# Reactions of 1-hydroxyindoles with p-toluenesulfonyl chloride and p-toluenesulfonic acid

# REACTIONS OF 1-HYDROXYINDOLES WITH *p*-TOLUENESULFONYL CHLORIDE AND *p*-TOLUENESULFONIC ACID[1]

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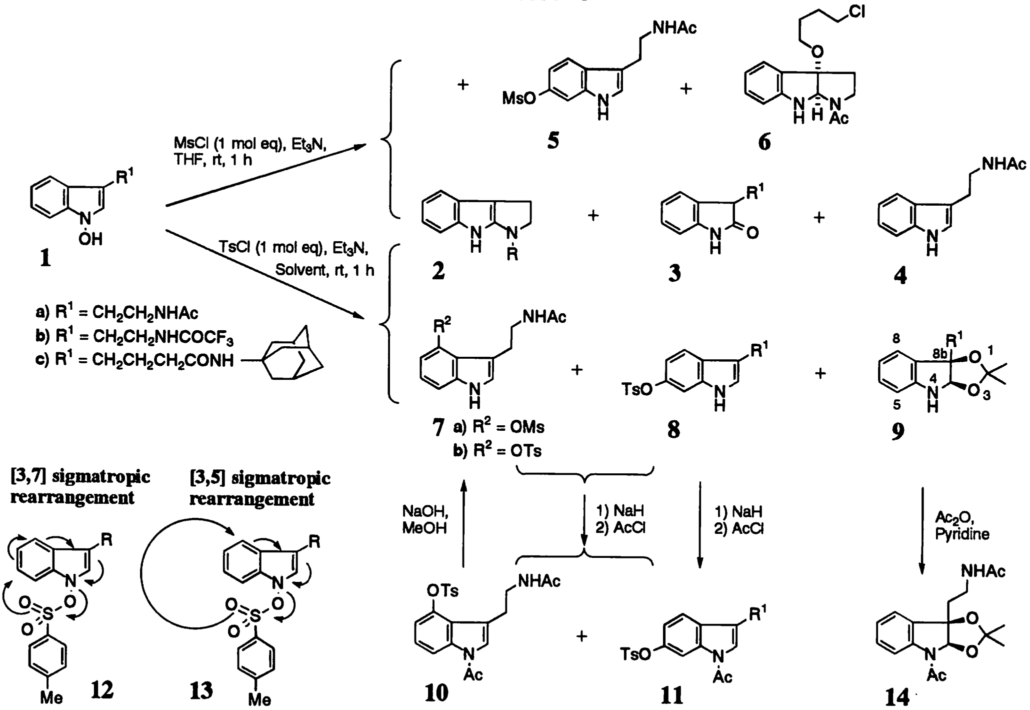
*Abstract* — 1-Hydroxyindoles produced novel types of compounds such as 4-substituted indoles and 4*H*-1,3-dioxolo[4,5-*b*]indoles upon reaction with *p*-toluenesulfonyl chloride in acetone. Contrastively, 5-tosyloxyindole and 2*H*-1,2-oxazino[2,3-*a*]indole were generated upon reaction with *p*-toluenesulfonic acid in acetone.

In our ongoing project to discover reactions characteristic to 1-hydroxyindoles,[2] we have thus far disclosed that they undergo various types of reactions[3,4] depending on their structures, reagents, and reaction conditions. Now, we wish to describe novel findings upon reactions of 1-hydroxyindoles (**1a-c**) with *p*-toluenesulfonyl chloride (TsCl) and *p*-toluenesulfonic acid (TsOH) in either THF or acetone.

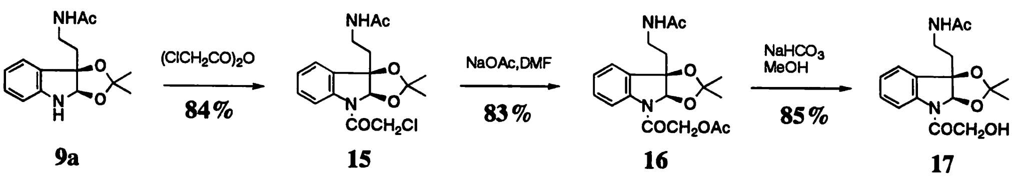
We reported[4] that 1-hydroxytryptamine (**1a**) led to **2a**, **3a**, **4**, **5**, and **6** by the reaction with methanesulfonyl chloride (MsCl) in THF in the presence of triethylamine ($Et_3N$) at room temperature (Scheme 1) and thereby formation of 4-mesyloxyindole (**7a**) was not observed at all. We therefore expected that under similar conditions TsCl would follow the same reaction pathways as those with MsCl to give the corresponding products. In fact, however, the reaction of **1a** with TsCl in THF provided **2a**, **3a**, **4**, **7b**, and **8a** in 42, 6, 3, 0.5, and 5% yields, respectively. Though the yield was low, 4-substituted indole (**7b**) was isolated for the first time among thus far variously examined reactions.[2,3] The complete absence of **6** in the products is another interesting finding.

Since the solvent plays an important role for governing reaction pathways, the reaction of **1a** with TsCl was next examined in acetone instead of THF in the presence of $Et_3N$ at room temperature, resulting in the formation of a novel 4*H*-1,3-dioxolo[4,5-*b*]indole derivative (**9a**) in 3% yield together with **2a**, **3a**, **4**, **7b**, and **8a** in 14, 6, 4, 0.2, and 3% yields, respectively. In the reaction of **1b**, the yield of the corresponding **9b** was raised up to 11% under the same reaction conditions together with **2b** and **8b** in the respective yields of 58 and 6%. In the case of **1c**, **9c** and **3c** were produced in 10 and 49% yields, respectively. Although chromatographical separation of **7b** from **8a** was quite difficult, the fractions containing **7b** and **8a** were readily obtained. So, the mixture of **7b** and **8a** was converted to the readily separable 1-acetyl derivatives (**10** and **11a**) by the reaction with NaH followed by treatment with AcCl. Alkaline hydrolysis of **10** afforded pure **7b** in 77% yield. In the $^1$H-NMR spectrum of **10**, *ortho*- and *meta*-coupled C(7)-proton (dd, $J$=0.7 and 8.3 Hz) appeared in lower magnetic field (δ 8.39) by *ca.* 1 ppm than that of **7b** (δ 7.25) by the anisotropy effect of the introduced 1-acetyl group. The results clearly prove

## Scheme 1



## Scheme 2



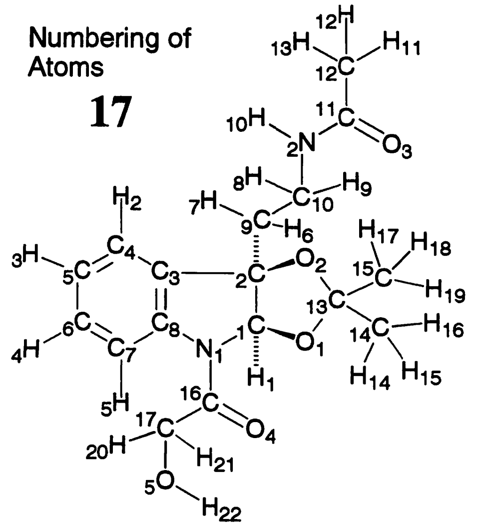
that these compounds are 4-substituted indoles. Structures of **11a,b** and **8a,b** are determined to be 6-substituted indoles based on the similar anisotropy effect observed on the *meta*-coupled C(7)-proton (d, $J$=2.2 Hz; δ 6.97→7.98 for **8a**→**11a**; δ 7.08→8.07 for **8b**→**11b**). Mechanisms for the formations of **7** and **8** might be explained by the [3,7] and [3,5] sigmatropic rearrangements of the initially formed 1-tosyloxytryptamine as shown in the general formulas (**12** and **13**). Structural determinations of **9a-c** were carried out using **9a** as a representative sample. The presence of secondary amine in the molecule was proved by obtaining **14** in 71% yield by treating **9a** with $Ac_2O$-pyridine. Based on the result, **9a** was further derived to chloroacetyl derivative (**15**) in 84% yield by reacting it with chloroacetic anhydride (Scheme 2). Subsequent nucleophilic substitution of chlorine of **15** for acetoxy group proceeded by treatment with sodium acetate in DMF to give **16** in 83% yield. Mild alkaline hydrolysis of ester (**16**) with sodium bicarbonate in MeOH produced hydroxyacetyl derivative (**17**) in 85% yield as colorless prisms. Although spectral and elemental analyses data of **9a** and **15** through **17** suggested 4*H*-1,3-dioxolo[4,5-*b*]indole structure, the unequivocal proof was obtained by X-Ray single crystallographic analysis of **17**.

The results and numbering of atoms are shown in Figure 1. Positional parameters and *B* (eq) for **17** are summarized in Table 1.

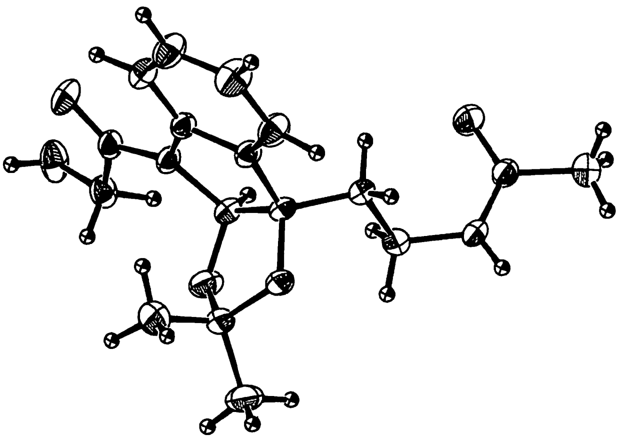
**Figure 1**

Numbering of Atoms

**17**



ORTEP Drawing of **17** (R = 0.042)

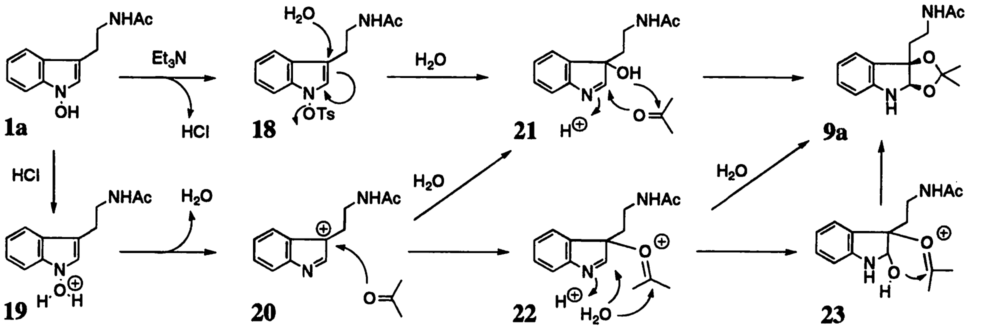


## Table 1. Positional Parameters and *B* (eq) for **17**

| atom | *x* | *y* | *z* | *B* (eq) | atom | *x* | *y* | *z* | *B* (eq) |
|---|---|---|---|---|---|---|---|---|---|
| O (1) | 0.7979 (1) | 0.3109 (1) | 1.2574 (2) | 4.58 (5) | C (17) | 1.0353 (2) | 0.4315 (2) | 1.1736 (3) | 4.21 (7) |
| O (2) | 0.6335 (1) | 0.1516 (1) | 1.1578 (1) | 3.72 (4) | H (1) | 0.769 (1) | 0.365 (2) | 1.030 (2) | 3.144 (8) |
| O (3) | 0.4207 (1) | 0.3866 (1) | 0.6575 (2) | 4.95 (5) | H (2) | 0.565 (2) | −0.046 (2) | 0.805 (3) | 5.33 (1) |
| O (4) | 1.0941 (1) | 0.2759 (1) | 0.9797 (2) | 5.15 (6) | H (3) | 0.676 (3) | −0.177 (2) | 0.652 (3) | 6.90 (2) |
| O (5) | 1.1487 (1) | 0.5058 (1) | 1.1673 (2) | 5.43 (6) | H (4) | 0.894 (2) | −0.109 (2) | 0.663 (3) | 6.25 (2) |
| N (1) | 0.8880 (1) | 0.2442 (1) | 1.0104 (2) | 3.19 (5) | H (5) | 1.009 (2) | 0.085 (2) | 0.827 (3) | 4.37 (1) |
| N (2) | 0.3573 (1) | 0.3258 (1) | 0.8872 (2) | 3.92 (6) | H (6) | 0.470 (2) | 0.140 (2) | 0.859 (3) | 4.05 (1) |
| C (1) | 0.7795 (2) | 0.2883 (2) | 1.0718 (2) | 3.30 (6) | H (7) | 0.555 (2) | 0.231 (2) | 0.778 (3) | 4.26 (1) |
| C (2) | 0.6621 (2) | 0.1839 (1) | 0.9984 (2) | 3.16 (5) | H (8) | 0.552 (2) | 0.397 (2) | 0.993 (3) | 4.27 (1) |
| C (3) | 0.7154 (2) | 0.0879 (1) | 0.8954 (2) | 3.27 (6) | H (9) | 0.484 (2) | 0.305 (2) | 1.104 (3) | 4.19 (1) |
| C (4) | 0.6518 (2) | −0.0242 (2) | 0.8007 (2) | 4.47 (7) | H (10) | 0.294 (2) | 0.312 (2) | 0.935 (3) | 4.50 (1) |
| C (5) | 0.7200 (2) | −0.0983 (2) | 0.7144 (3) | 5.50 (8) | H (11) | 0.188 (3) | 0.451 (3) | 0.621 (4) | 8.93 (3) |
| C (6) | 0.8488 (2) | −0.0589 (2) | 0.7240 (3) | 5.24 (8) | H (12) | 0.140 (2) | 0.335 (2) | 0.711 (3) | 5.74 (1) |
| C (7) | 0.9141 (2) | 0.0532 (2) | 0.8175 (3) | 4.16 (7) | H (13) | 0.170 (2) | 0.324 (2) | 0.539 (4) | 5.84 (1) |
| C (8) | 0.8451 (2) | 0.1269 (1) | 0.9033 (2) | 3.20 (5) | H (14) | 0.861 (3) | 0.094 (2) | 1.245 (4) | 7.77 (2) |
| C (9) | 0.5385 (2) | 0.2125 (2) | 0.8890 (2) | 3.74 (6) | H (15) | 0.785 (3) | 0.053 (3) | 1.368 (4) | 6.66 (2) |
| C (10) | 0.4879 (2) | 0.3163 (2) | 0.9821 (2) | 4.15 (7) | H (16) | 0.906 (3) | 0.166 (3) | 1.450 (4) | 8.62 (2) |
| C (11) | 0.3330 (2) | 0.3602 (2) | 0.7322 (2) | 3.58 (6) | H (17) | 0.613 (3) | 0.307 (2) | 1.429 (4) | 7.36 (2) |
| C (12) | 0.1961 (2) | 0.3673 (3) | 0.6485 (4) | 5.05 (9) | H (18) | 0.640 (3) | 0.180 (3) | 1.499 (4) | 7.61 (2) |
| C (13) | 0.7360 (2) | 0.2065 (2) | 1.3086 (2) | 4.08 (6) | H (19) | 0.742 (3) | 0.287 (2) | 1.565 (4) | 7.21 (2) |
| C (14) | 0.8298 (3) | 0.1226 (3) | 1.3520 (4) | 6.2 (1) | H (20) | 0.958 (2) | 0.473 (2) | 1.147 (3) | 4.41 (1) |
| C (15) | 0.6790 (3) | 0.2503 (3) | 1.4620 (3) | 6.1 (1) | H (21) | 1.044 (2) | 0.413 (2) | 1.285 (3) | 5.13 (1) |
| C (16) | 1.0100 (2) | 0.3118 (2) | 1.0447 (2) | 3.58 (6) | H (22) | 1.215 (3) | 0.473 (2) | 1.211 (3) | 6.26 (2) |

The mechanism for the formation of **9a** might be explained as shown in Scheme 3. Initially, TsCl leads **1a** to 1-tosyloxy derivative (**18**) with a concomitant formation of HCl, which works as a proton source and transforms 1-hydroxy moiety of the second molecule (**1a**) to a good leaving group as shown in **19**. Liberation of water from **19** leaves resonance stabilized indolyl cation[4,5] (**20**). Nucleophilic addition of water to **20** produces 3-hydroxyindolenine (**21**) and then a sequence of reactions, such as i) protonation of imine nitrogen, 2) nucleophilic addition of acetone to the imine carbon, and 3) addition of the 3-hydroxy group to the acetone carbonyl, leads to the formation of **9a**. Nucleophilic addition of acetone to **20** might take place to produce **23** through **22**. Subsequent cyclization of aminal oxygen to the positively charged carbonyl carbon affords **9a**. The attack of water at the positively charged carbonyl carbon of **22** followed by cyclization of the resultant hemiketal oxygen to the imine carbon could be another possible pathway.

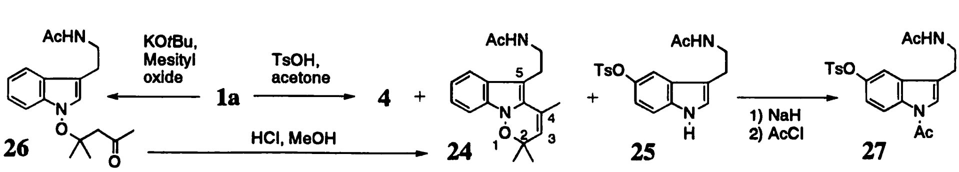
## Scheme 3



With an attempt to improve the yield of **9a**, we next examined the reaction of **1a** in acetone with *p*-toluenesulfonic acid (TsOH) as an acid catalyst. Interestingly, the result was completely different from the expectation. Thus, **1a** afforded 2*H*-1,2-oxazino[2,3-*a*]indole (**24**), 5-tosyloxyindole (**25**), **4**, and unreacted **1a** in 9, 10, 7, and 14% yields, respectively (Scheme 4).

The structure of **24** was proved by comparing it with the authentic sample prepared by the following alternative route. Michael addition reaction of **1a** to mesityl oxide in DMF in the presence of potassium *t*-butoxide afforded **26** and unreacted **1a** in 49 and 50% yields, respectively. Acid catalyzed cyclization of **26** with 8% HCl in MeOH provided **24** in 78% yield. The reaction of **1a** with mesityl oxide at 55°C also produced **24** directly in 53% yield. For the structural determination of **25**, it was converted to **27** in 69% yield by the sequential treatment with NaH and then with AcCl.

## Scheme 4



Comparison of the $^1$H-NMR spectrum of **27** with that of **25** exhibited the anisotropy effect of the 1-acetyl group on the *ortho*-coupled C-7 proton (d, *J*=7.5 Hz) by *ca.* 1 ppm (δ 7.22→8.30), proving these compounds are 5-substituted indoles. The formation of **25** can be explained by the regioselective nucleophilic attack of *p*-toluenesulfonate at the 5-position as the 1-hydroxy leaving group departs upon protonation. This is an additional example of nucleophilic substitution reactions characteristic to 1-hydroxyindoles.[2]

In conclusion, we have found that 1-hydroxyindoles provide unprecidented types of compounds such as 4-substituted indoles and 4*H*-1,3-dioxolo[4,5-*b*]indoles upon reaction with TsCl in acetone, while the reaction with TsOH in acetone contrastively produces 2*H*-1,2-oxazino[2,3-*a*]indole and 5-tosyloxyindole. By choosing reaction conditions and substrates, whether we could control the reaction pathways to obtain individual products selectively and in better yields is the next facing subject.

## EXPERIMENTAL

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were determined with a Shimadzu IR-420 spectrophotometer, and $^1$H-NMR spectra with a JEOL GSX-500 spectrometer with tetramethylsilane as an internal standard. MS were recorded on JEOL SX-102A and JMS-GCmate spectrometers. Column chromatography was performed on silica gel ($SiO_2$, 100—200 mesh, from Kanto Chemical Co. Inc.) throughout the present study.

**1-Acetyl-1,2,3,8-tetrahydropyrrolo[2,3-*b*]indole (2a), *Nb*-Acetyl-2,3-dihydro-2-oxo-tryptamine (3a), *Nb*-Acetyltryptamine (4), *Nb*-Acetyl-4-tosyloxytryptamine (7b), and *Nb*-Acetyl-6-tosyloxytryptamine (8a) from *Nb*-Acetyl-1-hydroxytryptamine (1a)** — TsCl (181.8 mg, 0.96 mmol) was added to a solution of **1a** (208.8 mg, 0.96 mmol) in anhydrous THF (8.0 mL) and $Et_3N$ (0.8 mL, 5.7 mmol) at 0 °C with stirring. After additional stirring at rt for 1 h, ice and $H_2O$ was added to the reaction mixture. The whole was extracted with $CHCl_3$–MeOH (95:5, v/v). The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ repeatedly with $CHCl_3$–MeOH (98:1—98:2, v/v) to give **2a**[4] (80.3 mg, 42%), **4**[4] (4.9 mg, 3%), **7b** (1.7 mg, 0.5%), **8a** (16.5 mg, 5%), and **3a**[4] (12.4 mg, 6%) in the order of elution. **7b**: mp 178—182 °C (pale yellow prisms, recrystallized from EtOAc–hexane). IR (KBr): 3303, 3216, 1624, 1570, 1371, 1177, 1023, 858 cm$^{-1}$. $^1$H-NMR ($CDCl_3$) δ: 1.94 (3H, s), 2.48 (3H, s), 3.08 (2H, t, *J*=7.1 Hz), 3.58 (2H, q, *J*=7.1 Hz), 5.85 (1H, br s), 6.48 (1H, dd, *J*=0.7, 8.0 Hz), 6.98 (1H, t, *J*=8.0 Hz), 7.04 (1H, d, *J* =2.4 Hz), 7.25 (1H, dd, *J*=0.7, 8.0 Hz), 7.37 (2H, br d, *J*=8.2 Hz), 7.83 (2H, br d, *J*=8.2 Hz), 8.23 (1H, br s). HR–MS *m/z*: Calcd for $C_{19}H_{20}N_2O_4S$: 372.1135. Found: 372.1144. **8a**: mp 190—191 °C (colorless prisms, recrystallized from EtOAc). IR (KBr): 3400, 3182, 1660, 1542, 1361, 945 cm$^{-1}$. $^1$H-NMR ($CD_3OD$) δ: 1.88 (3H, s), 2.43 (3H, s), 2.88 (2H, dt, *J*=0.8, 7.5 Hz), 3.41 (2H, t, *J*=7.5 Hz ), 6.57 (1H, dd, *J*=2.2, 8.5 Hz), 6.97 (1H, dd, *J*=0.5, 2.2 Hz), 7.10 (1H, s), 7.37 (2H, br d, *J*=8.5 Hz), 7.42 (1H, dd, *J*=0.5, 8.5 Hz), 7.67 (2H, br d, *J*=8.5 Hz). MS *m/z*: 372 ($M^+$). *Anal.* Calcd for $C_{19}H_{20}N_2O_4S$: C, 61.27; H, 5.41; N, 7.52. Found: C, 61.17; H, 5.47; N, 7.23. Although chromatographical separation of **7b** from **8a** was quite difficult, the fractions containing **7b** and **8a** were readily obtained. So, the pure sample of **7b** was prepared by the following alkaline hydrolysis of *Na,Nb*-diacetyl-4-tosyloxyindole (**10**).

***Na,Nb*-Diacetyl-4-*p*-tosyloxytryptamine (10) and *Na,Nb*-Diacetyl-6-*p*-tosyloxytryptamine (11a) from the Fractions Containing 7b and 8a** — The fractions containing **7b** and **8a** were collected after the similar reactions and work-up as described above. The mixture (27.5 mg, 0.07 mmol) was dissolved in anhydrous DMF (1.5 mL). The solution was added to 60% NaH (5.9 mg, 0.14 mmol, washed with dry benzene) at 0℃ with stirring. After additional stirring at rt for 10 min, a solution of AcCl (19.8 mg, 0.22 mmol) in anhydrous DMF (0.5 mL) was added to the resultant solution. The mixture was stirred at rt for 30 min. After addition of $H_2O$ under ice cooling, the whole was extracted with EtOAc. The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with $CHCl_3$–MeOH (99:1, v/v) to give **11a** (13.3 mg, 44%) and **10** (10.6 mg, 35%) in the order of elution. **10**: mp 151.5—152.5 °C (colorless needles, recrystallized from EtOAc–hexane). IR (KBr): 3298, 1705, 1639, 1434, 1379 $cm^{-1}$. $^1$H-NMR ($CDCl_3$) δ: 1.98 (3H, s), 2.49 (3H, s), 2.61 (3H, s), 3.08 (2H, t, *J*=7 Hz), 3.62 (2H, q, *J*=7 Hz, collapsed to t, *J*=7 Hz, on addition of $D_2O$), 5.85 (1H, br s, disappeared on addition of $D_2O$), 6.58 (1H, dd, *J*=0.7, 8.1 Hz), 7.15 (1H, t, *J*=8.1 Hz), 7.32 (1H, s), 7.39 (2H, d, *J*=8.1 Hz), 7.80 (2H, d, *J*=8.3 Hz), 8.39 (1H, dd, *J*=0.7, 8.3 Hz). HR – MS *m/z*: Calcd for $C_{21}H_{22}N_2O_5S$: 414.1250. Found: 414.1251.

***Nb*-Acetyl-4-tosyloxytryptamine (7b) from 10** — Sat. aq. $NaHCO_3$ (1.0 mL, 1.05 mmol) was added to a solution of **10** (6.4 mg, 0.015 mmol) in MeOH (1.0 mL) and the mixture was stirred at rt for 45 min. After addition of $H_2O$, the whole was extracted with $CHCl_3$–MeOH (95:5, v/v). The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with $CHCl_3$ – MeOH (97:3, v/v) to give pure **7b** (4.4 mg, 77%).

**1-Acetyl-1,2,3,8-tetrahydropyrrolo[2,3-*b*]indole (2a), *N*b-Acetyl-2,3-dihydro-2-oxotryptamine (3a), *Nb*-Acetyltryptamine (4), *Nb*-Acetyl-4-*p*-tosyloxytryptamine (7b), *Nb*-Acetyl-6-*p*-tosyloxytryptamine (8a), and 8b-(2-Acetylaminoethyl)-2,2-dimethyl-4*H*-1,3-dioxolo[4,5-*b*]indole (9a) from 1a** —*p*-Toluenesulfonyl chloride (88.5 mg, 0.47 mmol) was added to a solution of **1a** (101.6 mg, 0.47 mmol) in anhydrous acetone (20.0 mL) and $Et_3N$ (0.65 mL, 4.7 mmol) at 0 °C with stirring. After additional stirring at rt for 1 h, $H_2O$ was added to the reaction mixture. The whole was extracted with $CHCl_3$–MeOH (95:5, v/v). The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ repeatedly with $CHCl_3$–MeOH (99:1, v/v) and then with $CHCl_3$–MeOH–28% aq.$NH_3$ (46:2:0.2, v/v) to give **2a**[4] (12.8 mg, 14%), **9a** (3.7 mg, 3%), **4**[4] (3.7 mg, 4%), **7b** (0.3 mg, 0.2%), **8a** (5.2 mg, 3%), and **3a**[4] (6.5 mg, 6%) in the order of elution. **9a**: pale yellow oil. IR (film): 3300, 1640 (br), 1550 (br), 1027, 750 $cm^{-1}$. $^1$H-NMR (DMSO-$d_6$) δ: 1.02 (3H, s), 1.35 (3H, s), 1.76 (3H, s), 1.87 (1H, ddd, *J*= 5.1, 10.1, 13.5 Hz), 2.05 (1H, ddd, *J*=6, 11, 13.5 Hz), 2.91—2.99 (1H, m), 3.04—3.12 (1H, m), 5.44 (1H, d, *J*=2.5 Hz), 6.53 (1H, d, *J*=7.5 Hz), 6.64 (1H, dt, *J*=1.3, 7.5 Hz), 6.88 (1H, d, *J*=2.5 Hz), 7.07 (1H, dt, *J*=1.3, 7.5 Hz), 7.15 (1H, br d, *J*=7.5 Hz), 7.77 (1H, br t, *J*=5.0 Hz). HR–MS *m/z*: Calcd for $C_{15}H_{20}N_2O_3$: 276.1474. Found: 276.1477.

**1-Trifluoroacetyl-1,2,3,8-tetrahydropyrrolo[2,3-*b*]indole (2b), *Nb*-Trifluoroacetyl-6-*p*-**

**tosyloxytryptamine (8b), and 8b-(2-Trifluoroacetylaminoethyl)-2,2-dimethyl-4*H*-1,3-dioxolo[4,5-*b*]indole (9b) from *N*b-Trifluoroacetyl-1-hydroxytryptamine (1b)** — TsCl (36.0 mg, 0.19 mmol) was added to a solution of **1b** (51.1 mg, 0.19 mmol) in acetone (2.0 mL) and $Et_3N$ (0.26 mL, 1.9 mmol) at 0 °C with stirring. After additional stirring at rt for 1 h, ice and $H_2O$ was added to the reaction mixture. The whole was extracted with $CHCl_3$–MeOH (95:5, v/v). The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with $CHCl_3$–hexane (2:1, v/v), then with $CHCl_3$ to give **2b**[4] (27.7 mg, 58%), **9b** (6.9 mg, 11%), and **8b** (4.7 mg, 6%) in the order of elution. **9b**: mp 104—105 °C (colorless fine needles, recrystallized from EtOAc–hexane). IR (KBr): 3407, 3342, 1700, 1613, 1551, 1160 (br) $cm^{-1}$. $^1H$-NMR ($CDCl_3$) δ: 1.10 (3H, s), 1.47 (3H, s), 2.12 (1H, ddd, *J*=14.9, 7.1, 4.6 Hz), 2.27 (1H, ddd, *J*=14.9, 8.1, 4.7 Hz), 3.38—3.46 (1H, m), 3.68—3.75 (1H, m), 4.73 (1H, br s), 5.41 (1H, s), 6.66 (1H, br d, *J*=7.6 Hz), 6.85 (1H, dt, *J*=1.0, 7.6 Hz), 7.20 (1H, dt, *J*=1.2, 7.6 Hz), 7.25 (1H, br d, *J*=7.6 Hz), 7.28 (1H, br s). *Anal.* Calcd for $C_{15}H_{17}N_2O_2F_3$: C, 54.54; H, 5.19; N, 8.48. Found: C, 54.56; H, 5.15; N, 8.44. **8b**: mp 167—168 °C (colorless plates, recrystallized from $CHCl_3$). IR (KBr): 3304, 1717, 1368, 1173, 1087 $cm^{-1}$. $^1H$-NMR ($CDCl_3$) δ: 2.45 (3H, s), 3.01 (2H, t, *J*=6.7 Hz), 3.65 (2H, q, *J*=6.7 Hz), 6.33 (1H, br s), 6.62 (1H, dd, *J*=8.6, 2.3 Hz), 7.08 (1H, d, *J*=2.3 Hz), 7.17 (1H, d, *J*=2 Hz), 7.30 (2H, br d, *J*=8.6 Hz), 7.40 (1H, d, *J*=8.6 Hz), 7.71 (2H, br d, *J*=8.6 Hz), 8.17 (1H, br s). *Anal.* Calcd for $C_{19}H_{17}N_2O_4F_3S$: C, 53.52; H, 4.02; N, 6.57. Found: C, 53.55; H, 4.03; N, 6.47.

***N*-Adamantyl-4-(2-oxyindol-3-yl)butanamide (3c) and *N*-Adamantyl-4-(2,2-dimethyl-4*H*-1,3-dioxolo[4,5-*b*]indol-8b-yl)butanamide (9c) from *N*-Adamantyl-4-(1-hydroxyindol-3-yl)butanamide (1c)** — TsCl (16.6 mg, 0.08 mmol) was added to a solution of **1c** (29.3 mg, 0.08 mmol) in acetone (1.5 mL) and $Et_3N$ (0.12 mL, 0.9 mmol) at 0 °C with stirring. After additional stirring at rt for 30 min, ice and $H_2O$ was added to the reaction mixture. The whole was extracted with $CHCl_3$–MeOH (95:5, v/v). The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with EtOAc–hexane (1:2—1:1, v/v) to give **9c** (3.4 mg, 10%) and **3c** (14.3 mg, 49%) in the order of elution. **3c**: mp 227.0—228.5 °C (colorless powder, recrystallized from $CHCl_3$). IR (KBr): 3292, 2904, 1712, 1628, 1550, 750 $cm^{-1}$. $^1H$-NMR ($CDCl_3$) δ: 1.64—1.68 (6H, m), 1.67—1.72 (2H, m), 1.96—1.99 (6H, m), 1.97—2.03 (2H, m), 2.06 (3H, br s), 2.10 (2H, t, *J*=7.4 Hz), 3.47 (1H, br t, *J*=6.1 Hz), 5.18 (1H, br s), 6.85 (1H, d, *J*=7.6 Hz), 7.02 (1H, dt, *J*=1.0, 7.6 Hz), 7.20 (1H, br t, *J*=7.6 Hz), 7.25 (1H, t, *J*=7.6 Hz), 7.79 (1H, br s, disappeared on addition of $D_2O$). MS *m/z*: 352 ($M^+$). *Anal.* Calcd for $C_{22}H_{28}N_2O_2 \cdot 1/2\ H_2O$: C, 73.10; H, 8.09; N, 7.75. Found: C, 72.97; H, 7.81; N, 7.70. **9c**: pale yellow oil. IR (KBr): 3292, 1643, 1613, 1543, 1017, 746 $cm^{-1}$. $^1H$-NMR ($CDCl_3$) δ: 1.11 (3H, s), 1.45 (3H, s), 1.49—1.61 (1H, m), 1.64—1.68 (6H, m), 1.64—1.78 (1H, m), 1.85—2.03 (3H, m), 1.95—1.98 (6H, m), 2.06 (3H, br s), 2.03—2.16 (1H, m), 4.66 (1H, br s), 5.06 (1H, br s), 5.44 (1H, s), 6.61 (1H, d, *J*=7.5 Hz), 6.79 (1H, dt, *J*=0.9, 7.5 Hz), 7.14 (1H, dt, *J*=1.2, 7.5 Hz), 7.23 (1H, dd, *J*=0.9, 7.5 Hz). HR–MS *m/z*: Calcd for $C_{25}H_{34}N_2O_3$: 410.2569. Found: 410.2578.

***Na,Nb*-Diacetyl-6-*p*-tosyloxytryptamine (11a) from 8a** — A solution of **8a** (39.8 mg, 0.11

mmol) in DMF (1.5 mL) was added to 60% NaH (9.3 mg, 0.23 mmol, washed with dry benzene) at 0 °C with stirring. After additional stirring at rt for 10 min, a solution of AcCl (30.2 mg, 0.38 mmol) in DMF (0.5 mL) was added to the resultant solution and the mixture was stirred at rt for 1 h. After addition of $H_2O$ under ice cooling, the whole was extracted with EtOAc. The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with EtOAc to give unreacted **8a** (5.9 mg, 14.8%) and **11a** (37.6 mg, 84.9%) in the order of elution. **11a**: mp 155.0—156.5 °C (colorless prisms, recrystallized from EtOAc–hexane). IR (KBr): 3256, 1706, 1658, 1634, 1172, 905, 834 $cm^{-1}$. $^1H$-NMR ($CD_3OD$) δ: 1.89 (3H, s), 2.44 (3H, s), 2.58 (3H, s), 2.87 (2H, dt, *J*=1.0, 7.1 Hz), 3.47 (2H, t, *J*=7.1 Hz), 6.91 (1H, dd, *J*=2.2, 8.5 Hz), 7.39 (2H, br d, *J*=8.5 Hz), 7.51 (1H, d, *J*=8.5 Hz), 7.57 (1H, s), 7.68 (2H, br d, *J*=8.5 Hz), 7.98 (1H, d, *J*=2.2 Hz). *Anal.* Calcd for $C_{21}H_{22}N_2O_5S$: C, 60.85; H, 5.35; N, 6.76. Found: C, 60.63; H, 5.38; N, 6.65.

***Na*-Acetyl-*Nb*-trifluoroacetyl-6-*p*-tosyloxytryptamine (11b) from 8b** — A solution of **8b** (40.2 mg, 0.09 mmol) in DMF (2.0 mL) was added to 60% NaH (8.0 mg, 0.18 mmol, washed with dry benzene) at 0 °C with stirring. After additional stirring at rt for 15 min, a solution of AcCl (24.0 mg, 0.31 mmol) in DMF (1.0 mL) was added to the resultant solution and the mixture was stirred at rt for 1 h. After addition of $H_2O$ under ice cooling, the whole was extracted with EtOAc. The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with EtOAc-hexane (1:1, v/v) to give unreacted **8b** (9.4 mg, 23%) and **11b** (15.5 mg, 35%) in the order of elution. **11b**: mp 162.5—164.0 °C (colorless powder, recrystallized from $CHCl_3$–hexane). IR (KBr): 3328, 1698, 1371, 1174 $cm^{-1}$. $^1H$-NMR ($CDCl_3$) δ: 2.45 (3H, s), 2.54 (3H, s), 2.98 (2H, dt, *J*=1.0, 7.1 Hz), 3.68 (2H, q, *J*=7.1 Hz, collapsed to t, *J*=7.1 Hz on addition of $D_2O$), 6.45 (1H, br s, disappeared on addition of $D_2O$), 7.01 (1H, dd, *J*=2.2, 8.5 Hz), 7.29 (1H, br s), 7.33 (2H, br d, *J*=8.5 Hz), 7.42 (1H, d, *J*=8.5 Hz), 7.75 (2H, br d, *J*=8.5 Hz), 8.07 (1H, br s). *Anal.* Calcd for $C_{21}H_{19}N_2O_5F_3S$: C, 53.84; H, 4.09; N, 5.98. Found: C, 53.56; H, 4.03; N, 5.87.

**4-Acetyl-8b-(2-acetylaminoethyl)-2,2-dimethyl-4*H*-1,3-dioxolo[4,5-*b*]indole (14) from 9a** — $Ac_2O$ (1 mL) was added to a solution of **9a** (23.3 mg, 0.08 mmol) in pyridine (2.0 mL) and the mixture was stirred at rt for 8.5 h. Evaporation of the solvent under reduced pressure afforded an oil, which was column-chromatographed on $SiO_2$ with $CHCl_3$–MeOH (98:2, v/v) to give **14** (19.0 mg, 71%). **14**: colorless oil. IR (film): 3300, 1663 (br), 1553 (br), 760 $cm^{-1}$. $^1H$-NMR ($CDCl_3$) δ: 1.00 (3H, s), 1.50 (3H, s), 1.96 (3H, s), 2.07—2.14 (1H, m), 2.28—2.35 (1H, m), 2.43 (3H, s), 3.25—3.33 (1H, m), 3.43—3.52 (1H, m), 5.85 (1H, br s), 5.87 (1H, s), 7.13 (1H, t, *J*=7.5 Hz), 7.32—7.37 (2H, m), 8.20 (1H, d, *J*=7.5 Hz). HR-MS *m/z*: Calcd for $C_{17}H_{22}N_2O_4$: 318.1580. Found: 318.1580.

**8b-(2-Acetylaminoethyl)-4-chloroacetyl-2,2-dimethyl-4*H*-1,3-dioxolo[4,5-*b*]indole (15) from 9a** — A solution of chloroacetic anhydride (28.1 mg, 0.15 mmol) in $CHCl_3$ (0.5 mL) was added to a solution of **9a** (14.1 mg, 0.05 mmol) in $CHCl_3$ (1.0 mL) and the mixture was stirred at rt for 3 h. Sat. aq. $NaHCO_3$ and $CHCl_3$ were added to the reaction mixture. The organic layer was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with EtOAc to give **15** (17.0 mg, 84%). **15**: colorless oil. IR (film): 3292, 1656 (br), 1550, 1480, 1400, 1059, 760 cm$^{-1}$. $^{1}$H-NMR ($CDCl_3$) δ: 1.01 (3H, s), 1.50 (3H, s), 1.95 (3H, s), 2.11—2.18 (1H, m), 2.31—2.38 (1H, m), 3.25—3.32 (1H, m), 3.41—3.49 (1H, m), 4.34 (1H, d, *J*= 13.2 Hz), 4.55 (1H, d, *J*=13.2 Hz), 5.76 (1H, br s), 6.04 (1H, s), 7.19 (1H, dt, *J*=1.0, 7.4 Hz), 7.37 (1H, br d, *J*=7.4 Hz), 7.38 (1H, ddd, *J*=8.1, 7.4, 1.3 Hz), 8.21 (1H, br d, *J*=8.1 Hz). HR–MS *m/z*: Calcd for $C_{17}H_{21}N_2O_4Cl$: 354.1160 and 352.1190. Found: 354.1189 and 352.1185.

**4-(2-Acetoxy)acetyl-8b-(2-acetylaminoethyl)-2,2-dimethyl-4*H*-1,3-dioxolo[4,5-*b*]indole (16) from 15** — A solution of NaOAc (7.6 mg, 0.09 mmol) in $H_2O$ (0.2 mL) was added to a solution of **15** (16.5 mg, 0.047 mmol) in DMF (2.0 mL) and the mixture was stirred at 55–57 °C for 8 h. After evaporation of the solvent under reduced pressure, $H_2O$ was added to the residue. The whole was extracted with $CHCl_3$–MeOH (95:5, v/v). The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with $CHCl_3$–MeOH (98:2, v/v) to give **16** (14.6 mg, 83%). **16**: colorless oil. IR (film): 3287, 1747, 1691, 1655, 763 cm$^{-1}$. $^{1}$H-NMR ($CDCl_3$) δ: 1.02 (3H, s), 1.50 (3H, s), 1.96 (3H, s), 2.10—2.17 (1H, m), 2.24 (3H, s), 2.31—2.38 (1H, m), 3.20—3.27 (1H, m), 3.44—3.52 (1H, m), 4.93 (1H, d, *J*=15.1 Hz), 5.06 (1H, d, *J*=15.1 Hz), 5.82 (1H, br s, disappeared on addition of $D_2O$), 5.97 (1H, s), 7.16 (1H, dt, *J*= 1.0, 7.4 Hz), 7.36 (1H, dd, *J*=7.4, 1.3 Hz), 7.36 (1H, ddd, *J*=8.5, 7.4, 1.3 Hz), 8.18 (1H, br d, *J*=8.5 Hz). HR–MS *m/z*: Calcd for $C_{19}H_{24}N_2O_6$: 376.1634. Found: 376.1630.

**8b-(2-Acetylaminoethyl)-4-hydroxyacetyl-2,2-dimethyl-4*H*-1,3-dioxolo[4,5-*b*]indole (17) from 16** — Sat. aq. $NaHCO_3$ (0.5 mL, 0.5 mmol) was added to a solution of **16** (3.3 mg, 0.009 mmol) in MeOH (0.5 mL) and the mixture was stirred at rt for 45 min. After addition of $H_2O$ to the reaction mixture, the whole was extracted with $CHCl_3$–MeOH (95:5, v/v). The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with $CHCl_3$–MeOH (95:5, v/v) to give **17** (2.5 mg, 85%). **17**: mp 130.0—130.5 °C (colorless prisms, recrystallized from EtOAc). IR (KBr): 3455, 3284, 1676, 1625, 1562, 1055, 756 cm$^{-1}$. $^{1}$H- NMR ($CDCl_3$) δ: 1.00 (3H, s), 1.49 (3H, s), 1.95 (3H, s), 2.07—2.15 (1H, m), 2.28—2.36 (1H, m), 3.23—3.31 (1H, m), 3.35 (1H, br t, *J*=4 Hz, disappeared on addition of $D_2O$), 3.41—3.49 (1H, m), 4.46 (1H, dd, *J*=4.3, 16.1 Hz, collapsed to d, *J*=16.1 Hz on addition of $D_2O$), 4.58 (1H, dd, *J*=4.5, 16.1 Hz, collapsed to d, *J*=16.1 Hz on addition of $D_2O$), 5.75 (1H, br s, disappeared on addition of $D_2O$), 5.80 (1H, br s), 7.18 (1H, dt, *J*=1.0, 7.6 Hz), 7.38 (1H, br d, *J*=7.9 Hz), 7.39 (1H, ddd, *J*=7.9, 7.6, 1.2 Hz), 8.21 (1H, br d, *J*=7.6 Hz). *Anal.* Calcd for $C_{17}H_{22}N_2O_5$: C, 61.06; H, 6.63; N, 8.38. Found: C, 60.90; H, 6.58; N, 8.26.

***N*b-Acetyl-1-(1,1-dimethyl-3-oxo)butoxytryptamine (26) from 1a** — Potassium *t*-butoxide (74.8 mg, 0.67 mmol) was added to a solution of **1a** (50.0 mg, 0.23 mmol) in DMF (2.5 mL) under Ar atmosphere and then mesityl oxide (9 mL) was added to the reaction mixture at 0 °C. The mixture was stirred at rt for 72 h. After addition of $H_2O$ under ice cooling, the whole was extracted with EtOAc. The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with $CHCl_3$–MeOH (98:2, v/v) and then with EtOAc to give **26** (35.5 mg, 49%) and unreacted **1a** (25.1 mg, 50%) in the order of elution. **26**: pale yellow oil. IR (film) : 3300, 1713, 1653, 1553, 745 cm$^{-1}$. $^{1}$H-NMR ($CDCl_3$) δ: 1.53 (6H, s), 1.98 (3H, s), 2.22 (3H, s), 2.93 (2H, s), 2.93 (2H, t, *J*=6.3 Hz), 3.56 (2H, t, *J*=6.3 Hz), 7.06 (1H, s), 7.11 (1H, t, *J*=7.5 Hz), 7.24 (1H, t, *J*=7.5 Hz), 7.38 (1H, d, *J*=7.5 Hz), 7.53 (1H, d, *J*=7.5 Hz). HR−MS *m/z*: Calcd for $C_{18}H_{24}N_2O_3$: 316.1787. Found: 316.1791.

**5-(2-Acetylaminoethyl)-2,2,4-trimethyl-2*H*-1,2-oxazino[2,3-*a*]indole (24), *Nb*-Acetyl-5-tosyloxytryptamine (25) and 4 from 1a** — *p*-Toluenesulfonic acid (181 mg, 1.05 mmol) was added to a solution of **1a** (202 mg, 0.93 mmol) in acetone (16.0 mL) and the mixture was refluxed for 24 h with stirring. Evaporation of the solvent under reduced pressure afforded an oil, which was column-chromatographed repeatedly on $SiO_2$ with $CHCl_3$−MeOH−28% aq.$NH_3$ (46:1:0.1, v/v) and $CHCl_3$−MeOH (95:5, v/v) to give **24** (25.1 mg, 9%), **4** (16.2 mg, 7%), **25** (33.3 mg, 10%), and unreacted **1a** (27.6 mg, 14%) in the order of elution. **24**: pale yellow oil. IR (film) : 3250, 1653, 1553, 755, 735 $cm^{-1}$. $^1H$-NMR ($Me_2SO$-$d_6$) δ: 1.41 (6H, s), 1.77 (3H, s), 2.20 (3H, d, *J*=1.9 Hz), 2.98 (2H, dd, *J*= 6.9, 7.5 Hz), 3.22 (2H, dt, *J*=6.9, 7.5 Hz), 5.76 (1H, q, *J*=1.9 Hz), 7.02 (1H, ddd, *J*=1.3, 6.9, 7.5 Hz), 7.16 (1H, ddd, *J*=1.3, 6.9, 7.5 Hz), 7.27 (1H, d, *J*=7.5 Hz), 7.57 (1H, d, *J*=7.5 Hz), 8.00 (1H, t, *J*=6.9 Hz). HR−MS *m/z*: Calcd for $C_{18}H_{22}N_2O_2$: 298.1681. Found: 298.1685. **25**: Pale yellow oil. IR (film) : 3400, 3250, 1645, 1360, 930 $cm^{-1}$. $^1H$-NMR ($CDCl_3$) δ: 1.94 (3H, s), 2.44 (3H, s), 2.85 (2H, t, *J*=6.3 Hz), 3.48 (2H, q, *J*=6.3 Hz), 5.50 (1H, br s), 6.79 (1H, dd, *J*=2.5, 8.1 Hz), 7.07 (1H, d, *J*=2.5 Hz), 7.18 (1H, d, *J*=2.5 Hz), 7.22 (1H, d, *J*=8.1 Hz), 7.30 (2H, d, *J*=7.5 Hz), 7.72 (2H, d, *J*=7.5 Hz), 8.20 (1H, br s). HR–MS *m/z*: Calcd for $C_{19}H_{20}N_2O_4S$: 372.1144. Found: 372.1125.

**5-(2-Acetylaminoethyl)-2,2,4-trimethyl-2*H*-1,2-oxazino[2,3-*a*]indole (24) from 1a** — A solution of **1a** (70.5 mg, 0.32 mmol) and *p*-toluenesulfonic acid (70.4 mg, 0.41 mmol) in mesityl oxide (5.5 mL) was heated at 55 °C for 2 h with stirring. Evaporation of the solvent under reduced pressure afforded an oil, which was column-chromatographed on $SiO_2$ with $CHCl_3$ to give **24** (51.2 mg, 53%).

**5-(2-Acetylaminoethyl)-2,2,4-trimethyl-2*H*-1,2-oxazino[2,3-*a*]indole (24) from 26** — 8% Aq. HCl (2.5 mL) was added to a solution of **26** (34.0 mg, 0.11 mmol) in MeOH (5.0 mL) at 0 °C and the mixture was stirred at rt for 1 h. After addition of $H_2O$ to the reaction mixture under ice cooling, the whole was extracted with $CHCl_3$−MeOH (95:5, v/v). The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with $CHCl_3$–MeOH (99:1, v/v) to give **24** (25.0 mg, 78%).

***Na*,*Nb*-Diacetyl-5-*p*-tosyloxytryptamine (27) from 25** — A solution of **25** (31.6 mg, 0.09 mmol) in anhydrous DMF (3.0 mL) was added to 60% NaH (10.0 mg, 0.25 mmol, washed with dry benzene) at 0 °C with stirring. After additional stirring at rt for 10 min, a solution of AcCl (31.2 mg, 0.39 mmol) in anhydrous DMF (0.5 mL) was added to the resultant solution. The mixture was stirred at rt for 30 min. After addition of $H_2O$ under ice cooling, the whole was extracted with EtOAc. The extract was washed with brine, dried over $Na_2SO_4$, and evaporated under reduced pressure to leave an oil, which was column-chromatographed on $SiO_2$ with $CHCl_3$−MeOH (98:2, v/v) to give **27** (24.2 mg, 69%) and unreacted **25** (9.5 mg, 30%) in the order of elution. **27**: mp 66 °C (colorless needles, recrystallized from $CH_2Cl_2$–hexane). IR (KBr): 3380, 1698, 1680, 1660, 1550 $cm^{-1}$. $^1H$-NMR ($CDCl_3$) δ: 1.99 (3H, s), 2.45 (3H, s), 2.60 (3H, s), 2.87 (2H, t, *J*=6.3 Hz), 3.56 (2H, q, *J*=6.3 Hz, collapsed to t, *J*=6.3 Hz on addition of $D_2O$), 5.66 (1H, br s, disappeared on addition of $D_2O$), 6.79 (1H, dd, *J*=2.5, 7.5 Hz), 7.28

(1H, d, $J$=2.5 Hz), 7.31 (2H, d, $J$=7.5 Hz), 7.35 (1H, s), 7.70 (2H, d, $J$=7.5 Hz), 8.30 (1H, d, $J$=7.5 Hz). *Anal.* Calcd for $C_{21}H_{22}N_2O_5S$: C, 60.86; H, 5.35; N, 6.76. Found: C, 60.80; H, 5.45; N, 6.75.

**X-Ray Single Crystallographic Analysis of 17** — The reflection data were collected on a Rigaku AFC5R diffractometer over the range of 79.66°<2$\theta$<80.03° using Cu$K_{\alpha}$ radiation ($\lambda$=1.54178 Å) and the $\omega$–2$\theta$ scan method at a 2$\theta$ scan speed of 6°/min. The structure of **17** was solved by the direct method using MITHRIL[6] and refined by the full-matrix least-squares method with anisotropic thermal factors for non-hydrogen atoms and with isotropic ones for hydrogen atoms. The final $R$- and $R_w$-factors were 0.042 and 0.063 for 2511 observed reflections [$I$>3.00$\sigma$ ($I$)], respectively. The atomic parameters are listed in Table 1. Crystal data for **17**: $C_{17}H_{22}N_2O_5$; $M$=334.37; triclinic; space group, $P\bar{1}$ (#2); $a$=10.7201 (9) Å, $b$=11.4019 (9) Å, $c$=7.8385 (6) Å; $\alpha$=99.204 (6)°, $\beta$=102.615 (7)°, $\gamma$=97.892 (6)°; $V$=908.1 (1) Å$^3$, $Z$=2, $D_{calc.}$=1.223 g/cm$^3$.

## REFERENCES AND NOTES

1. This is Part 102 of a series entitled "The Chemistry of Indoles". Part 101: F. Yamada, T. Hayashi, K. Yamada, and M. Somei, *Heterocycles*, 2000, **53**, 1881.
2. M. Somei, *Heterocycles*, 1999, **50**, 1157 and references cited therein.
3. M. Somei, M. Nakajou, T. Teramoto, A. Tanimoto, and F. Yamada, *Heterocycles*, 1999, **51**, 1949; M. Hasegawa, K. Yamada, Y. Nagahama, and M. Somei, *ibid.*, 1999, **51**, 2815; M. Somei, K. Noguchi, R. Yamagami, Y. Kawada, K. Yamada, and F. Yamada, *ibid.*, 2000, **53**, 7; T. Kurauchi, Y. Nagahama, M. Hasegawa, K. Yamada, and M. Somei, *ibid.*, 2000, **53**, 1017; F. Yamada, A. Goto, and M. Somei, *ibid.*, 2000, **53**, 1255.
4. M. Hasegawa, Y. Nagahama, K. Kobayashi, M. Hayashi, and M. Somei, *Heterocycles*, 2000, **52**, 483.
5. M. Somei, N. Oshikiri, M. Hasegawa, and F. Yamada, *Heterocycles*, 1999, **51**, 1237.
6. C. J. Gilmore, *J. Appl. Cryst.*, 1984, **17**, 42.

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