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Inverted Prenylation of N_b-Methoxycarbonyltryptamine. Synthesis of 3a-(1,1-Dimethylallyl)pyrrolo[2,3-*b*]indole and 2-(1,1-Dimethylallyl)tryptamine Derivatives

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Reaction of the indolyl anion of N_b-methoxycarbonyltryptamine (**4**) with 2-chloro-2-methyl-3-butyne (**2**) gave the 3a-(1,1-dimethylpropargyl)pyrrolo[2,3-*b*]indole (**6**) along with the allene derivative (**7**) and N_a-(1,1-dimethylpropargyl)tryptamine (**8**). Partial reduction of **6** gave the 3a-(1,1-dimethylallyl) derivative (**10**), which rearranged to the 2-(1,1-dimethylallyl)tryptamine (**11**) and the N_a-(3,3′-dimethylallyl)tryptamine (**12**) on acid treatment. On the other hand, acid treatment of **6** gave the 2-(1,1-dimethylpropargyl)tryptamine (**14**) in poor yield.

Keywords——N_b-methoxycarbonyltryptamine; inverted prenylation; 2-chloro-2-methyl-3-butyne; acid-catalyzed rearrangement; (1,1-dimethylallyl)tryptamine; (1,1-dimethylpropargyl)-tryptamine; pyrrolo[2,3-*b*]indole 3a-substituted

Many natural products derived from prenylated tryptophans have been found, mostly from fungi. An inverted prenyl (1,1-dimethylallyl) group is often observed at the 1-,2-, or 3-position of the indole ring in these natural products, *e.g.*, echinulines,[1] brevianamide E,[2] LL-S490β,[3] roquefortine,[4] flustramines,[5] and amauromine,[6] For the synthesis of simple 1,1-dimethylallylindoles, the thio-Claisen rearrangement of 2- or 3-(3,3-dimethylallylthio)-indoles has been employed.[7] Furthermore 2-(1,1-dimethylallyl)indole derivatives have been obtained by acid-catalyzed rearrangement of 1-(3,3-dimethylallyl)indoles[8] or by stepwise indole ring synthesis.[9] Direct introduction of the inverted prenyl group into indoles has not been reported, although normal prenylation of simple indoles and tryptamine derivatives was reported by Casnati's group[10] and our group.[11]

Nucleophilic substitution of 1,1-dimethylallyl chloride with nucleophiles generally gives S_N2' type products. However, the reaction of the cyclopentanone enamine (**1**) with 2-chloro-2-methyl-3-butyne (**2**) has been reported[12] to give α-(1,1-dimethylpropargyl)cyclopentanone (**3**), an S_N2 type product. Therefore we examined the reaction of N_b-methoxycarbonyl-tryptamine (**4**) with **2** under various conditions. The reaction of **4** with **2**[13] in dimethylformamide (DMF) in the presence of triethylamine and cuprous chloride, following to the above example,[12] failed to give the expected compound **6**, and **4** was recovered unchanged. The reaction of **4** with **2** in acetate buffer, under conditions where prenylation of **4** with dimethylallyl bromide proceeded smoothly to give the 3a,8-diprenylpyrrolo[2,3-*b*]indole (**5**), also did not proceed. However, the addition of **2** to the sodium salt of **4**, prepared by treatment of **4** with sodium hydride in DMF, gave the expected product, 3a-(1,1-dimethylpropargyl)pyrrolo[2,3-*b*]indole (**6**), in 27% yield along with the allene (**7**, 11%) and the *N*-propargyl derivative (**8**, 23%). The structure of **6** was confirmed by the following spectral data. The ultraviolet (UV) spectrum showed typical hexahydropyrrolo[2,3-*b*]indolic chromophore absorptions (λ_{max} 245 and 301 nm)[11] and the mass spectrum (MS) showed the molecular ion peak at *m/z* 284. The infrared (IR) spectrum showed the C≡CH band at

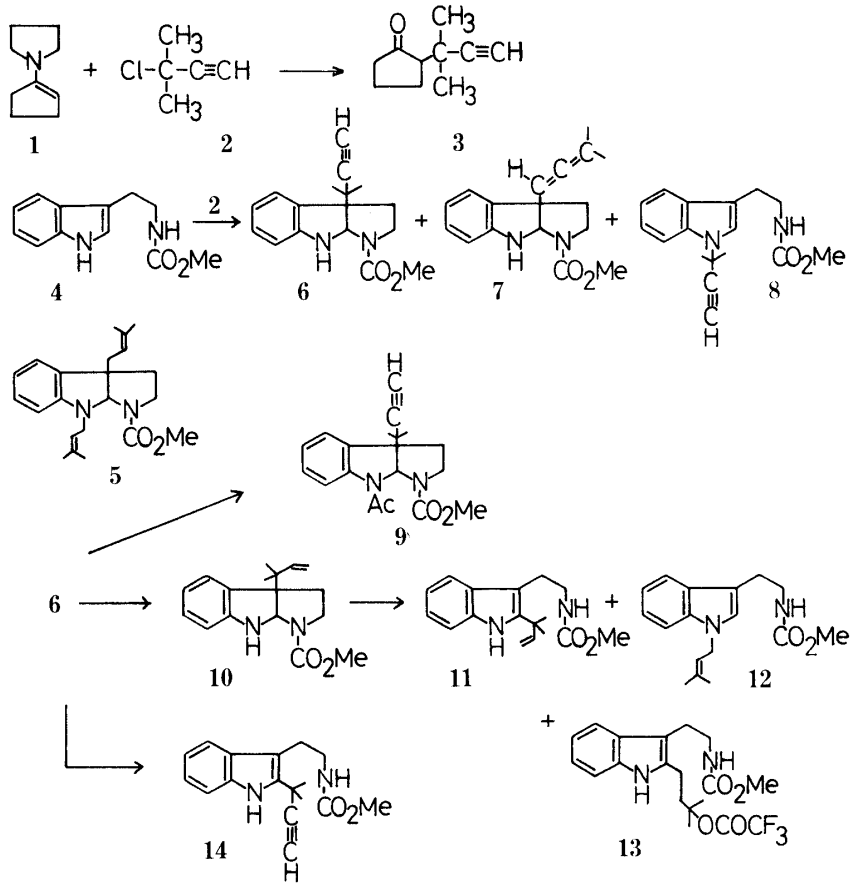

Chart 1

3325 cm^{-1} and C≡C band at 2100 cm^{-1}. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed two singlets due to the 8a-proton at 5.44 and 5.48 ppm and two singlets for the methoxy at 3.70 and 3.78 ppm, indicating the presence of rotamers due to slow rotation of the C–N bond of the amide group. A similar phenomenon has been observed in other 1-methoxycarbonylpyrrolo[2,3-*b*]indoles.[14] Further confirmation of the structure **6** was obtained by acetylation of **6** to give **9**, mp 148—149.5 °C (see Experimental for the spectral data). The structure of the allene derivative (**7**), mp 105.5—106.5 °C, was confirmed by the following spectral data. The UV spectrum was similar to that of **6**, but the IR spectrum showed a band at 1960 cm^{-1} due to C=C=C, and lacked the acetylenic band. The NMR spectrum showed a multiplet at between 5.00 and 5.32 ppm due to the 8a proton and –CH=C=C<. The presence of rotamers was also observed, as in the case of **6**. The structure of the *N*-propargyltryptamine (**8**), mp 90—90.5 °C, was confirmed by its spectral data (see Experimental). These results indicated that the reaction of **4** with **2** proceeded not only *via* S_N2 type substitution reaction, but also *via* S_N2' type reaction. However, only the S_N2 type reaction product (**8**) was isolated in the case of the substitution at the indole nitrogen.

Partial catalytic hydrogenation of **6** with Lindlar catalyst in benzene smoothly gave 3a-(1,1-dimethylallyl)pyrrolo[2,3-*b*]indole (**10**), mp 89—90.5 °C, whose structure was confirmed by the typical ABX vinyl proton signals at 5.04 (d, J=18 Hz), 5.08 (d, J=10 Hz), and 6.02 ppm (dd, J=10 and 18 Hz) in the NMR spectrum. In order to obtain 2-(1,1-dimethylallyl)tryptamines we examined acid catalyzed rearrangement of **6** and **10**. In the case of 3a,8-diprenylpyrrolo[2,3-*b*]indole (**5**), 1,2-diprenyltryptamine was obtained by treatment with trifluoroacetic acid in methylene chloride in good yield.[11] We attempted a similar acid treatment of **6**, but the rearranged compound **14** was not obtained. However, refluxing of **6** in

ethanolic concentrated hydrochloric acid (3 : 1) [conditions, under which 3a-benzylpyrrolo-[2,3-*b*]indole rearranged to the 2-benzyltryptophan derivative[15]] gave the desired 2-(1,1-dimethylpropargyl)trytamine (**14**) in 8% yield. These results suggest that these rearrange-

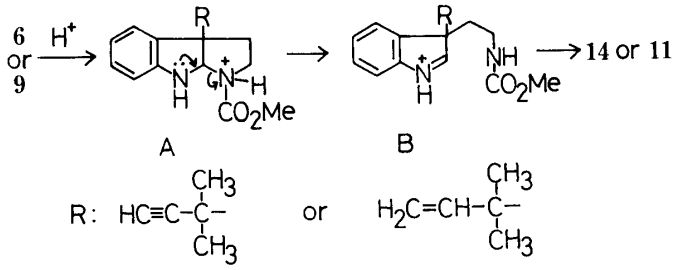

Chart 2

ments may proceed *via* intermediates A and B, and indicated that the migratory aptitude of the 1,1-dimethylpropargyl group is less than that of the prenyl group or benzyl group. Therefore we next examined the rearrangement of the 1,1-dimethylallyl derivative **10**. Treatment of **10** with trifluoroacetic acid in methylene chloride (1 : 1) at room temperature for 2 h gave the desired 2-(1,1-dimethylallyl)tryptamine (**11**) in only 15% yield, and the N_a-(3,3-dimethylallyl)tryptamine (**12**, 30%) and 2-(3-methyl-3-trifluoroacetoxybutyl)tryptamine (**13**, 35%) were obtained as major products. Rearrangement of **10** in trifluoroacetic acid or trifluoroacetic acid–methylene chloride (1 : 3) did not improve the yeild of **11**. Furthermore, the reaction of **10** in acetic acid at 60 °C gave **12** as the major product (53%) and **11** became the minor product (10%). The UV spectrum of **11** showed an indolic chromophore, λ_{max} 225, 284, and 291.5^{sh} nm. The NMR spectrum of **11** showed the presence of vinyl group, two doublets at 5.12 ppm (J = 10 and 18 Hz) and a double doublet at 6.12 ppm (J = 10 and 18 Hz), and lacked the 2-proton signal at 6.96 ppm observed in **4**. On the other hand, the spectral data (see Experimental) of **12** indicated that it is the N_a-dimethylallyltryptamine derivative. The structure of **12** was unequivocally confirmed by direct comparison with a sample prepared by prenylation of **4** with 3,3-dimethylallyl bromide in the presence of sodium hydride in DMF. The IR spectrum of **13** showed two carbonyl bands at 1780 and 1720 cm^{-1}; the former band suggested the presence of trifluoroacetoxy group. The NMR spectrum of **13** showed two singlets due to a geminal methyl group at 1.62 and 1.66 ppm, and two multiplets due to CH_2CH_2–$\overset{|}{C}$–$OCOCF_3$ at 2.04—2.32 and 2.64—3.20 ppm. Neither an olefinic proton nor an α-proton of the indole ring was observed. These data confirmed the structure of **13**. The formation of **12** might be interpreted in terms of [3,3]-sigmatropic rearrangement of the intermediate B (R = –CMe_2–CH = CH_2), giving **11** by 1,2-shift or [1,5]-sigmatropic rearrangement. On the other hand, **13** might be formed by 1,2-shift with allylic rearrangement or by [3,5]-sigmatropic rearrangement of the intermediate B followed by addition of trifluoroacetic acid. Although the yields of the reactions described above are not satisfactory, 3a-(1,1-dimethylallyl)pyrrolo[2,3-*b*]indole and 2-(1,1-dimethylallyl)tryptamine can be prepared by the propargylation of **2**.

Further investigations along this line are now in progress.

Experimental

All melting points are uncorrected. The UV spectra were taken with Hitachi-323 and 340 spectrophotometers, and IR spectra with Hitachi IR-295 and 260 spectrophotometers. The NMR spectra were recorded on a JEOL MH-100 and MS on a HItachi M-60. Merck Kieselgel 60, 70—230 mesh, was used for column chromatography.

Reaction of N_b-Methoxycarbonyltryptamine (4) with 2-Chloro-2-methyl-3-butyne (2)——Tryptamine carbamate (**4**, 2.18 g, 10 mmol) in DMF (90 ml) was added to NaH (50%, 730 mg, 15 mmol) in DMF (40 ml) during 35 min under

ice cooling and the mixture was stirred for 40 min. Then 2-chloro-2-methyl-3-butyne (**2**, 1.25 g, 12 mmol)[13] in DMF (40 ml) was added during 10 min under ice cooling. The mixture was stirred for 21 h at room temperature, then poured into H_2O (250 ml). The mixture was extracted with CH_2Cl_2 and the extract was washed with H_2O and saturated NaCl solution, then dried. Removal of the solvent by evaporation left a brown oil (3.38 g) which was chromatographed on a silica gel column (40 g). Elution with CH_2Cl_2–acetone (1 : 1) gave a mixture (1.82 g) of **6**, **7**, and **8**. Further elution with the same solvent gave recovered **4** (471 mg, 22%). The first fraction was re-chromatographed on a silica gel column (30 g). Elution with AcOEt–hexane (1 : 3) gave a mixture of **6** and **7** (1.07 g, 38%). The ratio of **6** and **7** was determined from the NMR spectrum and was found to be 3 : 1. Pure samples of **6** and **7** were obtained by repeated silica gel column chromatography. Further elution with the same solvent gave **8** (644 mg, 23%).

3a-(1,1-Dimethylpropargyl)-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole (**6**): A colorless oil. UV λ_{max}^{EtOH} nm: 245, 301. IR ($CHCl_3$) cm^{-1}: 3450 (NH), 3325 (≡CH), 2100 (C≡C), 1680 (C=O). MS *m/z* (%): 284 (M^+, 18), 217 (100), ^{1}H-NMR ($CDCl_3$) δ: 1.12, 1.34 (3H, each s, *gem* CH_3), 2.04—2.36, 2.36—2.86 (2H, m, CH_2), 2.20 (1H, s, ≡CH), 2.88—3.20, 3.58—4.00 (2H, m, CH_2N), 3.70, 3.78 (total 1H, each s, CO_2Me), 4.0 (exchangeable, br, NH), 5.44, 5.48 (total 1H, each s, N–CH–N), 6.50—6.88, 7.00—7.24 (4H, m, arom H).

3a-(3,3-Dimethylallenyl)-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole (**7**): Colorless prisms, mp 105.5—106.5 °C (from acetone–hexane). UV λ_{max}^{EtOH} nm: 245, 298. IR (KBr) cm^{-1}: 3350 (NH), 1960 (C=C=C), 1695 (C=O). MS *m/z* (%): 284 (M^+, 34), 229 (100). ^{1}H-NMR ($CDCl_3$) δ: 1.68, 1.70 (3H, each s, *gem* CH_3), 2.22 (2H, t, CH_2), 3.16, 3.60 (2H, m, NCH_2), 3.68, 3.76 (total 3H, each s, CO_2Me), 4.68, 5.08 (br, NH), 6.44—7.20 (4H, m, arom H).

N_a-(1,1-Dimethylpropargyl)-N_b-methoxycarbonyltryptamine (**8**): Colorless needles, mp 90—90.5 °C (from acetone–hexane). UV λ_{max}^{EtOH} nm (ε): 226 (32300), 276^{sh} (5680), 285 (6200), 294.5^{sh} (5400). IR (KBr) cm^{-1}: 3320 (NH), 3300 (C≡CH), 1700 (C=O), 1545 (amide II). MS *m/z* (%): 284 (M^+, 39), 130 (100). ^{1}H-NMR ($CDCl_3$) δ: 1.92 (6H, s, *gem* CH_3), 2.52 (1H, s, C≡C–H), 2.90 (2H, t, J=6 Hz, CH_2), 3.44 (2H, q, J=6 Hz, NCH_2), 3.62 (3H, s, OCH_3), 4.68 (1H, br s, NH), 6.92—7.88 (5H, m, arom H). *Anal.* Calcd for $C_{17}H_{20}N_2O_2$: C, 71.80; H, 7.09; N, 9.85. Found: C, 71.81; H, 7.10; N, 9.68.

8-Acetyl-3a-(1,1-dimethylpropargyl)-1-methoxycarbonyl-1,2,3,3a-8,8a-hexahydropyrrolo[2,3-*b*]indole (9). Acetylation of 6——A mixture (504 mg) of **6** and **7** in acetic anhydride (12 ml) and pyridine (5 ml) was stirred for 51 h at room temperature and then for 4 h at 70—90 °C. Evaporation of the solvent *in vacuo* gave a residue, which was dissolved in CH_2Cl_2. The CH_2Cl_2 solution was washed with H_2O and dried. Evaporation of the solvent gave a residue (529 mg), which was recrystallized from acetone–hexane to give the acetyl derivative (**9**, 63 mg). Recrystallization from acetone–hexane gave colorless prisms, mp 148—149.5 °C. UV λ_{max}^{EtOH} nm (ε): 247.5 (7900), 276.5^{sh} (1200), 284.5^{sh} (1000). IR (KBr) cm^{-1}: 3250 (C≡C–H), 1710 (C=O), 1680 (C=O). MS *m/z* (%): 326 (M^+, 25), 217 (100). ^{1}H-NMR ($CDCl_3$) δ: 1.00, 1.32 (6H, each s, *gem* CH_3), 2.24 (1H, s, C≡C–H), 2.00—3.00 (4H, m, CH_2, N–CH_2), 2.58 (3H, s, $COCH_3$), 3.68 (3H, s, CO_2Me), 6.12 (1H, s, NCHN), 6.94—7.40 (3H, m, arom H), 7.98 (1H, d, J=8 Hz, 7-H). *Anal.* Calcd for $C_{19}H_{22}N_2O_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 70.02; H, 6.77; N, 8.56.

2-(1,1-Dimethylpropargyl)-N_b-methoxycarbonyltryptamine (14)——A mixture of **6** (200 mg, 0.7 mmol) in EtOH (9 ml) and concentrated HCl (3 ml) was refluxed for 10 h under an Ar atmosphere. The mixture was poured into H_2O (50 ml) and extracted with CH_2Cl_2. The extracts were washed with sat. $NaHCO_3$ solution, H_2O, and sat. NaCl solution, then dried. Evaporation of the solvent *in vacuo* gave a dark brown residue (181 mg), which was separated by silica gel preparative thin layer chromatography (TLC) to give the 2-propargyl derivative (**14**, 16 mg, 8%) and the starting material (**6**, 81 mg, 41%).

14: A colorless oil. UV λ_{max}^{EtOH} nm: 222, 276^{sh}, 284.5, 292^{sh}. IR ($CHCl_3$) cm^{-1}: 3450 (NH), 3300 (C≡CH), 1710 (C=O), 1520 (amide II). MS *m/z* (%): 284 (M^+, 20), 196 (100). ^{1}H-NMR ($CDCl_3$) δ: 1.74 (6H, s, *gem* CH_3), 2.46 (1H, s, C≡CH), 3.0—3.24 (2H, m, CH_2), 3.32—3.64 (2H, m, NCH_2), 3.64 (3H, s, OCH_3), 4.82 (1H, br s, NH, exchangeable), 7.00—7.64 (4H, m, arom H), 8.30 (1H, br s, NH, exchangeable). Reaction of the 3a-propargyl derivative with CF_3COOH in CH_2Cl_2 resulted in recovery of the starting material together with a small amount of unknown compounds.

3a-(1,1-Dimethylallyl)-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indole (10): Reduction of 6——A solution of the 3a-propargyl derivative (**6**, 1.27 g, 4.5 mmol) in benzene (15 ml) was hydrogenated in the presence of Lindlar catalyst (60 mg) and quinoline (0.12 ml) under an H_2 atmosphere (1 atm pressure) for 5.5 h. The catalyst was removed and washed with CH_2Cl_2. The combined filtrate was evaporated *in vacuo* to give a residue which was chromatographed on a silica gel column to give the 1,1-dimethylallyl derivative (**10**, 1.17 g, 92%) as colorless oil. Recrystallization from hexane gave colorless fine needles (950 mg). Repeated recrystallization from MeOH gave colorless prisms, mp 89—90.5 °C. UV λ_{max}^{EtOH} nm (ε): 244.5 (7800), 300 (3000). IR (KBr) cm^{-1}: 3340 (NH), 1690 (CO). MS *m/z* (%): 286 (M^+, 10), 217 (100). ^{1}H-NMR ($CDCl_3$) δ: 1.00, 1.08 (6H, each s, *gem* CH_3), 1.84—2.48, 2.76—3.12 (4H, 2×CH_2), 3.66, 3.76 (3H, each s, OCH_3), 4.58 (1H, br s, NH), 5.04 (1H, d, J=18 Hz, $H\!>\!C\!=\!C\!<^{H}_{H}$), 5.08 (1H, d, J=10 Hz, $H\!>\!C\!=\!C\!<^{H}_{H}$), 5.22, 5.88 (1H, each s, NCHN), 6.02 (1H, dd, J=10 and 18 Hz, $H\!>\!C\!=\!C\!<^{H}_{H}$), 6.44—6.84, 6.96—7.20 (4H, m, arom H). *Anal.* Calcd for $C_{17}H_{22}N_2O_2$: C, 71.30; H, 7.74; N, 9.78. Found: C, 71.35; H, 7.73; N, 9.74.

2-(1,1-Dimethylallyl)-N_b-methoxycarbonyltryptamine (11)——A mixture of **10** (101 mg, 0.35 mmol) in CH_2Cl_2 (5 ml) and CF_3COOH (5 ml) was stirred for 2.5 h at room temperature under an Ar atmosphere. The mixture was poured into sat. $NaHCO_3$ solution (50 ml) and extracted with CH_2Cl_2. The extracts were washed with H_2O and sat. NaCl solution, then dried. Evaporation of the solvent *in vacuo* gave a yellow oil (131 mg), which was separated by silica gel preparative TLC (EtOAc : hexane = 1 : 3) to give a mixture of **11** and **12** (45 mg, fraction 1), and **13** (49 mg, 35%). Further separation of fraction 1 by alumina preparative TLC (CH_2Cl_2) gave pure **11** and **12** as an oil. The yields of **11** and **12** were calculated from the NMR spectrum of fraction 1 based on the integral ratio of *gem*-dimethyl signals of the compounds: **11** (15%) and **12** (30%).

11: A colorless oil. UV λ_{max}^{EtOH} nm: 225, 284, 291.5^{sh}. IR ($CHCl_3$) cm^{-1}: 3450 (NH), 1710 (CO), 1510 (amide II). MS *m/z* (%): 286 (M^+, 24), 198 (100). ^{1}H-NMR ($CDCl_3$) δ: 1.52 (6H, s, *gem* CH_3), 3.04 (2H, t-like, CH_2), 3.42 (2H, q, NCH_2), 4.80 (1H, br s, NH), 5.12 (1H, d, J = 10 Hz, $-C=CH_2$), 5.12 (1H, d, J = 18 Hz, $C=CH_2$), 6.12 (1H, dd, J = 10 and 18 Hz, $-CH=C<^{H}_{H}$), 7.00—7.36, 7.44—7.60 (4H, m, arom H), 7.96 (1H, br s, NH).

12: A colorless oil. UV λ_{max}^{EtOH} nm: 227, 292. IR (neat) cm^{-1}: 1710 (C=O), 1530 (amide II). MS *m/z* (%): 286 (M^+, 34), 130 (100). ^{1}H-NMR ($CDCl_3$) δ: 1.76, 1.80 (6H, each s, *gem* CH_3), 2.92 (2H, t, J = 8 Hz, CH_2), 3.48 (2H, q, J = 8 Hz, N_b-CH_2), 3.64 (3H, s, OCH_3), 4.62 (2H, d, J = 6 Hz, N_a-CH_2), 4.62 (1H, s, NH), 5.34 (1H, t, J = 6 Hz, $CH=C<$), 6.88 (1H, s, 2-H), 7.00—7.36, 7.48—7.64 (4H, arom H). This sample was identical with a sample obtained by N_a-prenylation of N_b-methoxycarbonyltryptamine (IR, NMR, TLC).

CF_3COOH Adduct (**13**): A colorless oil. UV λ_{max}^{EtOH} nm: 225.5, 275^{sh}, 282, 292^{sh}. IR ($CHCl_3$) cm^{-1}: 1780 (C=O), 1720 (C=O), 1520 (amide II). ^{1}H-NMR ($CDCl_3$) δ: 1.62, 1.66 (6H, each s, *gem* CH_3), 2.04—2.32 (2H, m, CH_2–C–OCO), 2.64—3.20 (4H, m, 2 × CH_2), 3.36—3.60 (2H, q, N–CH_2), 3.66 (3H, s, OCH_3), 4.80 (1H, br s, NH), 6.88—7.40 (4H, m, arom H), 8.14 (1H, br s, NH). Similar reaction of **10** under various acidic conditions gave the following results. CF_3COOH-room temperature 2 h; **11** (14%), **12** (27%), **13** (26%). CF_3COOH–CH_2Cl_2 (1 : 3)-room temperature-2 h; **11** (11%), **12** (28%), **13** (29%). AcOH-60 °C-6 h; **11** (10%), **12** (53%).

***N*-Prenylation of N_b-Methoxycarbonyltryptamine**——N_b-Methoxycarbonyltryptamine (**4**, 1.00 g, 4.6 mmol) in DMF (15 ml) was added to a suspension of NaH (52.9% in oil, 304 mg, 6.0 mmol) in DMF (5 ml) under ice cooling and the whole was stirred for 40 min. 3,3-Dimethylallyl bromide (1.04 g, 7.0 mmol) was added, and the mixture was stirred for 1 h at room temperature, poured into H_2O (100 ml) and extracted with CH_2Cl_2. The extracts were washed with H_2O and sat. NaCl solution, then dried. Evaporation of the solvent *in vacuo* gave a residue (1.38 g) which was chromatographed on a silica gel column to give **12** (628 mg, 48%) and the N_a, N_b-diprenyl derivative (369 mg, 23%).

The N_a-prenyl derivative was identical with the sample obtained above (NMR, IR, TLC).

The N_a, N_b-diprenyl Derivative: A yellow oil. UV λ_{max}^{EtOH} nm: 227, 292. IR (CCl_4) cm^{-1}: 1700 (C=O) no amide II band. MS *m/z* (%): 354 (M^+, 33), 198 (80), 130 (100).

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