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# A Facile Route to 2-Substituted Indoles

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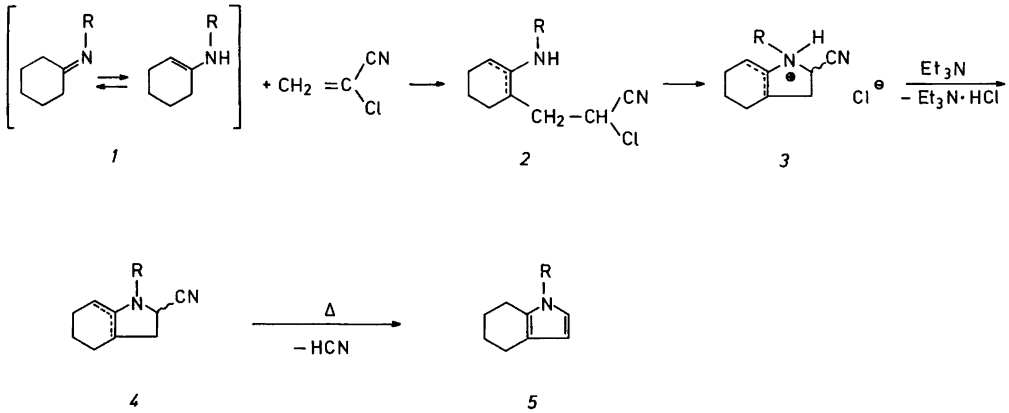
Imines, derived from cyclohexanone and alkylamines, react with α-chloroacrylonitrile in the presence of triethylamine to give products which upon pyrolysis afford 1-alkyl-4,5,6,7-tetrahydroindoles. Substitution at the 2-position of these compounds followed by catalytic dehydrogenation (Pd/C) leads to 2-substituted indoles. Thus, the Mannich base 2-dimethylaminomethyl-1-methyl-4,5,6,7-tetrahydroindole serves as an intermediate in the syntheses of 1-methylindol-2-ylacetonitrile and 2-amino-3-(1-methylindol-2-yl)propionic acid (1-methylisotryptophan).

Synthesis of 2-substituted indoles is difficult because electrophilic substitution of indoles normally proceeds at the 3-position. By alternative routes indole-2-carboxylic acid [1] and 2-dimethylaminomethylindole (isogramine) [2] are reasonably easily available and have been used for the preparation of isotryptophan.[2] In the present work a simple synthesis of 1-alkyl-4,5,6,7-tetrahydroindoles is presented. Being pyrroles, these can be substituted at the 2-positions; subsequent catalytic dehydrogenation of the substitution products affords 2-substituted indoles. The procedure is exemplified by syntheses of 1-methylisotryptophan and 1-methylindol-2-ylacetonitrile, in both cases with the Mannich base 2-dimethylaminomethyl-1-methyl-4,5,6,7-tetrahydroindole serving as a key intermediate.

## RESULTS

Tetrahydroindoles *5* could be prepared in good yields from cyclohexanone imines *1* and α-chloroacrylonitrile, Scheme 1. The reactions were performed in acetonitrile with an equivalent amount of triethylamine added. The residue, after removal of triethylamine hydrochloride and solvent, was subjected to pyrolysis in vacuum, whereby the product distils; hydrogen cyanide is eliminated and collected in a cold trap. In previous studies [3,4] enamines derived from cyclohexanone and secondary amines were found to react with α-chloroacrylonitrile to produce quaternary hexahydroindolium chlorides. Since unconjugated imines contain a few percent of the tautomeric enamines,[5] hexahydroindolium chlorides *3* are




*1* *2* *3* *4* *5*

*Scheme 1. a*, R = $CH_3$; *b*, R = cyclohexyl.

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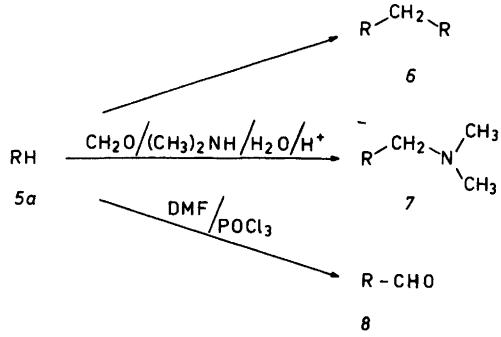
most likely similarly formed in the reaction with imines, the first step being alkylation of the enamine form of *1* to give the enamines *2*. Deprotonation of the intermediates *3* then leads to the hexahydroindoles *4*. The pyrolysis takes place in two stages: about half of the product, *5*, distils only slightly above its boiling point, while the rest is formed at considerably higher temperature. Probably the pyrroline isomer of *4* loses hydrogen cyanide readily, because an aromatic nucleus is directly generated, whereas the other isomer of *4* requires higher temperature or undergoes elimination only after isomerization to the pyrroline.

The reactions of imines with α-chloroacrylonitrile are strongly exothermic. Best yields are obtained when the temperature is kept moderately low. High temperature probably causes loss of the olefin reactant due to polymerization. Triethylamine hydrochloride was isolated in nearly quantitative yield, whereas the yield of pure, distilled tetrahydroindoles *5a* and *5b* were 79 and 70 %, respectively.

α-Chloroacrylonitrile is commercially available. For the present work, however, a laboratory synthesis was employed, in which dehydrohalogenation of α,β-dichloropropionitrile was effected simply by stirring with an equivalent amount of cold aqueous sodium hydroxide.

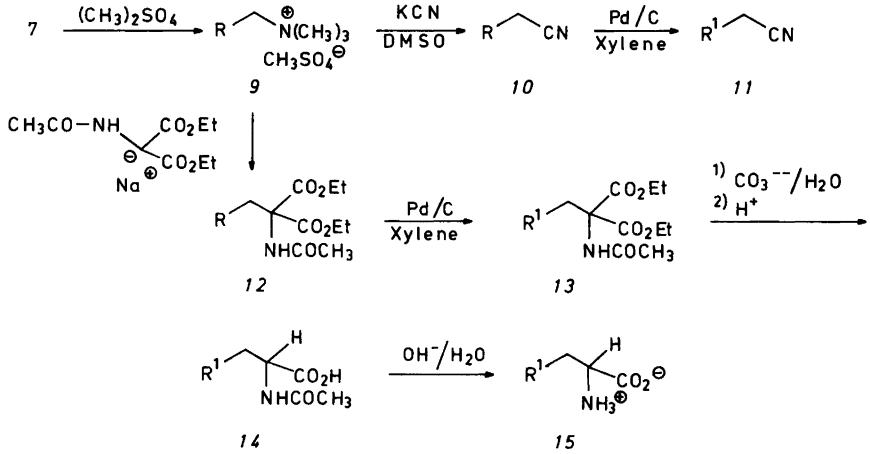
The utility of tetrahydroindoles in synthesis of 2-substituted indoles was demonstrated by the synthetic sequences presented in Schemes 2 and 3. The method for preparation of Mannich bases, in which the amine is introduced as its hydrochloride,




*Scheme 2.* R = 1-methyl-4,5,6,7-tetrahydroindol-2-yl.

applicable to, *e.g.*, 1-methylpyrrol,[6] failed in the case of the tetrahydroindole *5a*. From several attempts with aqueous formaldehyde and dimethylamine hydrochloride only bis-(tetrahydroindolyl)methane *6* was isolated (40 %) and characterized; examination by mass spectrometry revealed the additional presence of more complicated condensation products. However, replacing most of the amine hydrochloride by aqueous amine resulted in nearly quantitative formation of the desired Mannich base *7*. Apparently the tetrahydroindole is more nucleophilic than 1-methylpyrrole, so that dimethylamine must be present in free form to compete in the Mannich reaction.

Similarly to gramine,[7,8] the Mannich base *7* proved useful for synthesis of compounds with extended side-chains (Scheme 3). In order to obtain a good leaving grop the base was methylated with




*Scheme 3.* R = 1-methyl-4,5,6,7-tetrahydroindol-2-yl; $R^1$ = 1-methylindol-2-yl.

dimethyl sulfate in tetrahydrofuran solution.[7] The quaternary salt *9* precipitated in nearly quantitative yield. Conversion to the nitrile *10* (80 % yield) was carried out in dimethyl sulfoxide at room temperature. In other solvents (water, ethanol and dimethylformamide) large amounts of the coupling product *6* (Scheme 2), were formed. An analogous compound arises from 1-methylgramine methiodide in boiling aqueous base.[9] Dehydrogenation of the nitrile *10*, producing 1-methylindol-2-ylacetonitrile, *11*, takes place on treatment with palladium on charcoal in refluxing xylene. The yield is limited to about 65 %, probably owing to concomitant reduction of the cyano group. The major by-product, possessing molecular weight 325 according to mass spectrometry, is possibly formed by condensation of the primary product, *11*, and the corresponding amine with elimination of ammonia. A minor by-product proved to be 2-ethyl-1-methylindole. This obstacle could, in principle, be circumvented by performing the dehydrogenation at an earlier stage, *viz.* on the Mannich base 7. Unfortunately, however, the palladium catalyst seems incompatible with this amine. A similar, yet more serious, difficulty was encountered in dehydrogenation of the aldehyde *8* (Scheme 2) obtained by Vilsmeier-formylation in 74 % yield. The expected indole aldehyde could not be detected in the product mixture by mass spectrometry but the presence of 1-methylindole shows that dehydrogenation does, in fact, take place. Dehydrogenation of the oxime (see Experimental) was hardly more successful, the product mixture containing (GLC-MS) 1-methylindole, 1,2-dimethylindole, 2-cyano-1-methylindole, and only a small fraction of the indole aldehyde oxime. An imidazolidine derivative (see Experimental) could not be dehydrogenated by the palladium catalyst. The aldehyde derivatives might be useful in connection with other dehydrogenation techniques. With the palladium catalyst the tetrahydroindoles *5* are quantitatively converted into the corresponding 1-alkylindoles [10] (see Experimental).

The synthesis of 1-methylisotryptophan, *15*, followed a series of steps analogous to those employed for the syntheses of tryptophan [8] and isotryptophan,[2] except for the dehydrogenation step (*12–13*). This process is rapid and quantitative. The aromatization step was introduced as early as possible because indoles are more resistant to oxidation and mostly possess better crystallization properties then pyrroles. The yield of amino acid *15* was 37 %, based on the tetrahydroindole *5a*.

## EXPERIMENTAL

Mass spectra were recorded on a VG Micromass 70 70 F instrument; IP 70 eV, ion source temp. 220 °C. $^1$H NMR spectra were recorded on Varian 360, Varian HA 100 and Bruker HXE 90 instruments. Melting and boiling points are uncorrected.

*α-Chloroacrylonitrile*, α,β-Dichloropropionitrile,[11] 487 g (3.93 mol), was vigorously stirred with a solution of NaOH, 159 g, in 500 ml of water at 10 °C for 1.5 h. The layers were separated and the aqueous phase was washed with 2 × 30 ml of ether. The combined organic phases were dried over $Na_2SO_4$. Distillation gave 285 g (83 %) of pure (GLC, NMR) α-chloroacrylonitrile, b.p. 87.0–87.7 °C.

*Cyclohexylidenemethylamine*, *1a*, was prepared by condensation of cyclohexanone and methylamine with KOH as dehydrating agent. The distilled material contained about 20 % of cyclohexanone (GLC).

*Cyclohexylidenecyclohexylamine*, *1b*, was prepared by condensation of cyclohexanone and cyclohexylamine, with removal of the water of reaction by azeotropic distillation with benzene. Various methods for synthesis of ketimines are evaluated in Ref. 12.

*1-Methyl-4,5,6,7-tetrahydroindole*, 5a. To a stirred and nitrogen-swept solution of cyclohexylidenemethylamine, 176 g of 80 % pure material (~1.27 mol), and triethylamine, 154 g (1.5 mol), in acetonitrile, 1 l, α-chloroacrylonitrile, 111 g (1.27 mol) was added dropwise during 30 min. The temperature of the reaction mixture was kept at 25–30 °C by cooling. Precipitation of triethylamine hydrochloride commenced after a few min. The reaction mixture was stirred for an additional hour at room temperature, cooled to 5 °C and filtered, giving triethylamine hydrochloride in 86 % yield. To remove all of the hydrochloride, somewhat soluble in acetonitrile, the filtrate was evaporated in vacuum and the residue dissolved in 500 ml of ether. The solution was kept overnight at 5 °C, filtered and evaporated in vacuum. The residue was pyrolyzed in vacuum (2.6–4.0 kPa). The heating required caused the product to reflux. After the evolution of gas (HCN) had ceased the product was distilled. Yield 135 g (79 %), b.p. 93–95 °C/2.3 kPa. MS, *m/z* (% rel.int.): 135 (55, M), 134 (25), 133 (3), 132 (7), 131 (4), 130 (4), 107 (100, M – $C_2H_4$). $^1$H NMR data are given in Ref. 10.

*1-Cyclohexyl-4,5,6,7-tetrahydroindole*, *5b*, was prepared in the same way as *5a*. On a 0.1 mol scale the yield was 70 % of 99 % pure material (GLC), b.p. ~115 °C/80 Pa (lit.[13]:111–113 °C/0.13 Pa), m.p. (MeOH) 38–39 °C. Anal. $C_{14}H_{21}N$: C,H,N. $^1$H NMR (60 MHz, $CCl_4$): δ 1.0–2.7 (19 H, unresolved), 5.68 (1H, d, *J* 2.7 Hz), 6.35 (1H, d,

*J* 2.7 Hz), in agreement with published values.[13]

*1-Cyclohexylindole.* A solution of *5b*, 20.3 g (0.1 mol), in mesitylene, 70 ml, with 5 % Pd/C, 0.4 g, added was refluxed with nitrogen flushing for 24 h, when GLC showed dehydrogenation to be complete. The catalyst was filtered off and the product distilled. Yield 16.7 g (84 %), b.p. 112–115 °C/80 Pa, m.p. ~30 °C. Anal. $C_{14}H_{17}N$: C,H,N. MS, *m/z* (% rel. int.): 199 (67, M), 184 (2, M–$CH_3$), 170 (4, M–$C_2H_5$), 156 (34, M–$C_3H_7$), 143 (4), 130 (10), 117 (100, M–$C_6H_{10}$), 90 (13), 89 (12), 55(11), 43 (8). $^1$H NMR (60 MHz, $CDCl_3$): $\delta$ 1.0–2.5 (10 H, unresolved), 3.9–4.5 (1H, broad s), 6.50 (1H, d, *J*3,4 Hz), 6.7–7.7 (5H, m).

*Bis(1-methyl-4,5,6,7-tetrahydroindol-2-yl)methane*, 6. A mixture of dimethylamine hydrochloride, 4.3 g (0.053 mol) and 40 % formalin, 4.0 g (0.053 mol) was added dropwise to 1-methyl-4,5,6,7-tetrahydroindole, *5a*, 6.75 g (0.050 mol) with stirring during 10 min. After further stirring for 45 min at 30 °C (ice cooling) the reaction mixture was made alkaline with 15 % aqueous NaOH and extracted with 3 × 15 ml of ether. The ether extract was dried over $MgSO_4$ and evaporated in vacuum, leaving a viscous, dark oil, which on treatment with cold ethanol gave a yellow crystalline material. Recrystallization from ethanol afforded the colourless title compound. Yield 2.92 g (41 %), m.p. 93–95 °C. Anal. $C_{19}H_{26}N_2$: C,H,N. MS, *m/z* (% rel.int.): 282 (100, M), 281 (45), 267 (7), 254 (8), 253 (17), 148 (58), 147 (60), 146 (23), 145 (10), 144 (14). $^1$H NMR (100 MHz, $CDCl_3$): $\delta$ 1.8 (8H, m), 2.5 (8H, m), 3.39 (6H, s), 3.83 (2H, s), 5.64 (2H, s).

*2-Dimethylaminomethyl-1-methyl-4,5,6,7-tetrahydroindole*, 7. A mixture of conc. hydrochloric acid, 1.5 ml (0.018 mol), 40 % aqueous dimethylamine, 8.2 g (0.073 mol) and 26 % formalin, 4.3 g (0.037 mol) was added dropwise to 1-methyl-4,5,6,7-tetrahydroindole, *5a*, 5.0 g (0.037 mol) with stirring under nitrogen. The temperature was kept at 30 °C during the weakly exothermic reaction. The reaction mixture was left at room temperature for 20 h, made alkaline with 33 % NaOH, 2.2 ml (0.025 mol), and extracted successively with 20, 10, and 5 ml of ether. The ether extract was dried over $Na_2SO_4$ and evaporated in vacuum. The crude product thus obtained was pure according to NMR, whereas the residue after distillation contained some of the coupling product *6*. Yield of distilled product 6.0 g (85 %), b.p. 70.0–70.5 °C/13 Pa. Anal. $C_{12}H_{20}N_2$: C,H,N. MS, *m/z* (% rel. int.): 192 (20, M), 191 (1), 148 (100, M–$N(CH_3)_2$). $^1$H NMR (60 MHz, $CDCl_3$): $\delta$ 1.8 (4H, m), 2.20 (6H, s), 2.5 (4H, m), 3.30 (2H, s), 3.45 (3H, s), 5.78 (1H, s).

*1-Methyl-4,5,6,7-tetrahydroindole-2-aldehyde*, 8, was prepared by the procedure for indole-3-aldehyde.[14] From 27.9 g (0.207 mol) of 1-methyl-4,5,6,7-tetrahydroindole, *5a*, 24.9 g (74 %) of recrystallized aldehyde was obtained, m.p. (EtOH) 67.5–68.5 °C. Anal. $C_{10}H_{13}NO$: C,H,N. MS, *m/z* (% rel. int.): 163 (100, M), 162 (32), 135 (91), 134 (34), 107 (25). $^1$H NMR (100 MHz, $CCl_4$): $\delta$ 1.8 (4H, m) 2.5 (4H, m), 3.73 (3H, s), 6.42 (1H, s), 9.22 (1H, s).

*Oxime of aldehyde 8* crystallized from a solution of equimolar amounts of the aldehyde *8*, hydroxylammonium chloride and sodium acetate in water. M.p. (50 % aqueous EtOH) 158–160 °C. Anal. $C_{10}H_{14}N_2O$: C,N,N. $^1$H NMR indicates the presence of two isomers. MS, *m/z* (% rel.int.): 178 (100, M), 161 (40), 150 (52), 135 (27), 134 (30), 133 (45), 132 (43).

*1,3-Dimethyl-2-(1-methyl-4,5,6,7-tetrahydroindol-2-yl)-imidazolidine.* A mixture of *N,N'*-dimethylethylenediamine, 5.0 g (0.057 mol), aldehyde *8*, 5.8 g (0.036 mol) and *p*-toluenesulfonic acid, 300 mg, was refluxed under nitrogen for 2 h, cooled to room temperature and then mixed with light petroleum, 50 ml, and anhydrous $K_2CO_3$, 10 g. After standing at 5 °C for 12 h the drying agent was filtered off and the filtrate evaporated in vacuum at 70 °C, to give 7.1 g (85 %) of crude product, which was purified by chromatography on silica (light petroleum, ethyl acetate, triethylamine 15:15:1). M.p. 51–55 °C. Found: C 72.06; H 9.72; N 17.37. Calc. for $C_{14}H_{23}N_3$: C 72.06 H 9.93 N 18.01. MS, *m/z* (% rel.int.): 233 (52, M), 232 (27), 190 (69), 189 (39), 175 (34), 99 (100).

*(1-Methyl-4,5,6,7-tetrahydroindol-2-ylmethyl)-trimethylammonium methylsulfate*, 9. A solution of 2-dimethylaminomethyl-1-methyl-4,5,6,7-tetrahydroindole, 7, 20.0 g (0.104 mol), in freshly distilled, peroxide free tetrahydrofuran, 150 ml, was added dropwise with stirring under nitrogen during 20 min to a solution of dimethyl sulfate, 10.9 ml (0.115 mol), in tetrahydrofuran, 50 ml, initially at 5 °C. The temperature of the reaction mixture was kept below 15 °C. After standing at 5 °C for 3.5 h the mixture was filtered under nitrogen. The crystalline crude product was thoroughly washed with ice-cold, dry ether. Yield 32.0 g (97 %). Elemental analysis was not performed because the salt deteriorates within a few h.

*1-Methyl-4,5,6,7-tetrahydroindol-2-ylacetonitrile*, 10. Freshly prepared quaternary amine *9*, from the Mannich base 7, 2.00 g (10.4 mmol), was added in small portions with stirring under nitrogen to a solution of potassium cyanide, 1.0 g (15.6 mmol) in dimethyl sulfoxide, 100 ml, at room temperature. The homogeneous reaction mixture was left for 20 h, water, 350 ml, was added dropwise with stirring. The mixture was seeded with a crystal of the product when it became milky. Filtration, followed by drying in vacuum, gave 1.45 g (80 %) of crude product, m.p. 71–75 °C. Recrystallization

from 60 % aqueous MeOH afforded an analytically pure sample, m.p. 78.5–79.0 °C. Anal. $C_{11}H_{14}N_2$: C,H,N. MS, *m/z* (% rel.int.): 174 (51, M), 173 (22), 148 (5, M–CN), 146 (100, M–$C_2H_4$), 134 (15, M–$CH_2CN$), 133 (9), 132 (9), 131 (7), 130 (3). $^1$H NMR (60 MHz, $CCl_4$): $\delta$ 1.8 (4H, m), 2.5 (4H, m), 3.43 (3H, s), 3.68 (2H, s), 5.92 (1H, s).

*1-Methylindol-2-ylacetonitrile*, 11. The tetrahydro derivative *10*, 249 mg, and 10 % Pd/C, 155 mg, were refluxed for 17 h in xylene, 50 ml, with nitrogen flushing. The crude product, obtained after removal of catalyst and solvent, was recrystallized from 70 % aqueous MeOH. Yield 164 mg (67 %), m.p. 80–89 °C. Chromatography on silica (AcOEt, light petroleum 3:1) gave 120 mg (54 %) of pure product, m.p. 92.0–92.5 °C. Anal. $C_{11}H_{10}N_2$: C,H,N. MS, *m/z* (% rel.int.): 170 (100, M) 169 (62), 144 (27, M–CN). $^1$H NMR (90 MHz, $CDCl_3$): $\delta$ 3.63 (3H, s), 3.78 (2H, s), 6.49 (1H, s), 6.95–7.35 (3H, m), 7.56 (1H, dd, *J*7 and 1Hz).

*Ethyl 2-acetamino-2-carboethoxy-3-(1-methyl-4,5,4,5,6,7-tetrahydroindol-2-yl)-propionate*, 12. Sodium, 2.40 g (0.104 mol) and diethyl acetaminomalonate, 22.5 g (0.104 mol), were refluxed with vigorous stirring in freshly distilled, dry dioxan, 163 ml, for 3.5 h. To the resulting solution, kept under nitrogen at 95 °C, was added freshly prepared quaternary amine *9*, from the Mannich base *7*, 20.0 g. The mixture was stirred for 18 h at 95 °C and then refluxed for 3 h. The inorganic material was filtered off from the hot mixture and the solvent evaporated in vacuum. The crude material thus obtained was recrystallized from MeOH to give 23.5 g (62 %) of pure product (MS), m.p. 148.5–149.5 °C. A second crystallization raised the m.p. to 151.5–152.0 °C. Anal. $C_{19}H_{28}N_2O_5$: C,H,N. MS, *m/z* (% rel.int.): 364 (3, M), 305 (3, M–$H_2NCOCH_3$), 148 (100). $^1$H NMR (60 MHz, $CDCl_3$): $\delta$ 1.21 (6H, t) 1.7 (4H, m), 1.97 (3H, s), 2.4 (4H, m), 3.20 (3H, s), 3.61 (2H, s), 4.22 (4H, q), 5.46 (1H, s).

*Ethyl 2-acetamino-2-carboethoxy-3-(1-methylindol-2-yl)-propionate*, 13. The tetrahydro compound *12*, 14.6 g, 10 % Pd/C, 0.5 g, and xylene, 125 ml, were refluxed with nitrogen flush for 20 h. After filtering off the catalyst from the *hot* mixture, most of the product crystallized on cooling to 5 °C. A second crop was obtained by concentrating the solution to one-tenth of its volume. Yield 13.7 g (95 %), m.p. 148.5–150.0 °C. Recrystallization from MeOH raised the m.p. to 151.5–152.0 °C. Anal. $C_{19}H_{24}N_2O_5$: C,H,N. MS, *m/z* (% rel.int.): 360 (8, M), 301 (26, M–$H_2NCOCH_3$), 144 (100). $^1$H NMR (90 MHz, $CDCl_3$): $\delta$ 1.26 (6H, t), 1.97 (3H, s). 3.56 (3H, s), 3.87 (2H, s), 4.26 (4H, q), 6.11 (1H, s), 6.9–7.6 (4H, m).

*2-Acetamino-3-(1-methylindol-2-yl)-propionic acid*, *14*, was prepared from compound *13* by the method for synthesis of the corresponding indolyl compound.[2] Yield of crude product 95 %, m.p. 196–198 °C. An analytically pure sample was obtained by recrystallization from 50 % aqueous EtOH. M.p. 199–201 °C. Anal. $C_{14}H_{16}N_2O_3$: C,H,N. MS, *m/z* (% rel.int.): 260 (9, M), 242 (3, M–$H_2O$), 201 (18, M–$H_2NCOCH_3$), 144 (100).

*2-Amino-3-(1-methylindol-2-yl)-propionic acid*, 15. The acetyl derivative *14*, 6.0 g, was boiled with NaOH, 9.6 g, in water, 80 ml, for 24 h. The resulting solution was diluted with water, 80 ml, cooled on an ice-bath, and acidified with conc. hydrochloric acid, 18 ml. The precipitate, heavily contaiminated with inorganic material, was filtered off and extracted with 2 l of MeOH. Evaporation of the extract yielded 5.2 g of crude product. Recrystallization from 800 ml of 50 % aqueous EtOH gave 3.2 g (67 %) of the pure amino acid, m.p. (decomp.) 233–234.5 °C. Anal. $C_{12}H_{14}N_2O_2$: C,H,N. MS, *m/z* (% rel.int.): 218 (13, M), 201 (2), 144 (100).

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