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CARBON TRANSFER REACTIONS WITH HETEROCYCLES-IV[1]. SYNTHETIC EQUIVALENCE OF PERHYDROOXAZINES WITH CARBONYL COMPOUNDS. A FACILE SYNTHESIS OF STREPTINDOLE AND ANALOGUES

HARJIT SINGH* and KAMALJIT SINGH

Department of Chemistry, Guru Nanak Dev University,
Amritsar - 143 005, India

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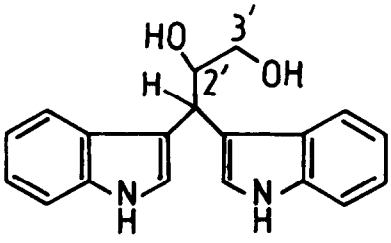
Abstract - Oxazolidines and tetrahydro-(2H)-1,3-oxazines transfer their C(2) units at the carbonyl group oxidation level to indoles and provide diindolylmethane derivatives. 2-Acetoxymethyl-4,4,6-trimethyltetrahydro-(2H)-1,3-oxazine and indole give streptindole.

Diindolylmethane moiety constitutes the structural unit of 1,1-di(1H-3-indolyl) propane-2',3'-diol 1 isolated[2] from Balansia epichloe' and 2,2-di(1H-3-indolyl) ethylacetate (streptindole) 2, a genotoxic metabolite isolated from intestinal bacteria. The synthesis[3,4] of these compounds, to have their sufficient amounts and their analogs for biological studies, is of importance. The use of conventional acid catalysed condensations of carbonyl compounds[5] or Schiff's bases[6] with indole are plagued by drawbacks of practicability, nonavailability of desired additional functionality and formation of polymeric products. Recently, carbon transfer reactions of tetrahydrofolate models-imidazolidines[7] have advantageously been used for incorporating an sp^3 hybridized carbon inbetween two indole moieties. In continuation of our interest in one carbon unit transfer reactions with perhydro-1,3-heterocycles,[1,8] here, we report synthesis of streptindole 2 and 15 i.e., 2'-deoxy compound 1, and their analogues by acid catalysed transfer of appropriate C-2 carbon units of oxazolidines and tetrahydro-(2H)-1,3-oxazines to indoles[9].

3-Phenyloxazolidine 3a reacts with indole/1-methyl indole in refluxing acetonitrile : acetic acid (10:1) to furnish di(1H/1-methyl-3-indolyl)methane



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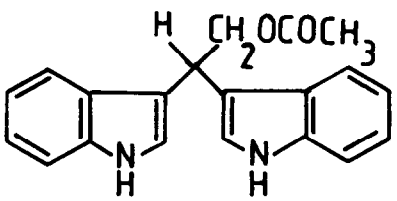

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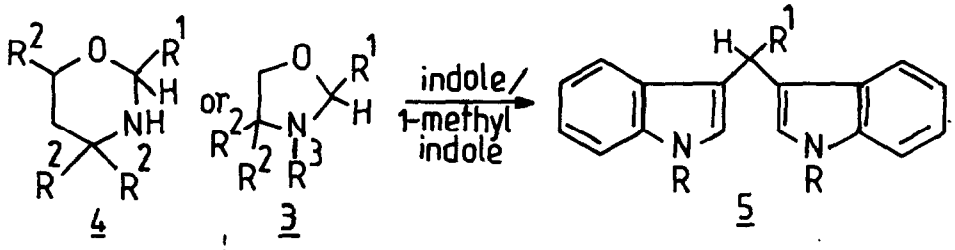
5a/5d (Table). Similarly, 2-phenyloxazolidines 3b/3c and 2-methyloxazolidine 3d with indole furnish 1,1-di(1H-3-indolyl)phenylmethane 5b and 1,1-di(1H-3-indolyl) ethane 5c respectively.

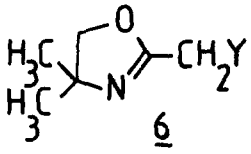
For the synthesis of streptindole and functionalized diindolylmethane derivatives, 2-hydroxymethyl/acetoxymethyl/carbethoxymethyl oxazolines 6, precursors of oxazolidines required for carbon transfer reactions, could not be obtained smoothly by the condensations[10] of glycolic, acetylglycolic and half ethyl esters of malonic-acids with 2-amino-2-methylpropan-1-ol. 4,4,6-Trimethyl-5,6-dihydro-(4H)-1,3-oxazines possessing such functionalized chains at C(2) are synthesized from diols and nitriles and are easily reduced with sodium borohydride to corresponding perhydro-1,3-oxazines 4. The carbonyl character of 4 has been amply demonstrated[12]. By the same argument as was advanced for oxazolidines[8], tetrahydro-(2H)-1,3-oxazines 4 could also function as carbon transfer reagents.



4 3 5

	R^1	R^2	R^1	R^2	R^3
a	H	H	H	H	C_6H_5
b	C_6H_5	H	C_6H_5	CH_3	H
c	C_6H_5	CH_3	C_6H_5	CH_3	CH_3
d	CH_3	CH_3	CH_3	H	C_6H_5

	R	R^1
a	H	H
b	H	C_6H_5
c	H	CH_3
d	CH_3	H
e	CH_3	CH_3
f	CH_3	C_6H_5



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Y = OH, OAc, $COOC_2H_5$

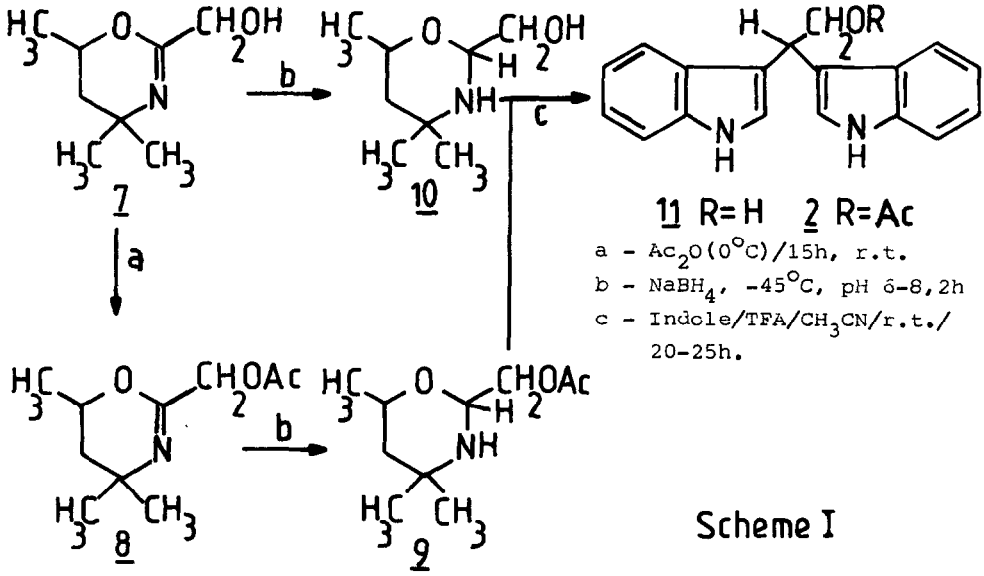
Table Reactions of indoles with 3 and 4

Reagent	Product	Time(h)	Yield(%)
3a/4a	5a	$4.0^a/3^a$	55/70
3b/3c/4b/4c	5b	$18^a/8^c/10^a/12^c$	55/53/65/66
3d/4d	5c	$0.25^b/24^c$	25/48
3a/4a	5d	$2.5^a/2.0^a$	57/60
4d	5e	$3\text{-}4^c$	48
4c	5f	7^c	80

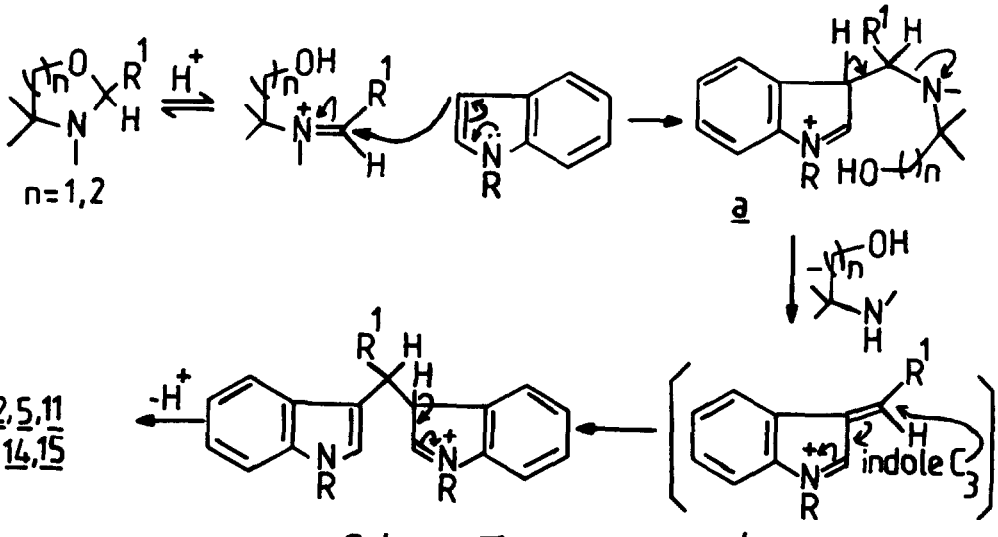
Reactions run in acetonitrile in the presence of, a - AcOH (reflux), b - TFA (r.t.), c - TFA (reflux).

1,3-Oxazine 4a reacts with indole and 1-methylindole in refluxing acetonitrile : acetic acid (10:1) to furnish 5a and 5d (Table). Likewise, 1,3-oxazines 4b/4c and 4d with indole/1-methylindole furnish 5b/5f and 5c/5e respectively. It is apparent from these results (Table) that tetrahydro-(2H)-1,3-oxazines are even more efficient carbon transfer reagents than oxazolidines[1].

2-Acetoxymethyl-4,4,6-trimethyltetrahydro-(2H)-1,3-oxazine 9 reacts with indole (Scheme I) to furnish streptindole 2. 9 has been obtained by sodium borohydride reduction of 5,6-dihydro-(4H)-1,3-oxazine 8 formed by acetylation of 2-hydroxymethyl-4,4,6-trimethyl-5,6-dihydro-(4H)-1,3-oxazine 7 which is obtained in an exothermic condensation of 2-methyl-2,4-pentanediol and freshly prepared glycolonitrile. 2,2-Di(1H-3-indolyl)ethanol 11 which has been acetylated[4] to streptindole has also been obtained by acid catalyzed (TFA) condensation of indole and 1,3-oxazine 10 formed smoothly by sodium borohydride reduction of 7 (Scheme I).



Scheme I

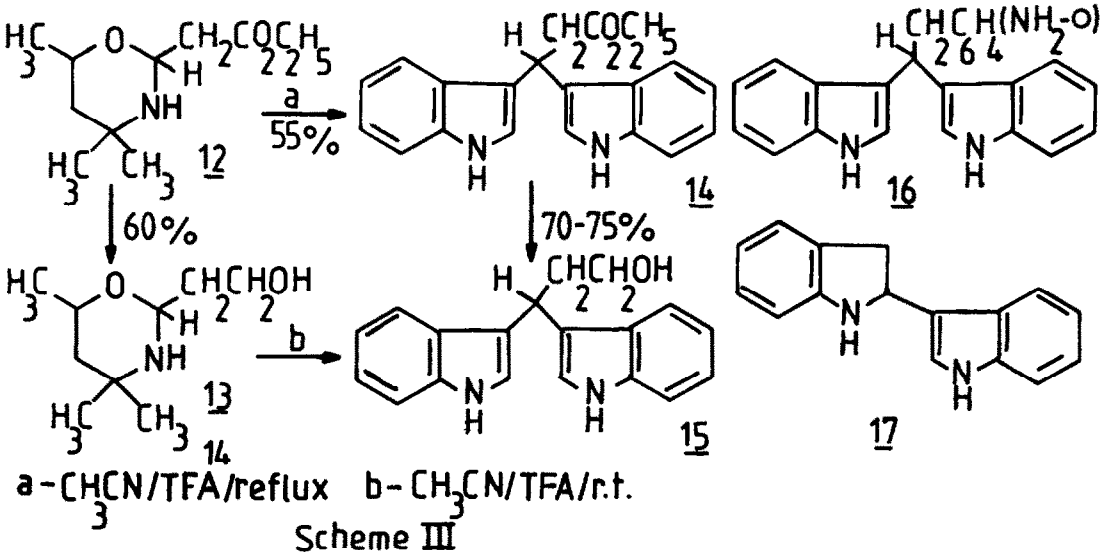


Scheme II

In comparison with the low yield (2%) synthesis[3] of streptindole from acetoxyacetaldehyde and indole which does not leave much scope for improvement and structural diversification and a four step approach[4] involving survival of labile indole moiety in all chemical transformations, the present approach is versatile enough for procuring a variety of its analogues through transformations on alpha carbon of C-2 substituent of 5,6-dihydro-(4H)-1,3-oxazines.

These reactions can be visualized through acid induced ring opening of oxazolidines/perhydro-1,3-oxazines followed by reaction with indole to form the adduct a which by loss of amino alcohol could generate an alkylidine indolinium cation b (Scheme II). The latter undergoes nucleophilic attack by second indole molecule to furnish diindolylmethane derivatives.

2-Carbethoxymethyl-1,3-oxazine 12 and indole furnish 2,2-di(1H-3-indolyl) ethylpropionate 14 which on lithium aluminium hydride reduction gives 3,3-di(1H-3-indolyl)propanol 15. 2-(β-Hydroxyethyl)-1,3-oxazine 13 formed by $LiAlH_4$ reduction of 12 upon reaction with indole gives 15 (Scheme III) as a minor component (15-20%) alongwith a major product m.p. 169°C[13]. FAB MS of the latter shows parent ion peak at 350 $(M-H)^+$ which could arise from a compound containing three indole units (3x117 = 351). A prominent peak at 245 constituting the highest mass ion in EIMS at 15/70 eV might be formed by the loss of $C_7H_{11}N$ (o-aminobenzyl) fragment. The ^1H nmr spectrum shows 21H comprising of D_2O exchangeable 4H, $-CH_2-CH<$ (δ 3.4(2H, d, J = 6.5Hz), 4.85(1H, t, J = 6.5Hz)) and aromatic 14H. The ^{13}C APT nmr reveals the presence of 9-CH = and 5 quaternary C in aromatic/olefinic region, a-CH_2- and a-CH-, corroborated by appearance of



Scheme III

only 11C signals in ^{13}C DEPT experiment. These data suggest the presence of two equivalent indole molecules joined through their C_3 to $>CH-CH_2-C_6H_4(NH_2-o)$ and the structure 1,1-di (1H-3-indolyl)-2-(2-aminophenyl)ethane 16.[13,15] For the formation of 16 from indole, the role of water emphasised earlier[17] is not apparent because in absolutely anhydrous acetonitrile containing P_2O_5 and TFA, indole gives 16 in 70% yield with ~10% recovery of indole. TLC monitoring of the progress of the reaction indicates initial formation of indole dimer 17 which could react with indole to give 16[16]. It is corroborated by the lack of formation of an analog of 16 from 2-methyl indole which does not form the dimer.

EXPERIMENTAL

All melting points are uncorrected. Infra-red spectra were recorded on PYE UNICAM SP3-300 instrument. ^{1}H and ^{13}C NMR spectra were run on JNM-PMX 60MHz and Bruker WM 250 MHz instruments using TMS as an internal standard. Mass spectra were recorded on a Jeol JMS-D 300 and Micromass 7070F spectrometers. TLC was performed on microplates, coated with silica gel G and spots were developed in iodine chamber. Acetonitrile was dried over P_2O_5.

Oxazolidines 3 and 1,3-oxazines 4

3-Phenyloxazolidine 3a[18], 2-phenyl-4,4-dimethyloxazolidine 3b[19], 2-phenyl-3,4,4-trimethyloxazolidine 3c[20], 2-methyl-3-phenyloxazolidine 3d[21], tetrahydro-(2H)-1,3-oxazine 4a[22], 2-phenyltetrahydro-(2H)-1,3-oxazine 4b[23], 2-phenyl-4,4,6-trimethyltetrahydro-(2H)-1,3-oxazine 4c[12], 2,4,4,6-tetramethyltetrahydro-(2H)-1,3-oxazine 4d[12] and 2-carbethoxymethyl-4,4,6-trimethyltetrahydro-(2H)-1,3-oxazine 12[12] were procured by methods reported in literature.

2-Hydroxymethyl-4,4,6-trimethyl-5,6-dihydro-(4H)-1,3-Oxazine 7

Freshly prepared glycolonitrile[24] (12g, 0.21 mol) was condensed with 2-methyl-2,4-pentanediol (22.58g, 0.19 mol) in concentrated sulphuric acid at -5° to $-10^{\circ}C$ in accordance with Meyers' procedure[12] to get 7(30.84g, 66%, b.p. $85-90^{\circ}/22mm$); IR(Neat): 3463, 3100, 1675 cm^{-1}. ^{1}H NMR ($CDCl_3$) : δ 1.1(6H, $2xCH_3$,s), 1.27(3H,CH_3, d, J = 6Hz), 1.6(2H, $-CH_2-$, d, J = 6Hz), 3.70(2H, $\underline{CH_2}$-OH, s), 3.8 (1H, OH, br, D_2O exchangeable), 4.0-4.21(1H, >CH-, m); Mass: $M^{+\cdot}$ m/z 157.

2-Acetoxymethyl-4,4,6-trimethyl-5,6-dihydro-(4H)-1,3-oxazine 8

Acetic anhydride (0.09 mol, 9 ml) was added dropwise to 7(10g, 0.06 mol) with stirring at $0^{\circ}C$. After the completion of reaction (10-15 h) excess of the reagent was removed under reduced pressure and residue was distilled to get 8(11.20g, 88%, b.p. $110^{\circ}/40$ mm); IR(Neat): 1737, 1657 cm^{-1}; ^{1}H NMR($CDCl_3$): δ 1.15 (6H, $2xCH_3$,s), 1.25(3H, CH_3, d, J = 6Hz), 1.65(2H, CH_2, d, J = 6Hz), 2.05 (3H, CH_3COO,s), 4.1-4.31(1H, >CH-, m), 4.4(2H, $\underline{CH_2}OAc$, s); Mass: $M^{+\cdot}$ m/z 199.

2-Hydroxymethyl/acetoxymethyl-4,4,6-trimethyltetrahydro-(2H)-1,3-oxazine 10/9

Sodium borohydride reduction of 1,3-oxazines 7/8 was performed using Meyers' procedure[12] to obtain 10/9. Compound 10(77%, b.p. $98-100^{\circ}/22$ mm); IR($CHCl_3$): 3450, 3100 cm^{-1}; ^{1}H NMR($CDCl_3$): δ 1.0(6H, $2xCH_3$, s), 1.28(3H, CH_3, d, J = 6Hz), 1.45(2H, CH_2, d, J = 6Hz), 3.30(2H, NH, OH, br, D_2O exchangeable), 3.45-3.55(2H, CH_2OH, m), 3.7-3.95(1H, >CH-, m), 4.25(1H, CH, t, J = 4Hz); Mass: $M^{+\cdot}$ m/z 159. Compound 9(69%, b.p. $100-10^{\circ}/22$ mm); IR($CHCl_3$): 3400, 2950, 1740 cm^{-1}; ^{1}H NMR($CDCl_3$): δ 1.1(6H, $2xCH_3$, s), 1.2(3H, CH_3, d, J = 6Hz), 1.28(2H, CH_2, d, J = 6Hz), 2.0(3H, CH_3CO, s), 2.2(1H, NH, br, D_2O exchangeable), 3.4-3.8(1H, >CH-,m), 4.0(2H, CH_2, d, J = 4Hz), 4.4(1H, CH, t, J = 4Hz); Mass: $M^{+\cdot}$ m/z 201.

2-(β-Hydroxyethyl)-4,4,6-trimethyltetrahydro-(2H)-1,3-oxazine 13

To a stirred suspension of $LiAlH_4$ (0.3 mol, 11.4 g) in anhydrous tetrahydrofuran (100 ml, dried over $LiAlH_4$) was added dropwise a solution of 1,3-oxazine 12(0.1 mol, 21.5 g) in THF (50 ml) under a stream of dry nitrogen. The reaction mixture was stirred at ambient temperature for 22 hours and cold saturated aqueous sodium potassium tartarate was introduced. Organic layer was separated and the aqueous portion extracted with chloroform. Combined organic phases were washed with water and dried (anhydrous Na_2SO_4). Removal of solvent furnished 13 as a yellow oil (60%, 10.4g), which was pure enough for further use. IR (Neat): 3400, 2900 cm^{-1}, ^{1}H NMR($CDCl_3$): δ 1.1(6H, $2xCH_3$, s), 1.2(3H, CH_3, s)

1.6(2H, CH_2, d, J = 6Hz), 2.6(2H, $>\underline{CH_2}-CH_2OH$, q, J = 6Hz), 3.6(2H, $\underline{CH_2}-OH$, t, J= 6Hz), 3.7-4.0(2H, NH, OH, br, D_2O exchangeable), 4.1(1H, CH, t, merged with broad signal), 4.2-4.32(1H, CH, m); Mass: $M^{+\cdot}$ m/z 173.

Reduction of 14 to 15

To a stirred suspension of $LiAlH_4$(.004 mol, 0.15 g) in THF (20-25 ml), 14(.001 mol, 0.33 g) in THF (5 ml) was introduced at 0°C, under a stream of dry nitrogen followed by stirring at ambient temperature for 15-20 hrs. 3,3-Di(1H, 3-indolyl) propanol 15 was isolated as in the case of 13 as a thick liquid, IR($CHCl_3$): 3100, 1600 cm^{-1}. ^1H NMR($CDCl_3$): δ 1.60(1H, OH, br, D_2O exchangeable), 2.42(2H, CH_2, t, J = 7Hz), 3.65(2H, CH_2, t, J = 7Hz), 4.59(1H, CH, t, J = 7Hz), 6.65-7.60(10H, ArH and C_2/C_2' H, m), 7.75(2H, NH, br, D_2O exchangeable); Mass: $M^{+\cdot}$ m/z 290.

Reactions of oxazolidines 3 and 1,3-oxazines 4 with indoles

General Procedure :

A solution of indole (0.02 mol) and 3/4 (0.01 mol) in dry acetonitrile (25-30 ml) containing an acid (2-3 ml) (Table) was stirred at ambient temperature/ refluxed till the reaction was completed (tlc). The solvent was distilled off and residue chromatographed over silica gel using hexane, benzene, or benzene-ethylacetate mixtures as eluents to get following diindolylmethane derivatives.

Di(1H-3-indolyl)methane (5a) : m.p. 164° (Lit. 164°)[5]; IR(KBr): 3400, 1620 cm^{-1}; ^1H NMR($CDCl_3$): δ 4.17(2H, CH_2, s), 6.8-7.6(10H, ArH and C_2/C_2' H, m), 7.65(2H, NH, br, D_2O exchangeable).

1,1-Di(1H-3-indolyl)phenylmethane(5b): m.p. 125° (Lit. 125°)[5]; IR(KBr): 3100, 1390 cm^{-1}; ^1H NMR($CDCl_3$): δ 5.92(1H, >CH-, s), 6.57(2H, C_2/C_2' H, s), 6.8-7.82 (13H, ArH and C_2/C_2' H, m), 7.83(2H, NH, br, D_2O exchangeable); Mass: $M^{+\cdot}$ m/z 322.

1,1-Di(1H-3-indolyl)ethane (5c): m.p. 155°(Lit. 156°)[5]; IR(KBr): 3400, 3100 cm^{-1}; ^1H NMR($CDCl_3$): δ 1.55(3H, CH_3, d, J = 6Hz), 4.55(1H, CH, q, J = 6Hz), 6.7-7.40 (10H, ArH and C_2/C_2' H, m), 7.55(2H, NH, br, D_2O exchangeable).

Di(1-methyl-3-indolyl)methane (5d): m.p. 110° (Lit. 108-10°)[25]; IR(KBr) : 3100, 1600 cm^{-1}; ^1H NMR($CDCl_3$): δ 3.30(6H, 2x CH_3, s), 4.15(2H, CH_2, s), 6.55(2H, C_2/C_2' H, s), 7.1-7.54(8H, ArH, m).

1,1-Di(1'-methyl-3-indolyl)ethane (5c): colourless glass[26]; IR($CHCl_3$): 3100, 2900 cm^{-1}; ^1H NMR($CDCl_3$): δ 1.7(3H, CH_3, d, J = 6Hz), 3.4(6H, 2 x N-CH_3, s), 4.5(1H, CH, q, J = 6Hz), 6.2-7.3(10H, ArH and C_2/C_2' H, m).

1,1-Di(1-methyl-3-indolyl)phenylmethane (5f): m.p. 202°(Lit. 202°)[27]; IR(KBr): 3100, 2900 cm^{-1}; ^1H NMR($CDCl_3$): δ 3.55(6H, 2xNCH_3, s), 5.65(1H, CH, s), 6.3-7.35 (15H, ArH and C_2/C_2' H, m).

2,2-Di(1H-3-indolyl)ethylacetate (2)[28]: IR($CHCl_3$): 3400, 1720 cm^{-1}; ^1H NMR($CDCl_3$): δ1.93(3H, $\underline{CH_3}$, s), 4.72(2H, CH_2, d, J = 4Hz), 4.93(1H, CH, t, J = 4Hz). 6.85 (2H, C_2/C_2' H, s), 6.9-7.3(8H, ArH, m), 7.85(2H, NH, br, D_2O exchangeable); Mass: $M^{+\cdot}$ m/z 318.

2,2'-Di(1H-3-indolyl)ethanol (11)[28]: m.p. 54° (Lit.50°)[4]; IR($CHCl_3$): 3100, 1390 cm^{-1}; ^1H NMR($CDCl_3$): δ 2.6(1H, OH, br, D_2O exchangeable), 3.05(2H, $\underline{CH_2}OH$, d, J = 8Hz), 4.5(1H, CH, t, J = 8Hz), 6.1-7.25(10H, ArH and C_2/C_2' H, m), 7.40 (2H, NH, br, D_2O exchangeable).

2,2-Di(1H-3-indolyl)ethylpropionate (14): m.p. 80°; IR(KBr): 3250, 1720, 1600 cm^{-1}; ^1H NMR($CDCl_3$): δ 1.05(3H, CH_3, t, J = 6Hz), 3.07(2H, CH_2, d, J = 6Hz), 3.90(2H,

CH_2, q, J = 6Hz), 5.0(1H, CH, t, J = 6Hz), 6.7-7.6(10H, ArH and C_2/C_2' H, m), 7.71(2H, NH, br, D_2O exchangeable); Mass $M^{+\bullet}$ m/z 332.

1,1-Di(1H-indolyl)-2(2-aminophenyl)ethane (16): m.p. 169°(Lit. 169°)[13]; IR(KBr): 3400, 3375(ν_{sym}, ν_{asym} NH_2), 1620, 1610 cm^{-1}; ^1H NMR($CDCl_3$): δ 3.15(2H, NH_2, br, D_2O exchangeable), 3.4(2H, CH_2, d, J = 6.5Hz), 4.85(1H, CH, t, J = 6.5Hz), 6.51(1H, ArH, d, J = 6.5Hz), 6.63(1H, ArH, t, J = 6.5Hz), 6.83(2H, ArH, s), 6.9-7.05(4H, ArH, m), 7.13(2H, ArH, t, J = 6.5Hz), 7.15-7.35(2H, ArH, m), 7.45(2H, ArH, d, J = 6.5Hz), 7.8(2H, NH, br, D_2O exchangeable). DEPT ^{13}C NMR ($CDCl_3$): δ 34.28(2.51, CH), 37.06(-1.73, CH_2), 111.07(5.75), 115.69(3.09), 118.74(2.47), 119.02(5.79), 119.50(6.22), 121.70(5.44), 121.87(4.46), 126.79 (2.47), 130.23(3.20); APT ^{13}C NMR($CDCl_3$): δ 34.29(5.27, CH), 37.07(-4.64, CH_2), 111.06(10.43), 115.69(5.57), 118.72(6.11), 119.02(12.58), 119.40(-5.83, quat.C), 119.50(10.72), 121.70(10.08), 121.86(5.89), 125.96(-5.10, quat.C), 126.78(5.11), 126.80(-1.91), 130.23(7.14), 136.45(-6.20, quat.C), 144.56(-4.35, quat.C); FAB MS : 351$(M-H)^+$.

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