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Reactions of *N*- and *C*-Alkenylanilines: IX.* Synthesis, Oxidation, and Nitration of Some 7-Methyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indoles

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Abstract—Heating of 4-acyl-3-iodo-7-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indoles in piperidine gave 4-acyl-7-methyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indoles which were oxidized with $KMnO_4$ to obtain the corresponding 4-acyl-7-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole-1,2-diols. Oxidation of 4-acyl-7-methyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indoles at the olefinic double bond with hydrogen peroxide in acetonitrile in the presence of formic acid afforded stereoisomeric epoxides with *cis* and *trans* orientation of the nitrogen-containing and oxirane rings. Nitration with a mixture of ammonium nitrate and trifluoroacetic anhydride produced 5-nitro derivatives. The structure of 1-{(1a*R**,1b*R**,6b*S**,7a*S**)-5-methyl-1a,1b,2,6b,7,7a-hexahydrooxireno[4,5]cyclopenta[1,2-*b*]indol-2-yl}ethanone was determined by X-ray analysis.

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Some cyclopenta[*b*]indoloquinones were reported [2, 3] to exhibit cancer-specific antitumor activity, in particular against melanoma. The scheme of their synthesis included nitration of the aromatic ring and subsequent reduction of the nitro group to amino. For example, 3-acetoxy-1-acetyl-7-methylcyclopenta[*b*]indole was thus converted into aziridinyl-substituted indoloquinones.

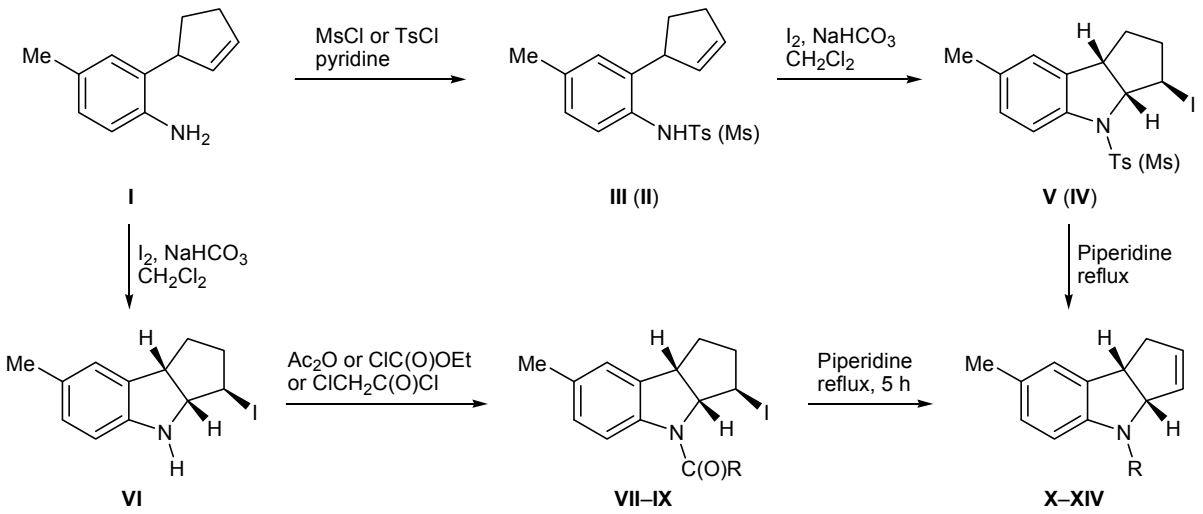
With a view to obtain other oxygen-containing cyclopenta[*b*]indole derivatives we made an attempt to synthesize cyclopenta[*b*]indoles from 2-(cyclopent-2-en-1-yl)-4-methylaniline (**I**). The tricyclic skeleton was built up as a result of formation of C–N bond via intramolecular amination by the action of iodine. For this purpose, compound **I** [4] was treated with methanesulfonyl and *p*-toluenesulfonyl chlorides, and sulfonanilides **II** and **III** thus obtained reacted with iodine to produce 3-iodo-1,2,3,3a,4,8b-hexahydrocyclopenta-[*b*]indoles **IV** and **V**. Their analogs **VII**–**IX** having an acetyl, ethoxycarbonyl, or chloroacetyl group on the nitrogen atom were synthesized by reaction of cyclization product **VI** with acetic anhydride, ethyl chloroformate, or chloroacetyl chloride, respectively. Heating of compounds **IV**, **V**, and **VII**–**IX** in boiling piperidine afforded dehydrohalogenation products **X**–**XIV** in good yields (Scheme 1).

While studying spectral properties of the synthesized compounds we found that signals from some protons in the ^{1}H NMR spectrum of **XII** are doubled, their intensity ratio being 100:28 (in $CDCl_3$; Fig. 1a). Replacement of the solvent by acetone-d_6 changed the intensity ratio to 100:13 (Fig. 1b). Taking into account the lack of essential structural reasons, we presumed that the observed signal doubling results from different orientations of the *N*-acyl substituent [5].

The oxidation of **XI** and **XII** with potassium permanganate gave diols **XV** and **XVI**, respectively. *N*-Acetyl derivative **XV** was poorly soluble in organic solvents used to extract it from the reaction mixture. Therefore, the yield of diol **XV** was as poor as 10–42% against 63% for *N*-tosyl analog **XVI**. Acetylation of diols **XV** and **XVI** with acetic anhydride in pyridine afforded diacetates **XVII** and **XVIII**. The latter was also synthesized by reaction of diol **XVI** with isopro-

* For communication VIII, see [1].

Scheme 1.



I **III** (**II**) **V** (**IV**)

VI **VII–IX** **X–XIV**

VII, R = Me; **VIII**, R = EtO; **IX**, R = $ClCH_2$; **X**, R = $MeSO_2$; **XI**, R = 4-$MeC_6H_4SO_2$; **XII**, R = MeC(O); **XIII**, R = EtOC(O); **XIV**, R = (piperidin-1-yl)acetyl.

penyl acetate in acetonitrile in the presence of TsOH; in this case the yield of **XVIII** was comparable with that in the reaction with acetic anhydride. By nitration of triacetyl derivative **XVII** with a mixture of ammonium nitrate and trifluoroacetic anhydride in methylene chloride at –20°C we obtained 5-nitrocyclopenta[*b*]indole **XIX**. *N*-Tosyl derivative **XVIII** failed to undergo nitration under similar conditions. Hydrogenation of **XIX** over Raney nickel produced a mixture of approximately equal amounts of 5-amino and 5-hydroxyamino

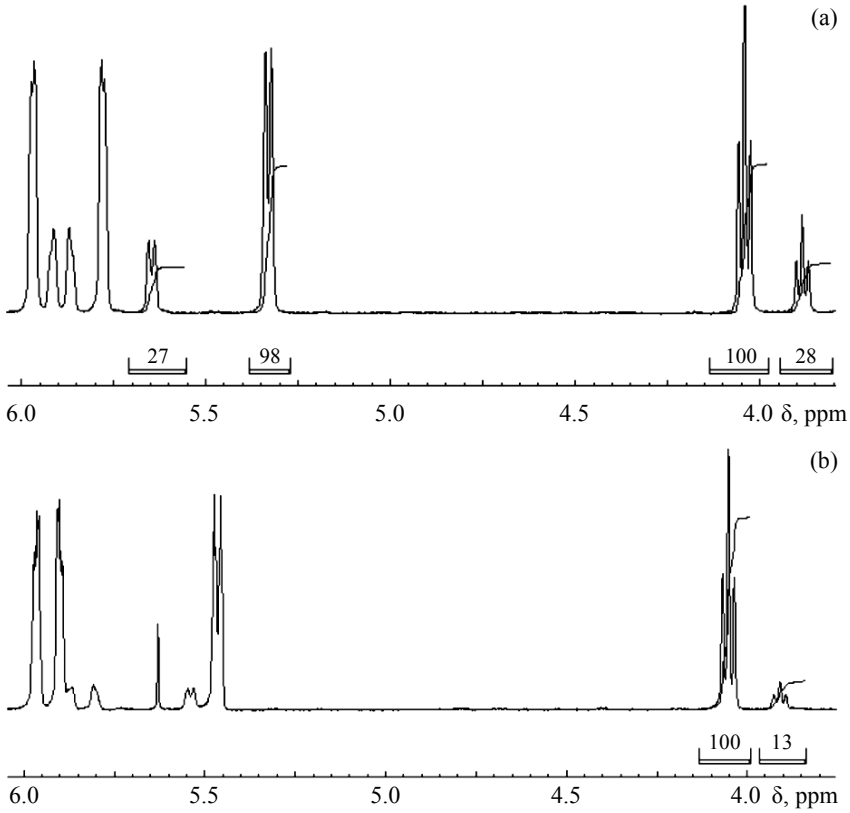
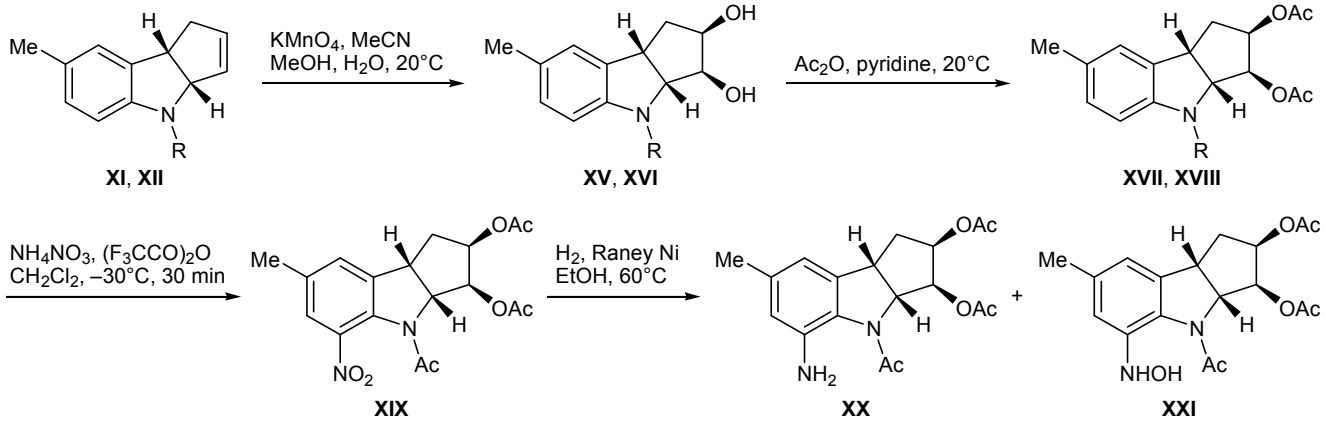


Fig. 1. Fragments of the ^1H NMR spectra of compound **XII** in (a) $CDCl_3$ and (b) acetone-d_6 in the resonance region of the 8b-H, 3a-H, 2-H, and 3-H protons.

Scheme 2.



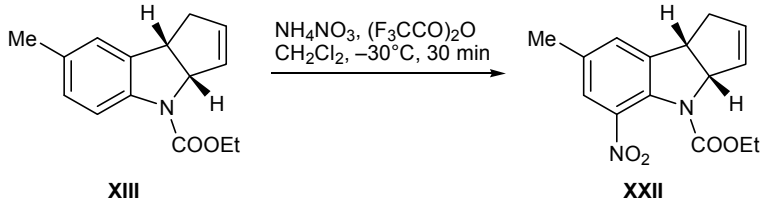
XII, **XV**, **XVII**, R = Ac; **XI**, **XVI**, **XVIII**, R = Ts.

derivatives **XX** and **XXI**. Compounds **XX** and **XXI** are almost insoluble in low-boiling organic solvents, and we did not succeed in isolating them as pure substances (Scheme 2).

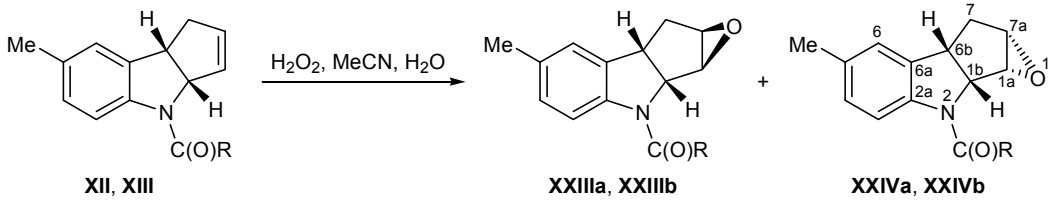
A mixture of ammonium nitrate with trifluoroacetic anhydride used as nitrating agent turned out to be inactive toward the double bond in the cyclopentene ring. The nitration of *N*-ethoxycarbonyl derivative under analogous conditions gave 90% of 5-nitrocyclopenta[*b*]indole **XXII** (Scheme 3). The use of sodium nitrate in sulfuric acid resulted in tarring. Oxidation of compounds **XII** and **XIII** with hydrogen peroxide in the presence of formic acid led to the formation of *trans*- and *cis*-epoxides **XXIIIa**/**XXIVa** and **XXIIIb**/**XXIVb** at ratios of about 1:1, which were similar to the corresponding isomer ratios obtained previously [1] from *N*-mesyl and *N*-tosyl derivatives (Scheme 4).

The structure of epoxide **XXIVb** was unambiguously determined by X-ray analysis. We failed to obtain single crystals of its analogs **XXIIIa**, **XXIIIb**, and **XXIVa**, and their structure was confirmed by elemental analyses and spectral data. According to the X-ray diffraction data (Fig. 2), both five-membered rings in molecule **XXIVb** occur in a flattened *envelope* conformation with the C^{1b} (in the pyrrole ring) and C^{6b} (in the cyclopentane ring) atoms deviating from the planes formed by the four other atoms (see table). The oxirane ring is oriented *trans* with respect to the hydrogen atoms on C^{1b} and C^{6b}. The acetyl group on N^2 lies in the dihydropyrrole ring plane, but the intramolecular contact C^3–$H^3\cdots O^2$ cannot be unambiguously interpreted as hydrogen bond only on the basis of geometric parameters (the $H^3\cdots O^2$ distance is fairly long, and the $C^3H^3O^2$ angle is strongly different from 180°).

Scheme 3.



Scheme 4.



R = EtO (**a**), Me (**b**).

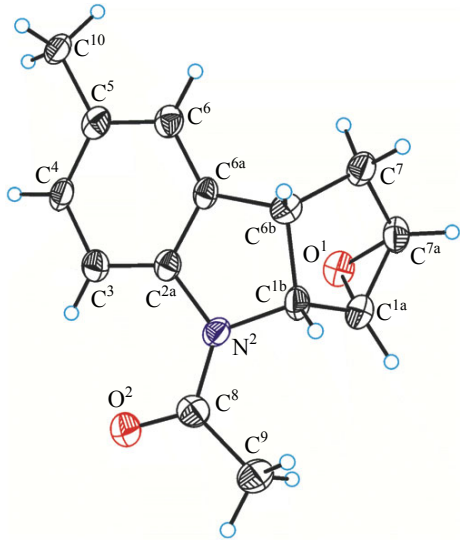


Fig. 2. Structure of the molecule of 1-{(1a*R**,1b*R**,6b*S**,7a*S**)-5-methyl-1a,1b,2,6b,7,7a-hexahydrooxireno[4,5]cyclopenta-[1,2-*b*]indol-2-yl}ethan-1-one (**XXIVb**) according to the X-ray diffraction data; non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

Geometric parameters of molecule **XXIVb** were calculated in terms of the density functional theory (M052X/6-31G**) using GAUSSIAN software package [6], followed by analysis in terms of the Atoms in Molecule (AIM) topological theory [7, 8]. This approximation was successfully used previously to analyze the structure of various heterocyclic and π-conjugated molecules [9, 10]. The results of calculations for structure **XXIVb** were very consistent with the experimental data (see table). The AIM analysis revealed a set of critical points (3, –1) corresponding to interatomic bonding interactions. Apart from expected chemical bonds (Fig. 2), a critical point (3, –1) was also found between H^3 and O^2; it was identified as corresponding to closed shell interaction. From the correlation between the potential energy density in critical point and contact energy [12, 13] we estimated the energy of interaction between the H^3 and O^2 atoms at 4.1 kcal/mol. These data allowed us to interpret the C^3–$H^3\cdots O^2$ contact as a weak intramolecular H-bond.

In the ^{1}H NMR spectra of **XXIIIa**/**XXIVa** and **XXIIIb**/**XXIVb**, the largest difference was observed between the position of signals from methylene protons on C^7 (*AB* spin system). *anti* Isomer **XXIIIa** displayed a difference Δδ of 0.80 ppm between the chemical shifts of 7-H_A and 7-H_B which resonated as doublets of doublets at δ 1.84 ($J_{7A,6b}$ = 4.0, ^2J = 14.4 Hz) and 2.64 ppm ($J_{7B,6b}$ = 9.0, ^2J = 14.4 Hz), respectively, which might be expected for interactions between the corresponding protons and *syn*- or *anti*-oriented epoxide ring. Presumably, the coupling constants of protons in the oxirane ring (7a-H and 1a-H) with 7-H_A, 7-H_B, and 1b-H are too small. Therefore, their signals in the ^{1}H NMR spectra of both stereoisomers appear as one-proton singlets at δ 3.55 and 3.92 ppm (*anti*- **XXIIIa**) and δ 3.63 and 3.88 ppm (*syn*-**XXIVa**). The 1b-H proton shows an appreciable

Principal experimental and calculated (M052X/6-31G**) geometric parameters of the molecule of 1-{(1a*R**,1b*R**,6b*S**,7a*S**)-5-methyl-1a,1b,2,6b,7,7a-hexahydrooxireno[4,5]cyclopenta[1,2-*b*]indol-2-yl}ethan-1-one (**XXIVb**)

Parameter	X-Ray diffraction	M052X/6-31G**
Deviation of C^{1b} from the $N^2C^{2a}C^{6a}C^{6b}$ plane, Å	0.188(7)	0.243
Deviation of C^{6b} from the $C^7C^{7a}C^{1a}C^{1b}$ plane, Å	0.263(8)	0.300
Dihedral angle between the $C^{1b}N^2C^{2a}C^{6a}C^{6b}$ and $C^{6b}C^7C^{7a}C^{1a}C^{1b}$ rings, deg	60.1(2)	63.4
Dihedral angles, deg		
$C^3C^{2a}N^2C^8$	–9.6(7)	–9.1
$C^{2a}N^2C^8O^2$	0.7(7)	2.5
Fragment[a] C^3–$H^3\cdots O^2$		
C^3–H^3, Å	1.08	1.08
$C^3\cdots O^2$, Å	2.857(6)	2.873
$H^3\cdots O^2$, Å	2.25	2.27
$\angle C^3H^3O^2$, deg	113.3	113.5

[a] Experimental geometric parameters were calculated for the C^3–H^3 bond normalized by a standard length of 1.08 Å [11] (neutron diffraction data), which coincided with the results of quantum-chemical calculations.

coupling constant ($J > 9$ Hz) only with 6b-H and gives a doublet in the spectra of both *syn* and *anti* isomers.

Like compound **XII** (see above), some signals in the ^{1}H NMR spectrum of *syn*-**XXIVa** were doubled. In $CDCl_3$ the intensity ratio for the 1b-H, 6b-H, OEt, 3-H, and 4-H protons was 1:2. The difference in the chemical shifts of the aromatic 6-H proton (doubled signal) was 0.4 ppm. The differences for the other protons were smaller, and their signals were poorly resolved in $CDCl_3$. Replacement of the solvent by acetone-d_6 changed the signal intensity ratio in the ^{1}H NMR spectrum of *syn*-**XXIVa** to the opposite (~20:1). In this solvent, signals from the geminal 7-H$_A$ and 7-H$_B$ protons were well resolved. The 7-H$_A$ proton resonated as a doublet of doublets ($J_{7A,7a}$ = 2.0, ^2J = 14.6 Hz) with no coupling from 6b-H, whereas the 7-H$_B$ signal was a double doublet of doublets at δ 2.41 ppm characterized by a fairly large coupling constant with 6b-H ($J_{7B,7a}$ = 1.8, $J_{7B,6b}$ = 9.6, ^2J = 14.6 Hz). Well resolved signals from 6b-H (d.d, $J_{6b,7B}$ = 9.6, $J_{6b,1a}$ = 10.1 Hz) and 1a-H (s, δ 3.82 ppm) were also observed in the spectrum recorded from a solution in acetone-d_6. The 7a-H proton gave rise to a doublet of doublets ($J_{7a,7A}$ = 1.8, $J_{7a,7B}$ = 2.0 Hz), while its coupling with 1a-H was likely to be too small to be detected. The 1b-H proton (d.d) displayed coupling only with 6b-H ($J_{1b,6b}$ = 10.1 Hz).

Analysis of the proton magnetic resonance spectra revealed the existence in solution of two forms of compound **XXIVb**, which were not identified. In the ^{1}H NMR spectrum of **XXIVb** in $CDCl_3$ the intensity ratio of the double signals was 1:1, and it changed to ~1:3 in going to acetone-d_6. The solvent nature did not affect resolution of signals from protons in the epoxide ring; in both cases, small coupling constants could not be estimated because of insufficiently high resolution of the NMR spectrometer, and the 1a-H and 7a-H signals appeared as singlets. The 6b-H signal of **XXIVb** ($CDCl_3$), as in the spectrum of **XXIVa**, was doubled, and it appeared as a doublet of triplets at δ 3.83 ppm and a triplet at δ 3.89 ppm. In the spectrum of **XXIVb** in acetone-d_6, the 6b-H signal was not doubled (t, δ 4.03 ppm, $J_{6b,7A}$ = 9.5, $J_{6b,1b}$ = 9.5 Hz), whereas the 1b-H signal in $CDCl_3$ was doubled with an appreciable difference in the chemical shifts (δ 4.75 ppm, d.d, $J_{1b,1a}$ = 1.75, $J_{1b,6b}$ = 9.5 Hz; δ 5.08 ppm, d.d, $J_{1b,1a}$ = 1.7, $J_{1b,6b}$ = 9.5 Hz; Δδ = 0.33 ppm). The corresponding difference in acetone-d_6 is much smaller (Δδ = 0.06 ppm), and the less intense signal is located in a weaker field (δ 5.04 ppm) relative to the more intense one (δ 4.98 ppm).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer at 300.13 and 75.47 MHz, respectively. The elemental compositions were determined on an M-185B CHN analyzer. Silica gel LS (40–100 μm, Lancaster) was used for column chromatography. Qualitative TLC analysis was performed on Sorbfil plates (*Sorbpolimer*, Krasnodar); spots were detected by treatment with iodine vapor.

Colorless whisker single crystals of **XXIVb** were obtained by slow crystallization from 95% ethanol. The X-ray diffraction data were acquired at 100 K from a 0.12×0.01×0.01-mm single crystal on a Bruker SMART APEX II diffractometer (λMoK_α radiation, θ_{max} = 52.0°). Rhombic crystals, $C_{14}H_{15}NO_2$ (*M* 229.27), with the following unit cell parameters (100 K): *a* = 5.068(4), *b* = 14.553(10), *c* = 14.898(10) Å; *V* = 1098.8(13) Å^3; space group $P2_12_12_1$; *Z* = 4, d_{calc} = 1.386 g/cm^3. Total of 10389 reflection intensities were measured and processed using SAINT and SADABS programs included into APEX2 software package [14]. The structure was solved by the direct method and was refined against F^2_{hkl} by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were placed into positions calculated on the basis of geometry considerations and were refined according to the riding model [U_{iso}(H) = nU_{eq}(C), where *n* = 1.5 for methyl carbon atoms and *n* = 1.2 for other carbon atoms]. The structure was refined using 1289 independent reflections. The final divergence factors were wR_2 = 0.1420 (all independent reflections) and R_1 = 0.0606 [860 reflections with $I > 2\sigma(I)$]. All calculations were performed on an IBM PC with the aid of SHELXTL software package [15]. The coordinates of atoms and their temperature factors were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 820748) and are available at *http://www.ccdc.cam.ac.uk/products/csd/request/*.

***N*-[2-(Cyclopent-2-en-1-yl)-4-methylphenyl]-methanesulfonamide (II).** Methanesulfonyl chloride, 1.26 g (11 mmol), was added to a solution of 1.73 g (10 mmol) of compound **I** in 20 ml of benzene and 4 ml of triethylamine, and the mixture was left to stand for 48 h at 20°C. The mixture was treated with 10 ml of water and stirred for 30 min to decompose excess methanesulfonyl chloride, 10 ml of benzene was added, the aqueous phase was separated, and the organic phase was washed with water (10 ml) and dried

over $MgSO_4$. The solvent was distilled off, and the residue was crystallized from ethanol. Yield 2.03 g (81%), mp 81–84°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.60–2.60 m (4H, CH_2), 2.33 s (3H, CH_3), 3.00 s (3H, CH_3), 4.02–4.12 m (1H, 1-H), 5.70–5.80 m (1H, 2-H), 6.10 quint (1H, 3′-H, J = 2.3 Hz), 6.50 s (1H, NH), 7.01 s (1H, 3-H), 7.04 d (1H, 5-H, J = 7.9 Hz), 7.32 d (1H, 6-H, J = 7.9 Hz). Found, %: C 61.95; H 6.72; N 5.35; S 12.56. $C_{13}H_{17}NO_2S$. Calculated, %: C 62.12; H 6.82; N 5.57; S 12.76.

***N*-[2-(Cyclopent-2-en-1-yl)-4-methylphenyl]-4-methylbenzenesulfonamide (III)** was synthesized in a similar way from 1.73 g (10 mmol) of **I** and 2.06 g (10.5 mmol) of *p*-toluenesulfonyl chloride. Yield 2.68 g (82%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.33–2.50 m (4H, CH_2), 2.20 s (3H, CH_3), 2.25 s (3H, CH_3), 3.78 m (1H, 1-H, J = 2.3 Hz), 5.44 d.q (1H, 3′-H, J = 2.0, 5.5 Hz), 5.95 d.quint (1H, 2-H, J = 2.3, 5.5 Hz), 6.50 s (1H, NH), 6.86 d (1H, 3-H, J = 1.8 Hz), 6.93 d.d (1H, 6-H, J = 1.8, 8.1 Hz), 7.17–7.25 m (3H, 5-H, 3″-H, 5″-H), 7.61 d (2H, 2″-H, 6″-H, J = 8.3 Hz). Found, %: C 69.59; H 6.25; N 4.09; S 9.59. $C_{19}H_{21}NO_2S$. Calculated, %: C 69.69; H 6.46; N 4.28; S 9.79.

(3*R,3a*R**,8b*S**)-3-Iodo-4-methylsulfonyl-7-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (IV).** Compound **II**, 0.478 g (2 mmol), was dissolved in 10 ml of methylene chloride, 0.508 g (2 mmol) of iodine and 2 g of $NaHCO_3$ were added, and the mixture was stirred for 48 h at room temperature, the progress of the reaction being monitored by TLC using benzene as eluent. The mixture was treated with 20 ml of methylene chloride and 10 ml of 5% aqueous $Na_2S_2O_3$ and stirred, the organic phase was separated, washed with 10 ml of 5% aqueous $Na_2S_2O_3$ and 10 ml of water, and dried over $MgSO_4$, the solvent was distilled off, and the residue was passed through a short column charged with silica gel for clarification using benzene as eluent. Yield 0.62 g (82%), mp 173–178°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.20 s (3H, CH_3), 2.87 s (3H, CH_3), 3.92 t (1H, 8b-H, J = 9.0 Hz), 4.25 m (1H, 3-H), 4.73 d (1H, 3a-H, J = 9.0 Hz), 6.47 d (1H, H_{arom}, J = 7.9 Hz), 6.82 d (1H, H_{arom}, J = 7.9 Hz), 6.90 s (1H, 8-H). Found, %: C 41.29; H 4.09; I 33.44; N 3.51; S 8.30. $C_{13}H_{16}INO_2S$. Calculated, %: C 41.39; H 4.28; I 33.64; N 3.71; S 8.50.

Compounds **V** and **VI** were synthesized in a similar way.

(3*R,3a*R**,8b*S**)-3-Iodo-4-methylphenylsulfonyl-7-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (V)** was synthesized from 4.3 g (13.13 mmol) of **II** and 3.3 g (13.13 mmol) of I_2 in the presence of 12 g of $NaHCO_3$. Yield 4.93 g (83%). Colorless crystals, mp 154–155°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.60–2.65 m (4H, CH_2), 2.25 s (3H, CH_3), 2.35 s (3H, CH_3), 3.65 t (1H, 8b-H, J = 8.5 Hz), 4.75 d (1H, 3a-H, J = 8.5 Hz), 4.90 d (1H, 3-H, J = 4.0 Hz), 6.85 s (1H, 8-H), 7.00 d (1H, H_{arom}, J = 8.0 Hz), 7.22 d (2H, 2′-H, 4′-H, J = 8.1 Hz), 7.50 d (1H, H_{arom}, J = 8.0 Hz), 7.65 d (2H, 3′-H, 5′-H, J = 8.1 Hz). Found, %: C 50.14; H 4.25; I 27.78; N 2.90; S 6.87. $C_{19}H_{20}INO_2S$. Calculated, %: C 50.34; H 4.45; I 27.99; N 3.09; S 7.07.

(3*R,3a*R**,8b*S**)-3-Iodo-7-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (VI)** was synthesized from 0.478 g (2 mmol) of **I** and 0.504 g (2 mmol) of I_2 in the presence of 2 g of $NaHCO_3$. The product was isolated by column chromatography on silica gel using benzene as eluent. Yield 0.352 g (59%), dark viscous material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.75–2.60 m (4H, CH_2), 2.20 s (3H, CH_3), 3.92 t (1H, 8b-H, J = 9.0 Hz), 4.25 m (1H, 3-H), 4.73 d (1H, 3a-H, J = 9.0 Hz), 6.47 d and 6.82 d (1H each, 6-H, 7-H, J = 7.9 Hz), 6.90 s (1H, 8-H). Found, %: C 47.98; H 4.52; I 42.22; N 4.48. $C_{12}H_{14}IN$. Calculated, %: C 48.18; H 4.72; I 42.42; N 4.68.

1-[(3*R,3a*R**,8b*S**)-3-Iodo-7-methyl-2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl]ethanone (VII).** *a*. Acetic anhydride, 2.08 g, was added to a solution of 0.478 g (2 mmol) of compound **VI** in 10 ml of methylene chloride, and the mixture was left to stand for 24 h at 20°C. The mixture was treated with 10 ml of water and stirred for 30 min to decompose excess acetic anhydride, the organic phase was separated and dried over $MgSO_4$, the solvent was distilled off, and the residue was crystallized from benzene. Yield 0.506 g (74%), mp 116°C (from benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.00–2.70 m (4H, CH_2), 2.43 s (3H, CH_3), 2.47 s (3H, CH_3), 4.00 t (1H, 8b-H, J = 8.2 Hz), 4.43 d (1H, 3-H, J = 5.1 Hz), 4.08 d (1H, 3a-H, J = 8.2 Hz), 6.95 m (2H, H_{arom}), 8.00 d (1H, H_{arom}, J = 7.9 Hz). Found, %: C 49.08; H 4.52; I 37.00; N 3.91. $C_{14}H_{16}INO$. Calculated, %: C 49.28; H 4.73; I 37.19; N 4.11.

b. *N*-[2-(1-Cyclopenten-3-yl)-4-methylphenyl]acetamide, 2.15 g (10 mmol), was dissolved in 50 ml of methylene chloride, 2.54 g (10 mmol) of I_2 and 10 g of $NaHCO_3$ were added, and the mixture was stirred for 48 h at room temperature, the progress of the reaction being monitored by TLC using benzene as eluent.

When the reaction was complete, the mixture was treated with 20 ml of water and stirred, 20 ml of 5% aqueous $Na_2S_2O_3$ was added, the mixture was stirred, the organic phase was separated, washed with 10 ml of 5% aqueous $Na_2S_2O_3$ and 10 ml of water, and dried over magnesium sulfate, the solvent was distilled off, and the residue was crystallized from ethanol. Yield 2 g (59%).

2-Chloro-1-[(3*R,3a*R**,8b*S**)-3-iodo-7-methyl-2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl]-ethanone (IX).** Compound **VI**, 5.1 g (17 mmol), was dissolved in methylene chloride, 5 g of K_2CO_3 was added, and 2.3 g (20.35 mmol) of chloroacetyl chloride was added dropwise under continuous stirring. The mixture was stirred until the reaction was complete (TLC), 20 ml of water was added, the mixture was stirred, the organic phase was separated and dried over $MgSO_4$, the solvent was removed, and the residue was crystallized from benzene. Yield 5.3 g (83%), mp 156–157°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.60–1.75 m, 2.00–2.10 m, and 2.55–2.70 m (4H, 1-H, 2-H); 4.05 m (1H, 8b-H), 4.20 d and 4.30 d (1H each, CH_2Cl, ^2J = 12.6 Hz), 4.45 d (1H, 3-H, J = 5.5 Hz), 5.20 d (1H, 3a-H, J = 8.0 Hz), 6.95 s (1H, 8-H), 7.05 d (1H, 5-H, J = 7.4 Hz), 8.00 d (1H, 6-H, J = 7.4 Hz). Found, %: C 44.68; H 3.98; Cl 9.37; I 33.68; N 3.69. $C_{14}H_{15}ClINO$. Calculated, %: C 44.77; H 4.02; Cl 9.44; I 33.78; N 3.73.

(3a*S,8b*S**)-7-Methyl-4-methylsulfonyl-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (X).** A mixture of 0.4 g (0.8 mmol) of compound **IV** and 2 ml of piperidine was heated for 10 h at 110°C. The solvent was distilled off under reduced pressure, the residue was dissolved in 50 ml of methylene chloride, the solution was washed with water and dried over $MgSO_4$, the solvent was removed, and the residue was crystallized from ethanol. Yield 0.165 g (83%), mp 123–125°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.32 s (3H, CH_3), 2.60 d.quint (1H, 1-H_A, J = 2.0, ^2J = 17.0 Hz), 2.85 s (3H, CH_3), 2.98 d.d.quint (1H, 1-H_B, J = 2.0, 8.7, ^2J = 17.0 Hz), 4.08 t (1H, 8b-H, J = 2.0, 8.7 Hz), 5.35 d.quint (1H, 3a-H, J = 2.0, 8.7 Hz), 5.87–5.97 m (2H, 2-H, 3-H), 7.01 d (1H, H_{arom}, J = 8.0 Hz), 7.04 s (1H, 8-H), 7.29 d (1H, H_{arom}, J = 8.0 Hz). Found, %: C 62.43; H 5.90; N 5.42; S 12.66. $C_{13}H_{15}NO_2S$. Calculated, %: C 62.63; H 6.06; N 5.62; S 12.86.

Compounds **XI** and **XII** were synthesized in a similar way.

(3a*S,8b*S**)-7-Methyl-4-(4-methylphenylsulfonyl)-1,3a,4,8b-tetrahydrocyclopenta[*b*]indole (XI)** was obtained from 3.5 g (7.8 mmol) of **V**. Yield 2.1 g (84%), mp 161–165°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 s (3H, CH_3), 2.38 s (3H, CH_3), 2.60 d.quint (1H, 1-H_A, J = 2.0, ^2J = 16.8 Hz), 2.95 d.d.quint (1H, 1-H_B, J = 2.0, 8.4, ^2J = 16.8 Hz), 3.55 t (1H, 8b-H, J = 8.0 Hz), 5.20–5.27 d.quint (1H, 3a-H, J = 2.0, 8.4 Hz), 5.83–5.91 m (2H, 2-H, 3-H), 6.87 s (1H, 8-H), 7.02 d.d (1H, 5-H, J = 0.8, 8.1 Hz), 7.18 d (2H, 3-H, 5′-H, J = 8.0 Hz), 7.51 d (1H, 6-H, J = 8.1 Hz), 7.59 d.d (2H, 2′-H, 6′-H, J = 8.0 Hz). Found, %: C 69.92; H 5.68; N 4.10; S 9.65. $C_{19}H_{19}NO_2S$. Calculated, %: C 70.13; H 5.88; N 4.30; S 9.85.

1-[(3a*S,8b*S**)-7-Methyl-3a,8b-dihydrocyclopenta[*b*]indol-4(1*H*)-yl]ethanone (XII)** was obtained from 0.4 g (1.1 mmol) of **VII**. Yield 0.208 g (89%), mp 133–135°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.31 s (3H, CH_3); 2.34 s and 2.42 s (3:1, CH_3); 2.65 d (1H, 1-H_A, J = 16.9 Hz), 2.95 d.d.q (1H, 1-H_B, J = 2.0, 8.3, 16.9 Hz), 3.82 t (minor signal, 1H, 8b-H, J = 8.3 Hz), 3.98 t (major signal, 1H, 8b-H, J = 9.0 Hz), 5.34 d.quint (major signal, 1H, 3a-H, J = 1.6, 8.3 Hz), 5.60 d (minor, 1H, 3a-H, J = 9.0 Hz), 5.68–5.75 m and 5.90–5.93 m (major, 1H each, 2-H, 3-H), 5.79–5.82 m and 5.83–5.88 m (minor, 1H each, 2-H, 3-H), 6.90–7.00 m (2H, H_{arom}), 8.00 d (1H, 6-H, J = 8.0 Hz). ^{13C} NMR spectrum (DMSO-d_6), δ_C, ppm: 20.6/20.8 and 23.6/24.5 (CH_3), 39.5/39.9 (CH_2), 40.4/42.3 (C^{8b}), 70.6/71.2 (C^{3a}), 114.0/117.1 (C^3); 124.6, 126.1, 128.0, 128.2, 128.3, 129.4, 132.5, 134.3 (C^2, C^5, C^6, C^8); 132.9, 133.4, 135.5, 137.8, 138.0, 138.9 (C^{4a}, C^7, C^{8a}); 176.67/176.68 (C=O). Found, %: C 78.64; H 6.90; N 6.37. $C_{14}H_{15}NO$. Calculated, %: C 78.84; H 7.09; N 6.57.

Ethyl (3a*S,8b*S**)-7-methyl-3a,8b-dihydrocyclopenta[*b*]indole-4(1*H*)-carboxylate (XIII).** Crude product **VI** (27.1 g), obtained by iodocyclization of 17.3 g of cyclopentenylaniline **I** and appropriate treatment of the reaction mixture, was dissolved 150 ml of methylene chloride, 46.6 g of potassium carbonate was added, and a solution of 12.7 ml of ethyl chloroformate in 50 ml of methylene chloride was added dropwise to the resulting suspension under stirring at room temperature. When the reaction was complete, the mixture was treated with 100 ml of water and stirred for 20 min, the organic phase was separated, washed with water, and dried over $MgSO_4$, the solvent was removed, the residue (32 g of crude product **VIII**) was dissolved in 50 ml of piperidine, and the solution was heated for 5 h under reflux. Excess piperidine was removed under reduced pressure, the residue was

dissolved in 150 ml of methylene chloride, and the organic phase was washed with water and with a solution of $NaHCO_3$ and dried over $MgSO_4$. Volatile substances were removed, and the residue was distilled in vacuo. Yield 11.5 g (47%), viscous material which gradually crystallized, bp 152°C (2 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 br.s (3H, CH_3), 2.30 s (3H, CH_3), 2.58 d (1H, 1-H_A, J = 17.0 Hz), 2.97 d.d (1H, 1-H_B, J = 8.0, 17.0 Hz), 3.95 t (1H, 8b-H, J = 8.0 Hz), 4.25–4.40 m (2H, CH_2), 5.33–5.45 m (1H, 3a-H), 5.85–6.03 m (2H, 2-H, 3-H), 6.90–7.05 m (2H, H_{arom}), 7.73 d (1H, H_{arom}, J = 7.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.6 and 20.8 (CH_3), 40.1 (C^1), 41,7 (C^{8b}), 60.9 (CH_2), 70.3 (C^{3a}), 114.7 (C^5); 124.8, 128.3, 129.3, 133.1 (C^6, C^8, C^2, C^3); 132.1, 135.1, 138.5 (C^{4a}, C^7, C^{8a}). Found, %: C 73.96; H 6.99; N 5.71. $C_{15}H_{17}NO_2$. Calculated, %: C 74.05; H 7.04; N 5.76.

1-[(3a*S,8b*S**)-7-Methyl-3a,8b-dihydrocyclopenta[*b*]indol-4(1*H*)-yl]-2-(piperidin-1-yl)ethanone (XIV).** Crude product **VI**, 5.5 g [obtained by iodocyclization of 3.46 g (20 mmol) of cyclopentenylaniline **I** and appropriate treatment of the reaction mixture] was dissolved in 50 ml of methylene chloride, 6.5 g of K_2CO_3 was added, and 2.3 g (20 mmol) of chloroacetyl chloride in 10 ml of methylene chloride was added dropwise under stirring at room temperature to the resulting suspension. The mixture was then treated with 15 ml of water and stirred for 20 min, and the organic phase was separated, washed with water, and dried over $MgSO_4$. Removal of the solvent gave 5.8 g of crude compound **XIV** which was dissolved in 20 ml of piperidine, the solution was heated for 5 h under reflux, and excess piperidine was distilled off under reduced pressure. The residue was dissolved in 150 ml of methylene chloride, the solution was washed with water, a saturated solution of $NaHCO_3$ until CO_2 no longer evolved, and water again, and dried over $MgSO_4$, the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel. Yield 3.61 g (61%, calculated on the initial aniline **I**). Compound **XIV** was isolated as a viscous material which gradually transformed into colorless powder, R_f = 0.2 (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.50–1.75 m, 2.55–2.75 m, and 3.15–3.26 m (10H, CH_2); 2.35 s (3H, CH_3), 2.70 d (1H, 1-H_A, J = 17.3 Hz), 3.05 d.d (1H, 1-H_B, J = 5.5, 17.3 Hz), 3.34 d and 3.49 d (2H, 4-CH_2, ^2J = 14.0 Hz), 4.08 t (1H, 8b-H, J = 8.0 Hz), 5.71 d (1H, 3a-H, J = 8.0 Hz), 5.89–5.93 m (1H, 2-H), 5.95–6.02 m (1H, 3-H), 7.06 s (1H, 8-H), 7.11 d (1H, 5-H, J = 8.0 Hz), 8.15 d (1H, 6-H, J = 8.0 Hz). Found, %: C 76.91; H 8.12; N 9.42. $C_{19}H_{24}N_2O$. Calculated, %: C 76.99; H 8.16; N 9.45.

1-[2,3-Dihydroxy-7-methyl-2,3,3a,8b-tetrahydrocyclopenta[*b*]indol-4(1*H*)-yl]ethanone (XV). A solution of 1.18 g (7.5 mmol) of $KMnO_4$ in 12 ml of water was added under stirring to a solution of 0.49 g (2.2 mmol) of **XII** in a mixture of 30 ml of acetonitrile and 17 ml of methanol. The mixture was stirred for 6 h at room temperature, the precipitate of MnO_2 was filtered off and washed with methylene chloride on a filter, organic solvents were evaporated from the filtrate, the residue was diluted with 25 ml of water, saturated with sodium chloride, and extracted with methylene chloride (3×50 ml). The extracts were dried over $MgSO_4$, the solvent was removed, and the residue was crystallized from benzene. Yield 0.25 g (46%), mp 246–248°C (from MeOH). ^{1}H NMR spectrum, δ, ppm: in ($CDCl_3$: 1.61 d.d.d (1H, 1-H_A, J = 3.6, 8.6, 14.0 Hz), 2.40 m (1H, 1-H_B), 2.25 s (3H, CH_3), 2.43 s (3H, CH_3), 3.87 d.d (1H, 3-H, J = 3.5, 6.2 Hz), 3.98 q (1H, 8b-H, J = 10.6 Hz), 4.12 m (1H, 2-H), 4.71 d.d (1H, 3a-H, J = 6.3, 10.6 Hz), 6.95 s (3H, H_{arom}); in DMSO-d_6: 1.81 d.t (1H, 1-H_A, J = 3.6, 12.6 Hz), 2.18 d.t (1H, 1-H_B, J = 9.0, 12.6 Hz), 2.25 s (3H, CH_3), 2.28 s (3H, CH_3), 3.60 m (1H, 2-H), 3.73 q (1H, 3-H, J = 3.8 Hz), 3.81 t (1H, 8b-H, J = 9.0 Hz), 4.51 d.d (1H, 3a-H, J = 3.6, 9.0 Hz), 4.78 d (1H, OH, J = 4.9 Hz), 5.07 d (1H, OH, J = 4.7 Hz), 6.90 d (1H, H_{arom}, J = 8.0 Hz), 7.02 s (1H, 8-H), 7.39 d (1H, H_{arom}, J = 8.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 20.05 and 23.6 (CH_3), 36.6 (C^1), 40.5 (C^{8b}); 69.3, 71.7, 78.6 (C^2, C^3, C^{3a}); 115.9, 124.5, 127.5 (C^5, C^6, C^8); 132.6, 135.7, 140.0 (C^{4a}, C^7, C^{8a}); 168.8 (C=O). Found, %: C 67.79; H 6.73; N 5.46. $C_{14}H_{17}NO_3$. Calculated, %: C 68.00; H 6.93; N 5.66.

7-Methyl-4-(4-methylphenylsulfonyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole-2,3-diol (XVI) was synthesized in a similar way from 0.72 g (2.2 mmol) of compound **XI**. Yield 0.49 g (63%), mp 165–166°C (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.65–1.67 m (1H, 1-H_A), 2.25 s (3H, CH_3), 2.37 s (3H, CH_3), 2.35–2.50 m (1H, 1-H_B), 2.70 br.s (1H, OH), 3.60 br.s (1H, OH), 3.80–3.90 m (1H, 8b-H), 4.20–4.35 m (3H, 2-H, 3-H, 3a-H), 6.85 s (1H, 8-H), 7.01 d (1H, H_{arom}, J = 7.9 Hz), 7.20 d (2H, H_{arom}, J = 8.2 Hz), 7.51 d (1H, H_{arom}, J = 7.9 Hz), 7.67 d (2H, H_{arom}, J = 8.2 Hz). Found, %: C 63.29; H 5.69; N 3.70; S 8.72. $C_{19}H_{21}NO_4S$. Calculated, %: C 63.49; H 5.89; N 3.90; S 8.92.

4-Acetyl-7-methyl-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole-2,3-diyl diacetate (XVII). Diol **XV**, 0.53 g (2.14 mmol), was dissolved in 3 ml of pyridine, 2 ml of acetic anhydride and 3 ml of chloroform were added, and the mixture was left to stand for 24 h at 20°C. The mixture was treated with 10 ml of water and shaken to decompose excess acetic anhydride, 60 ml of methylene chloride and 10 ml of water were added, and the mixture was shaken in a separatory funnel. The organic phase was washed with 20 ml of 2% hydrochloric acid, water, and 10 ml of a saturated aqueous solution of $NaHCO_3$, dried over $MgSO_4$, and evaporated. Yield 0.637 g (91%), mp 246–248°C (from MeOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.98 s, 2.08 s, 2.19 s, and 2.25 s (3H each, CH_3), 2.12–2.35 m (2H, CH_2), 4.05 m (1H, 8b-H), 4.80–4.90 m (2H, 2-H, 3a-H), 5.11 t (1H, 3-H, J = 3.7 Hz), 7.00 d (1H, H_{arom}, J = 8.2 Hz), 7.10 s (1H, 8-H), 7.85 d (1H, H_{arom}, J = 8.2 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 20.04, 20.05, 20.06, and 23.4 (CH_3); 34.1 (C^1), 40.2 (C^{8b}); 66.7, 71.9, 77.2 (C^2, C^3, C^{3a}); 116.3, 124.7, 128.1 (C^5, C^6, C^8); 133.2, 134.2, 139.7 (C^{4a}, C^7, C^{8a}); 168.6, 169.3, 169.7 (NCO, CO_2). Found, %: C 65.16; H 6.30; N 4.13. $C_{18}H_{21}NO_5$. Calculated, %: C 65.24; H 6.39; N 4.23.

7-Methyl-4-(4-methylphenylsulfonyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole-2,3-diyl diacetate (XVIII) was synthesized in a similar way from 0.225 g (0.63 mmol) of diol **XVI** and 0.6 ml of acetic anhydride using 0.6 ml of pyridine. The product was isolated by column chromatography on silica gel (4 g) using benzene as eluent. Yield 0.233 g (87%), amorphous substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.95 s, 2.05 s, 2.21 s, and 2.32 s (3H, CH_3), 1.90–2.40 m (2H, CH_2), 3.53 d.t (1H, 8b-H, J = 4.5, 9.7 Hz), 4.43 d.d (1H, 3a-H, J = 4.3, 9.7 Hz), 5.09 q (1H, 2-H, J = 4.3 Hz), 5.32 t (1H, 3-H, J = 4.3 Hz), 6.72 s (1H, 8-H), 6.95 d (1H, H_{arom}, J = 8.3 Hz), 7.12 d (2H, H_{arom}, J = 8.3 Hz), 7.43 d (1H, H_{arom}, J = 8.2 Hz), 7.52 d (2H, H_{arom}, J = 8.3 Hz). Found, %: C 62.09; H 5.48; N 2.95; S 7.03. $C_{23}H_{25}NO_6S$. Calculated, %: C 62.29; H 5.68; N 3.16; S 7.23.

4-Acetyl-7-methyl-5-nitro-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole-2,3-diyl diacetate (XIX). Trifluoroacetyl nitrate prepared by stirring 1.5 mmol of ammonium nitrate and 5 mmol of trifluoroacetic anhydride in 1 ml of methylene chloride was added to a solution of 0.332 g (1 mmol) of compound **XVII** in 1 ml of methylene chloride, and the mixture was stirred for 30 min at –30°C. The mixture was treated with 10 ml of water and extracted with methylene chloride (30 ml), the extract was washed with water and dried over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was crystallized from ethanol. Yield 0.341 g (90%), mp 235–237°C (from EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.10 s, 2.15 s, 2.30 s, and 2.39 s (3H each, CH_3), 2.13 d.d (1H, 1-H_A, J = 4.0, ^2J = 14.4 Hz), 2.54 d.d.d (1H, 1-H_B, J = 4.4, 8.4, ^2J = 14.4 Hz), 4.12 d.t (1H, 8b-H, J = 4.4, 9.2 Hz), 4.89 d.d (1H, 3a-H, J = 6.5, 9.2 Hz), 5.17 d.d (1H, 3-H, J = 4.0, 6.5 Hz), 5.28 q (1H, 2-H, J = 4.0 Hz), 7.20 s and 7.51 s (1H each, 6-H, 8-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 20.5, 20.6, 20.7, 22.8 (CH_3); 34.7 (C^1), 40.5 (C^{8b}), 67.6 (C^{3a}), 72.1 (C^3), 78.2 (C^2), 123.2 (C^6), 128.8 (C^8), 130.5 (C^{4a}), 135.8 (C^{8a}), 139.3 (C^7), 140.8 (C^5); 169.1, 169.6, 169.8 (C=O). Found, %: C 57.31; H 5.28; N 7.36. $C_{18}H_{20}N_2O_7$. Calculated, %: C 57.44; H 5.36; N 7.44.

Ethyl 7-methyl-5-nitro-3a,8b-dihydrocyclopenta-[*b*]indole-4(1*H*)-carboxylate (XXII) was obtained in a similar way from 0.245 (1 mmol) of compound **XII**. After removal of the solvent, the residue was purified by column chromatography on silica gel. Yield 0.26 g (90%), viscous material which gradually solidified; R_f 0.5 (C_6H_6–EtOAc, 15 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 t (3H, CH_3, J = 7.2 Hz), 2.36 s (3H, CH_3), 2.56 d (1H, 1-H_A, J = 16.0 Hz), 2.97 d.d (1H, 1-H_B, J = 8.3, 16.0 Hz), 4.03 t (1H, 8b-H, J = 8.3 Hz), 4.23 q (2H, CH_2, J = 7.2 Hz), 5.56 d (1H, 3a-H, J = 8.3 Hz), 5.92 s (2H, 2-H, 3-H), 7.19 s and 7.45 s (1H each, 6-H, 8-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.1, 20.5 (CH_3); 39.3 (C^1), 42.0 (C^{8b}), 62.5 (CH_2), 72.6 (C^{3a}), 123.3 (C^3), 129.4 (C^2); 129.8, 132.8 (C^6, C^8); 132.2, 134.1, 139.7, 140.9 (C^{4a}, C^{8a}, C^7, C^5); 153.2 (C=O). Found, %: C 62.42; H 5.54; N 7.67. $C_{15}H_{16}N_2O_4$. Calculated, %: C 62.49; H 5.59; N 9.72.

General procedure for epoxidatin of compounds XII and XIII. A solution of 3 mmol of compound **XII** or **XIII** in 135 ml of acetonitrile was added to a mixture of 6 ml of formic acid and 5 ml of water, and the mixture was heated for 10–12 h at 50–60°C. After cooling to room temperature, $NaHCO_3$ was added until carbon dioxide no longer evolved, the organic solvent was evaporated under reduced pressure, and the aqueous residue was extracted with methylene chloride. The extract was dried over $MgSO_4$ and evaporated under reduced pressure, and stereoisomeric epoxides **XXIIIa**/**XXIVa** and **XXIIIb**/**XXIVb** were separated by chromatography on silica gel using benzene as eluent.

Ethyl (1a*S*,1b*R***,6b*S***,7a*R***)-5-methyl-1a,1b,2,6b,7,7a-hexahydrooxireno[4,5]cyclopenta-[1,2-*b*]indole-2-carboxylate (XXIIIa).** Yield 0.22 g (29%), colorless amorphous crystals, R_f 0.26 (C_6H_6–EtOAc, 40:7). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 t (3H, CH_3, J = 7.1 Hz), 1.84 d.d (1H, 7-H$_A$, J = 4.0, 14.4 Hz), 2.30 s (3H, CH_3), 2.64 d.d (1H, 7-H$_B$, J = 9.0, 14.4 Hz), 3.55 s (1H, 7a-H), 3.67 d.t (1H, 6b-H, J = 4.0, 9.0 Hz), 3.92 s (1H, 1a-H), 4.35 q (2H, CH_2, J = 7.1 Hz), 4.80 d (1H, 1b-H, J = 9.0 Hz), 6.90 s (1H, 6-H), 7.00 d (1H, H$_{arom}$, J = 8.6 Hz), 7.75 br.s (1H$_{arom}$). Found, %: C 69.37; H 6.54; N 5.32. $C_{15}H_{17}NO_3$. Calculated, %: C 69.48; H 6.61; N 5.40.

Ethyl (1a*R*,1b*R***,6b*S***,7a*S***)-5-methyl-1a,1b,2,6b,7,7a-hexahydrooxireno[4,5]cyclopenta-[1,2-*b*]indole-2-carboxylate (XXIVa).** Yield 0.23 g (30%), amorphous crystals, R_f 0.17 (C_6H_6–EtOAc, 40:7). ^{1}H NMR spectrum, δ, ppm: in $CDCl_3$: 1.38 t and 1.44 t (3H, CH_3, J = 6.8 Hz), 2.33–2.47 m (2H, 7-H), 2.28 s (3H, CH_3), 3.63 s (1H, 7a-H), 3.88 s (1H, 1a-H), 3.91–4.01 m (1H, 6b-H), 4.32 q and 4.39 q (1H each, CH_2, J = 6.8 Hz), 4.79 d and 4.87 d (1H, 1b-H, J = 9.6 Hz), 6.83 s (1H, 6-H), 6.92–7.00 m (1H, H$_{arom}$), 7.33 d and 7.73 d (1H, H$_{arom}$, J = 8.0 Hz); in acetone-d_6: 1.31 t and 1.36 t (3H, CH_3, J = 7.0 Hz), 2.19 s (3H, CH_3), 2.28 d.d (1H, 7-H$_A$, J = 2.0, ^2J = 14,6 Hz), 2.41 d.d.d (1H, 7-H$_B$, J = 1.8, 9.6, ^2J = 14.6 Hz), 3.58 d.d (1H, 7a-H, J = 1.8, 2.0 Hz), 3.82 s (1H, 1a-H), 3.94 d.d (1H, 6b-H, J = 9.6, 10.1 Hz), 4.10–4.35 m (2H, CH_2), 4.30 d (1H, 1b-H, J = 10.1 Hz), 6.86 s (1H, 6-H), 6.89 d (1H, H$_{arom}$, J = 8.0 Hz), 7.64 d (1H, H$_{arom}$, J = 8.0 Hz). Found, %: C 69.36; H 6.53; N 5.30. $C_{15}H_{17}NO_3$. Calculated, %: C 69.48; H 6.61; N 5.40.

1-{(1a*S*,1b*R***,6b*S***,7a*R***)-5-Methyl-1a,1b,2,6b,7,7a-hexahydrooxireno[4,5]cyclopenta-[1,2-*b*]indol-2-yl}ethan-1-one (XXIIIb).** Yield 0.21 g (31%), R_f 0.3 (benzene); the product was not pure. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.32 s and 2.41 s (3H, CH_3), 2.00–2.11 m (1H, 7-H$_A$), 2.63 d.d (1H, 7-H$_B$, J = 9.0, 14.6 Hz), 3.55 s (1H, 7a-H), 3.65 d (1H, 1a-H, J = 1.2 Hz), 4.75 d (1H, 1b-H, J = 9.0 Hz), 6.95 s (1H, 6-H), 7.02 d (1H, 4-H, J = 8.0 Hz), 8.09 d (1H, 3-H, J = 8.0 Hz). Found, %: C 73.07; H 6.54; N 5.89. $C_{14}H_{15}NO_2$. Calculated, %: C 73.34; H 6.59; N 6.11.

1-{(1a*R*,1b*R***,6b*S***,7a*S***)-5-Methyl-1a,1b,2,6b,7,7a-hexahydrooxireno[4,5]cyclopenta-[1,2-*b*]indol-2-yl}ethan-1-one (XXIVb).** Yield 0.19 g (27%), transparent crystals, R_f 0.15 (benzene). ^{1}H NMR spectrum, δ, ppm (some signals are doubled): in $CDCl_3$: 2.29 s and 2.31 s (3H, CH_3), 2.35–2.52 m (5H, 7-H, CH_3), 3.60 s (1H), 7a-H), 3.66 t (1H, 7a-H, J = 1.0 Hz), 3.79 s and 4.00 s (1H, 1a-H), 3.83 d.t (J = 1.5, 9.5 Hz) and 3.89 t (J = 9.5 Hz) (1H, 6b-H), 4.75 d.d (J = 1.5, 9.5 Hz) and 5.09 d.d (J = 1.7, 9.5 Hz) (1H, 1b-H), 6.84 s and 6.90 s (1H, 6-H), 6.95–6.99 m (1H, 4-H), 8.04 d (1H, 3-H, J = 8.0 Hz); in acetone-d_6: 2.25 s (3H, CH_3), 2.35–2.50 m (5H, 7-H, CH_3), 3.59 s and 3.65 s (1H, 7a-H), 3.87 s and 3.90 s (1H, 1a-H), 4.03 t (1H, 6b-H, J = 9.5 Hz), 4.98 d and 5.04 d (1H, 1b-H, J = 9.5 Hz), 6.85–7.05 m (2H, 4-H, 6-H), 7.98 d (1H, 3-H, J = 8.0 Hz). Found, %: C 73.16; H 6.38; N 5.97. $C_{14}H_{15}NO_2$. Calculated, %: C 73.34; H 6.59; N 6.11.

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