H (exch.), d, J = 2.3 Hz). MS (EI): m/z (rel. intensity): 375 (M^+, base), 238 (M - $C_6H_3(OCH_3)_2$, 49).

Anal. Calcd. for $C_{21}H_{17}N_3O_4$: C, 67.19; H, 4.56; N, 11.19. Found: C, 67.22; H, 4.60; N, 11.25.

6-(2,4,6-Trimethoxyphenyl)-2,6,7,8,9,10-hexahydropyrrolo-[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10v**).

Yield 24 mg (18%): mp 277°C; ir (potassium bromide): (ν cm^{-1}) 3355 (NH), 3050 - 2970 (CH), 1750, 1700 (C=O), 1605, 1540, 1485 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.76 (6 H, s), 3.82 (3 H, s), 6.21 - 7.76 (8 H, m), 10.12 (1 H (exch.), s), 11.25 (1 H (exch.), d, J = 2.1 Hz); MS (EI): m/z (rel. intensity): 405 (M^+, base), 238 (M - $C_6H_2(OCH_3)_3$, 52).

Anal. Calcd. for $C_{22}H_{19}N_3O_5$: C, 65.18; H, 4.72; N, 10.36. Found: C, 64.93; H, 4.68; N, 10.31.

6-(4-Hydroxy-3-methoxyphenyl)-2,6,7,8,9,10-hexahydro-pyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10w**).

Yield 26 mg (22%): mp 261°C; ir (potassium bromide): (ν cm^{-1}) 3435, 3315 (NH, OH), 3050 - 2980 (CH), 1760, 1790

(C=O), 1615, 1595, 1545 (C=C); ^{1}H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.60 (3 H, s), 5.71 (1 H, d, J = 4.7 Hz), 6.20 - 7.75 (7 H, m), 7.63 (1 H (exch.), d, J = 4.6 Hz), 8.83 (1 H, br s), 10.25 (1 H (exch.), s), 11.44 (1 H (exch.), d, J = 2.4 Hz); MS (EI): m/z (rel. intensity): 361 (M^+, base), 238 (M - $C_6H_3(OH)(OCH_3)$, 46).

Anal. Calcd. for $C_{20}H_{15}N_3O_4$: C, 66.48; H, 4.18; N, 11.60. Found: C, 66.42; H, 4.12; N, 11.53.

6-(4-Hydroxy-3,5-dimethoxyphenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10x**).

Yield 26 mg (20%): mp 291°C; ir (potassium bromide): (ν cm^{-1}) 3410 (NH, OH), 3060 - 2980 (CH), 1765, 1700 (C=O), 1615, 1540, 1520, 1460 (C=C); ^{1}H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.52 (6 H, s), 5.70 (1 H, d, J = 4.6 Hz), 6.33 (2 H, s), 6.64 - 7.78 (5 H, m), 8.26 (1 H (exch.), s), 10.27 (1 H (exch.), s), 11.46 (1 H (exch.), d, J = 2.4 Hz); MS (EI): m/z (rel. intensity): 391 (M^+, base), 238 (M - $C_6H_2(OH)(OCH_3)_2$, 69).

Anal. Calcd. for $C_{21}H_{17}N_3O_5$: C, 64.45; H, 4.38; N, 10.74. Found: C, 64.50; H, 4.33; N, 10.80.

5-Methoxy-6-phenyl-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]-azepino[4,5,6-*cd*]indole-8,10-dione (**10y**).

Yield 24 mg (21%): mp 254°C; ir (potassium bromide): (ν cm^{-1}) 3425, 3365, 3215 (NH), 3060 - 2835 (CH), 1760, 1705 (C=O), 1680, 1585, 1495 (C=C); ^{1}H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.75 (3 H, s), 6.22 (1 H, d, J = 5.2 Hz), 6.94; 7.35 (2 H, AB, J = 8.7 Hz), 6.99 - 7.20 (5 H, m), 7.74 (1 H (exch.), d, J = 5.0 Hz), 7.76 (1 H, d, J = 2.8 Hz), 10.22 (1 H (exch.), s), 11.32 (1 H (exch.), d, J = 2.6 Hz); MS (EI) m/z (rel. intensity) = 345 (M^+, base), 330 (M - CH_3, 4), 314 (M - CH_3O, 6), 268 (M - Ph, 75), 253 (268 - CH_3, 30), 172.5 (M^{2+}, 2).

Anal. Calcd. for $C_{20}H_{15}N_3O_3$: C, 69.56; H, 4.38; N, 12.17. Found: C, 69.13; H, 4.21; N, 11.98.

6-(3,4-Dimethoxyphenyl)-2,6,7,8,9,10-hexahydro-5-methoxypyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10z**).

Yield 12 mg (9%): mp 275°C; ir (potassium bromide): (ν cm^{-1}) 3420, 3350 (NH), 3060 - 2840 (CH), 1755, 1705 (C=O), 1670, 1540, 1515 (C=C); ^{1}H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.59 (3 H, s), 3.61 (3 H, s), 3.75 (3 H, s), 6.17 (1 H, d, J = 5.0 Hz), 6.25 (1 H, ddd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, J_3 = 0.4 Hz), 6.67 (1 H, d, J = 8.4 Hz), 6.86 (1 H, d, J = 2.1 Hz), 6.94; 7.34 (2 H, AB; J = 8.8 Hz), 7.66 (1 H (exch.), d), 7.73 (1 H, d, J = 2.5 Hz), 10.20 (1 H (exch.), s), 11.29 (1 H (exch.); d, J = 2.6 Hz); MS (EI): m/z (rel. intensity): 405 (M^+, base), 390 (M - CH_3, 3), 374 (M - CH_3O, 9), 268 (M - $C_6H_3(OCH_3)_2$, 80), 253 (268 - CH_3, 27), 202.5 (M^{2+}, 2).

Anal. Calcd. for $C_{22}H_{19}N_3O_5$: C, 65.18; H, 4.72; N, 10.36. Found: C, 64.69; H, 5.14; N, 9.97.

5-Methoxy-6-(3,4,5-trimethoxyphenyl)-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10aa**).

Yield 14 mg (9%): mp 244°C; ir (potassium bromide): (ν cm^{-1}) 3410, 3325 (NH), 3075 - 2835 (CH), 1765, 1700 (C=O), 1670, 1540, 1455 (C=C); ^{1}H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.52 (6 H, s), 3.55 (3 H, s), 3.79 (3 H, s), 6.15 (1 H, d, J = 5.0 Hz), 6.33 (2 H, s), 6.96; 7.36 (2 H, AB, J = 8.8 Hz), 7.68 (1 H (exch.), d, J = 5.2 Hz), 7.76 (1 H, d, J = 2.4 Hz), 10.24 (1 H (exch.), s), 11.31 (1 H (exch.), d, J = 2.1 Hz); MS (EI): m/z (rel. intensity): 435 (M^+, base), 420 (M - CH_3, 4), 404 (M - CH_3O, 5), 268 (M - $C_6H_2(OCH_3)_3$, 63), 253 (268 - CH_3, 25), 217.5 (M^{2+}, 2).

Anal. Calcd. for $C_{23}H_{21}N_3O_6$: C, 63.44; H, 4.86; N, 9.65. Found: C, 63.07; H, 5.16; N, 9.52.

6-(4-Hydroxy-3,5-dimethoxyphenyl)-5-methoxy-2,6,7,8,9,10-hexahydropyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole-8,10-dione (**10bb**).

Yield 13 mg (9%): mp 238°C; ir (potassium bromide): (ν cm^{-1}) 3570, 3345 (OH, NH), 3060 - 2840 (CH), 1770, 1710 (C=O), 1670, 1515, 1490 (C=C); ^{1}H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 3.50 (6 H, s), 3.77 (3 H, s), 6.13 (1 H, d, J = 5.2 Hz), 6.28 (2 H, s), 6.95; 7.35 (2 H, AB, J = 7.8 Hz), 7.62 (1 H (exch.), d, J = 5.2 Hz), 7.74 (1 H, d, J = 2.5 Hz), 8.21 (1 H (exch.), s), 10.20 (1 H (exch.), s), 11.28 (1 H (exch.), d, J = 2.5 Hz); MS (EI): m/z (rel. intensity): 421 (M^+, base), 406 (M - CH_3, 3), 390 (M - CH_3O, 5), 268 (M - $C_6H_2(OH)(OCH_3)_3$, 64), 253 (268 - CH_3, 24), 210.5 (M^{2+}, 1).

Anal. Calcd. for $C_{22}H_{19}N_3O_6$: C, 67.70; H, 4.54; N, 9.97. Found: C, 67.31; H, 4.90; N, 9.59.

Spiro[cyclopentane-1,6'-(7',8',9',10'-tetrahydro-2'*H*-pyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole)]-8',10'-dione (**10cc**).

Yield 16 mg (17%): mp 267°C; ir (potassium bromide): (ν cm^{-1}) 3340, 3360 (NH), 3070 - 2965 (CH), 1750, 1685 (C=O), 1610, 1540, 1500 (C=C); ^{1}H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 1.66 - 2.09 (8 H, m), 6.20 (1 H (exch.), s), 6.97 - 7.71 (4 H, m), 10.29 (1 H (exch.), s), 11.42 (1 H (exch.), br s); MS (EI): m/z (rel. intensity): 293 (M^+, base), 264 (38).

Anal. Calcd. for $C_{17}H_{15}N_3O_2$: C, 69.61; H, 5.15; N, 14.33. Found: C, 69.55; H, 5.10; N, 14.28.

Spiro[cyclohexane-1,6'-(7',8',9',10'-tetrahydro-2'*H*-pyrrolo-[3',4':2,3]azepino[4,5,6-*cd*]indole)]-8',10'-dione (**10dd**).

Yield 23 mg (23%): mp 289°C; ir (potassium bromide): (ν cm^{-1}) 3375, 3345 (NH), 3110 - 2965 (CH), 1760, 1685 (C=O), 1535, 1490 (C=C); ^{1}H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ 1.46 - 2.02 (10 H, m), 5.83 - 7.70 (4 H, m) 7.06 (1 H (exch.), s), 10.38 (1 H (exch.), s), 11.46 (1 H (exch.), s); MS (EI): m/z (rel. intensity): 307 (M^+, base), 264 (55).

Anal. Calcd. for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.76. Found: C, 70.30; H, 5.51; N, 13.71.

Spiro[cycloheptane-1,6'-(7',8',9',10'-tetrahydro-2'*H*-pyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole)]-8',10'-dione (**10ee**).

Yield 20 mg (19%): mp 278°C; ir (potassium bromide): (ν cm^{-1}) 3365 (NH), 3050 - 2925 (CH), 1750, 1700 (C=O), 1540, 1510, 1440 (C=C); ^{1}H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 1.58 - 2.14 (12 H, m), 5.96 (1 H, s), 7.01 - 7.71 (4 H, m), 10.32 (1 H (exch.), s), 11.44 (1 H (exch.), d, J = 2.0 Hz); MS (EI): m/z (rel. intensity): 321 (M^+, base), 264 (50).

Anal. Calcd. for $C_{19}H_{19}N_3O_2$: C, 71.01; H, 5.96; N, 13.07. Found: C, 70.93; H, 5.60; N, 13.00.

4-Phenylspiro[cyclohexane-1,6'-(7',8',9',10'-tetrahydro-2'*H*-pyrrolo[3',4':2,3]azepino[4,5,6-*cd*]indole)]-8',10'-dione (**10ff**).

Yield 25 mg (20%): mp 257°C; ir (potassium bromide): (ν cm^{-1}) 3405, 3370, 3200 (NH), 3030 - 2875 (CH), 1750, 1700 (C=O), 1605, 1540, 1515, 1495 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 1.33 - 2.30 (9 H, m), 6.07 (1 H (exch.), s), 7.10 - 7.72 (9 H, m), 10.40 (1 H (exch.), s), 11.49 (1 H (exch.), d, J = 2.2 Hz); MS (EI): m/z (rel. intensity): 383 (M^+, base), 264 (75), 251 (89).

Anal. Calcd. for $C_{24}H_{21}N_3O_2$: C, 75.18; H, 5.52; N, 10.96. Found: C, 75.23; H, 5.45; N, 10.91.

4-*tert*-Butylspiro[cyclohexane-1,6'-(7',8',9',10'-tetrahydro-2'*H*-pyrrolo[3',4':2,3]azepino[4,5,6,-*cd*]indole]-8',10'-dione (**10gg**).

Yield 28 mg (23%): mp 264°C; ir (potassium bromide): (ν cm^{-1}) 3365 (NH), 3005 - 2950 (CH), 1750, 1690 (C=O), 1605, 1540, 1515, 1460 (C=C); ^1H nmr (250 MHz) (hexadeutero dimethyl sulfoxide): δ ppm 0.88 (9 H, s), 1.10 - 2.37 (9 H, m), 5.76 (1 H (exch.), s), 7.05 - 7.69 (4 H, m;), 10.36 (1 H (exch.), s), 11.46 (1 H (exch.), d, J = 2.0 Hz); MS (EI): m/z (rel. intensity): 363 (M^+, base), 306 (M - C_4H_8, 10), 264 (M - C_7H_{15}, 78), 251 (M - C_8H_{16}, 35).

Anal. Calcd. for $C_{22}H_{25}N_3O_2$: C, 72.70; H, 6.93; N, 11.56. Found: C, 72.76; H, 6.90; N, 11.85.

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