INTERNATIONAL JOURNAL OF APPLIED BIOLOGY AND PHARMACEUTICAL TECHNOLOGY

Volume: 2: Issue-4: Oct - Dec -2011 IJABPT *ISSN 0976-4550*

MICROWAVE ASSISTED SYNTHESIS AND SPECTRAL STUDIES OF 2-THIOPHEN-2-YLMETHYLENE-2,3,4,9-TETRAHYDRO-CARBAZOL-1-ONE, 3-THIOPHEN-2-YL-4,5-DIHYDRO-10*H*-2-OXA-1,10-DIAZA-CYCLOPENTA[*a*]CARBAZOLE AND 3-THIOPHEN-2-YL-2,4,5,10-TETRAHYDRO-1,2,10-TRIAZA-CYCLOPENTA[*a*]CARBAZOLE DERIVATIVES

R. Velmurugan[a], G. Vadivelan[a], R. Rajamani[b], A.V. Vijayasankar[c] and M. Sekar[a*]

[a]Post Graduate and Research Department of Chemistry, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore- 641 020, India

[b]Post Graduate and Research Department of Chemistry, Tamilavel Umamaheswaranar Karanthai Arts College, Thanjavur- 613 002, India

[c]Department of Engineering Chemistry, Christ University, Bangalore-560 029, Karnataka, India

ABSTRACT: Microwave assisted new aldol condensation reaction of 1-oxo-1,2,3,4-tetrahydrocarbazoles **1** with thiophene-2-carbaldehyde **2** in the presence of alcoholic KOH affords a single product 2-Thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one **3**. **3** on irradiation with hydroxylamine hydrochloride yielded 3-Thiophen-2-yl-4,5-dihydro-10*H*-2-oxa-1,10-diaza-cyclopenta[*a*]carbazole **4** and **3** on irradiation with hydrazine hydrate in ethanol medium to yielded 3-Thiophen-2-yl-2,4,5,10-tetrahydro-1,2,10-triaza-cyclopenta[*a*]carbazole **5**. The structures of the synthesized compounds were confirmed on the basis of physical and spectral analysis (FT-IR, ^{1}H, ^{13}C-NMR) and Mass spectral data.

Key words: Tetrahydrocarbazole; microwave irradiation; spectral analysis.

INTRODUCTION

Microwave-assisted organic synthesis (MAOS) in controlled conditions is an invaluable technique for medicinal chemistry and drug discovery applications. Indeed, in recent developments, the use of microwave irradiation to simplify and improve classic organic reactions has become a very popular method, because it often leads to higher yields, cleaner reactions, and shorter reaction times. In connection with the multi-step synthesis of some anticancer compounds of our interest, we adopted Fischer indole synthesis as the most suitable for obtaining key carbazole intermediate for novel planned substituted pyrido carbazoles. Apart from that, it is also one of the most important processes in heterocycle chemistry, leading to a large variety of hetero-polycycle biological active compounds containing the indole nucleus and in some cases is the only method reaching target structures. Simply, starting from an arylhydrazine, a cyclohexanone hydrazone compound can provide carbazole derivatives by a thermal cyclization reaction carried out in several different but mostly strong acidic conditions[1]. Successful results often depend on these specific conditions which, in turn, depend on the presence of certain groups on the starting hydrazine. In recent years, microwave indole synthesis has been useful in achieving rate acceleration and high yields in thermal cyclization with various ketones[2-4] More recently, one pot approaches to carbazoles or indoles under controlled microwave irradiation were reported in which efficient procedures for performing difficult Fischer syntheses in the presence of catalysts or NCW (near-critical region of water) have been established[5-7].

Carbazole and other annelated indole derivatives form the basic structure of many valuable and highly potent drugs like camptothecine and its derivatives topotecane and irinotecane used as inhibitors of the enzyme topoisomerase I against different types of cancer, or like vincamine used in the therapy of Alzheimer disease. Many synthetic procedures in this area start with the cycloaddition of appropriate dienes to substituted 2- or 3-vinylindoles.

* Corresponding author. Tel.: +91-422-2692461, Fax: +91-422-2693812; E-mail:mmsekar7@gmail.com.

We have described reactions of maleimides and related systems with cyclopentadiene and with 1-(1-siloxyvinyl) naphthalene and the synthesis of pyrrolo[3,4-*a*]carbazole derivatives by cycloadditions between maleimides and 3-(1-methoxyvinyl)indole derivatives[8]. Alkaloid ellipticine which was isolated from leaves of the plant *Ochrosia elliptica* Labill (the Apocynaceae family) and some of its synthetic analogs exhibit high antitumor activity[9].

Fused carbazoles, for example, the antidepressants pyrazidole and tetrindole, belonging to the pyrazino[3,2,1-*j*,*k*]carbazole series are among important pharmaceuticals that are widely used in medical practice[10]. The synthesis of substituted carbazoles and heterocyclo-[*b*]-fused indoles such as pyrido[2,3-*b*, 4,3-*b*, 3,4-*b*]-indoles has attracted considerable attention in recent years as this class of compounds constitute structural frameworks of several naturally occurring compounds displaying a wide range of biological activity. Many elegant approaches have been developed for the synthesis of benzo and heterocyclo-fused carbazoles, indoles and related natural products involving annulation of indoles. Our own interest in the synthesis of these compounds relies upon application of our aromatic and heteroaromatic annelation methodology involving novel (or known) a-oxoketene dithioacetals as three carbon synthons for developing efficient synthetic methods for a wide variety of aromatic and heterocyclic compounds of biological importance[11-15]. These compounds have been associated with good biological activities such as antiviral[16], antimalarial[17,18], antibacterial[19-21] and anticancer activities[22]. Hence, the aim of this work was to demonstrate the advantage obtained by the use of microwave irradiation in the one-pot synthesis of 2-Thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one, 3-Thiophen-2-yl-4,5-dihydro-10*H*-2-oxa-1,10-diaza-cyclopenta
[*a*]carbazole and 3-Thiophen-2-yl-2,4,5,10-tetrahydro-1,2,10-triaza-cyclopenta[*a*]carbazole.

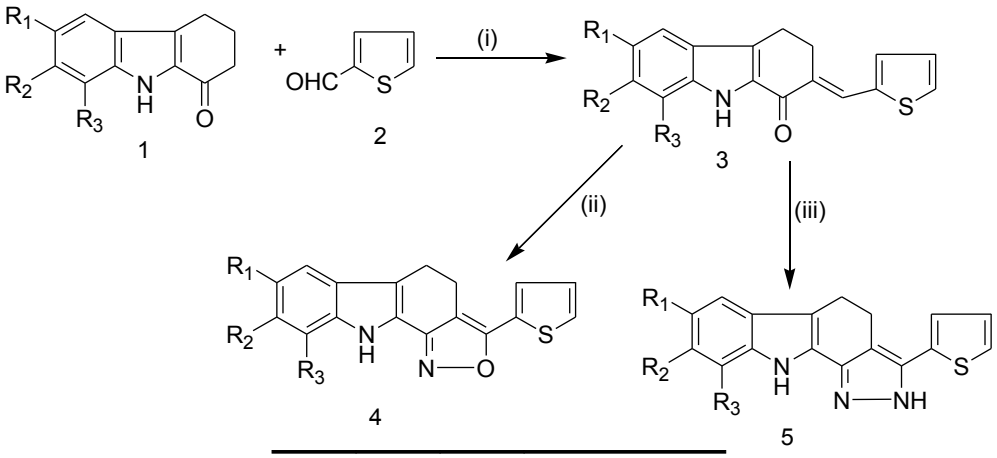
RESULTS AND DISCUSSION

2-Thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one (3a)

Mixed aldol condensation of 1-oxo-1,2,3,4-tetrahydrocarbazole (**1a**) with thiophene-2-aldehyde (**2**) under basic condition alcoholic KOH stirred well for 6 h. at room temperature gave a single product 2-Thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one (**3a**). The structure of the compound **3a** was established on the basis of elemental analysis and spectral data. The FT-IR spectrum of **3a** exhibited a sharp and strong absorption band at 1635 cm^{-1}, characteristic of an α,β-unsaturated carbonyl group and a band at 3434 cm^{-1}, ascribable to N-H asymmetric stretching vibration. The 3-H, 4-H protons appear as triplet centered at δ 3.30 and 3.14 ppm, respectively with J = 6.00, 5.66 Hz in the ^{1}H-NMR spectrum. A singlet peak appearing at δ 2.58 ppm is due to the benzylic proton and the carbazole NH appeared as a singlet at δ 11.77 ppm. The multiplet signal appearing in the range δ 7.09-7.85 ppm is attributed to the nine aromatic protons of carbazole nucleus. The appearance of seventeen distinct carbon signals in the ^{13}C-NMR spectrum of **3a** confirms it molecular structure. Two singlet peaks appearing at δ 20.20 and 27.65 ppm for two aliphatic CH_2 carbons respectively. A singlet peak at δ 179.17 ppm has been assigned to the carbonyl carbon. The remaining signals appearing in the aromatic region from δ 113.01 to 138.97 ppm owe to the aromatic carbons in the carbazole nucleus. Elemental analysis was compatible with the molecular formula $C_{17}H_{13}NOS$. The compounds **3b-e** were also synthesized and characterized in the same manner as **3a**.

3-Thiophen-2-yl-4,5-dihydro-10*H*-2-oxa-1,10-diaza-cyclopenta[*a*]carbazole (4a)

In another experiment the compound **3a** on microwave irradiation with hydroxylamine hydrochloride in dry pyridine yielded a single product **4a** which was purified by column chromatography. FT-IR spectrum of **4a** exhibited two absorption bands at 1631 and 3237 cm^{-1} owing to the C=N stretching and NH asymmetric stretching vibrations respectively. The ^{1}H-NMR spectrum in DMSO solution showed two multiplet peaks centered at δ 3.26, 3.06 ppm for C(4), C(5) protons respectively. The seven aromatic protons collectively stand responsible for the multiplet signal appearing in the range δ 6.98-7.93 ppm. A broad singlet appearing at 10.58 ppm is due to NH proton. The elemental analysis agreed well with the proposed molecular formula $C_{17}H_{12}N_2OS$. Based on the spectral data, the product was established as 3-Thiophen-2-yl-4,5-dihydro-10*H*-2-oxa-1,10-diaza-cyclopenta[*a*]carbazole **4a**. In a similar manner, the reaction was carried out for **3b-e** which yielded the corresponding *3*-Thiophen-2-yl-4,5-dihydro-10*H*-2-oxa-1,10-diaza-cyclopenta[*a*]carbazole derivatives **4b-4f** respectively (*Scheme 1*).



R_1	R_2	R_3	compounds
H	H	H	**1,3,4,5a**
CH_3	H	H	**1,3,4,5b**
H	H	CH_3	**1,3,4,5c**
Cl	H	H	**1,3,4,5d**
Br	H	H	**1,3,4,5e**

Scheme 1. Reagents and conditions i) alc. KOH, Stirring, ii) $NH_2OH.HCl$/Pyridine, iii) $NH_2NH_2.H_2O$/Ethanol

3-Thiophen-2-yl-2,4,5,10-tetrahydro-1,2,10-triaza-cyclopenta[*a*]carbazole (5a)

When the 2-Thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one (**3a**) and hydrazine hydrate in ethanol were irradiated in a microwave oven for 5 min. yielded the compound **5a**. The formation of the compound **5a** was confirmed by the absence of carbonyl absorption at around 1633 cm^{-1} with simultaneous appearance of a strong band at 1599 cm^{-1} for C=N in its FT-IR spectrum. The asymmetric NH stretching appears as a sharp band at 3236 cm^{-1}. The ^{1}H-NMR spectrum of the compound **5a** in DMSO solution showed two triplets centered at δ 3.07, and 3.17 ppm which are assigned to C(4), C(5) protons respectively. A singlet at δ 7.98 ppm is accountable for the pyrazolino NH proton. The ten aromatic protons resonate between δ 7.05 and 7.90 ppm and appear as a multiplet. The carbazole NH proton appeared as a broad singlet at δ 8.98 ppm. The mass spectrum of the compound has the molecular ion peak at m/z 294. Further the elemental analysis agreed well with the molecular formula $C_{17}H_{13}N_3S$. On the basis of the data given above, the product was established as 3-Thiophen-2-yl-2,4,5,10-tetrahydro-1,2,10-triaza-cyclopenta[*a*]carbazole **5a**. In the same manner, the reaction were carried out for **3b-e** to get the corresponding 3-Thiophen-2-yl-2,4,5,10-tetrahydro-1,2,10-triaza-cyclopenta[*a*]carbazole derivatives **5b-e** respectively (*Scheme 1*).

All the new compounds gave satisfactory FT-IR, ^{1}H-, ^{13}C - NMR, mass spectral and elemental analysis.

EXPERIMENTAL

3.1. Preparation of 2-Thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one 3a-e

The aldol condensation reaction of 1-oxo-1,2,3,4-tetrahydrocarbazoles (**1a-e**) reacted with thiophene-2-carbaldehyde (**2**) in the presence of alcoholic KOH afforded a single product, substituted 2-Thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one (**3a-e**). This was subjected to column chromatography over silica gel (mesh 60-80). During elution of the column with petroleum ether (60-80℃) and ethyl acetate [1:2] mixture, a yellowish solid was obtained. Finally it was recrystallised from the solvent mixture ethyl acetate and acetone (8:2).

2-Thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one (3a)

M.p: 231-235℃, Yield: 0.8 g, FT-IR (KBr): 3434, 1716, 1635, 1567, 1543, 1474, 1388, 1337, 735, 706, 577. ^{1}H-NMR (DMSO): 3.30 (2H, t, *J* 6.00 Hz, 3-H), 3.14 (2H, t, *J* 5.66 Hz, 4-H), 2.58 (1H, s,), 7.09-7.85 (7H, m, 5-H, 6-H, 7-H, 8-H, 3'-H, 4'-H and 5'-H)), 11.77 (1H, br s, N-H) ppm. (Found: C, 72.86; H, 5.05; N, 4.96%. Calc. for $C_{17}H_{13}NOS$ (280.29); C, 72.84; H, 5.01; N, 4.99%).

6-Methyl-2-thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one (3b)

M.p: 205-210℃, Yield: 0.6g, FT-IR (KBr): 3241, 2911, 2859, 1631, 1567, 1441, 1385, 1049, 820, 756, 711, 659. ^{1}H-NMR (DMSO): 2.45 (3H, s, 6-H), 3.09 (2H, t, *J* 6.50 Hz, 3-H), 3.26 (2H, t, *J* 5.00 Hz, 4-H), 2.41 (1H, *s*,), 7.15-7.84 (6H, m, 5-H, 7-H, 8-H, 3'-H, 4'-H and 5'-H), 11.64 (1H, br *s*, N-H) ppm. (Found: C, 73.38; H, 5.44; N, 4.73 %. Calc. for $C_{18}H_{15}NOS$ (294.45); C, 73.42; H, 5.49; N, 4.76%).

8-Methyl-2-thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one (3c)

M.p: 225-230℃, Yield: 0.7g, FT-IR (KBr): 3220, 2912, 2855, 1637, 1567, 1542, 1479, 1442, 1416, 1342, 1261, 1227, 1177, 1146, 1050, 912, 704. ^{1}H-NMR (DMSO): 2.64 (3H, s, 8-H), 3.10(2H, t, *J* 6.00 Hz, 3-H), 3.25(2H, t, *J* 5.00 Hz, 4-H), 2.41(1H, s,), 6.93-7.83(6H, m, 5-H, 6-H, 7-H, 3'-H, 4'-H and 5'-H), 11.62(1H, br s, N-H) ppm. (Found: C, 73.38; H, 5.46; N, 4.74%. Calc. for $C_{18}H_{15}NO_2$ (294.45): C, 73.42; H, 5.49; N, 4.76%).

6-Chloro-2-thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one (3d)

M.p: 240-245°C, Yield: 0.6g, FT-IR (KBr): 3229, 2923, 1630, 1563, 1485, 1443, 1383, 1314, 1050, 706. ^{1}H-NMR (DMSO): 3.26(2H, t, *J* 4.50 Hz, 3-H), 3.11(2H, t, *J* 6.00 Hz, 4-H), 2.41(1H, s,), 7.22-7.86(6H, m, 5-H, 7-H, 8-H, 3'-H, 4'-H and 5'-H), 11.97(1H, br s, N-H) ppm. (Found: C, 64.97; H, 3.94; N, 4.42%. Calc. for $C_{17}H_{12}NOSCl$ (314.15): C, 64.99; H, 3.96; N, 4.45%).

6-Bromo-2-thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one (3e)

M.p: 250-255°C, Yield: 0.7g, FT-IR (KBr): 3231, 1630, 1563, 1499, 1442, 1383, 1039, 705, 577. ^{1}H-NMR (DMSO): 3.28 (2H, t, *J* 5.00 Hz, 3-H); 3.12(2H, t, *J* 3.00 Hz, 4-H), 2.42(1H, s,), 7.23-7.95 (6H, m, 5-H, 7-H, 8-H, 3'-H, 4'-H and 5'-H), 11.98(1H, br s, N-H) ppm. (Found: C, 56.92; H, 3.44; N, 3.89%. Calc. for $C_{17}H_{12}NOSBr$ (358.61): C, 56.94; H, 3.47; N, 3.91%).

Preparation of 3-Thiophen-2-yl-4,5-dihydro-10*H*-2-oxa-1,10-diaza-cyclopenta[*a*] carbazoles (4a-e)

2-Thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one (**3,** 1mmol) was mixed with hydroxylamine hydrochloride (1g,14mmol) and pyridine (5 ml). The reaction mixture was irradiated in a microwave oven for 5 min. After the reaction was completed, the mixture was poured into the crushed ice. The resulting solid separated was filtered off, washed with dilute HCl and finally with water. The substance was dried and purified over CC with 1:5 petroleum-ether: ethyl acetate solvent mixture, to obtain **4**.

3-Thiophen-2-yl-4,5-dihydro-10*H*-2-oxa-1,10-diaza-cyclopenta[*a*]carbazole (4a)

M.p: 105-107℃, Yield: 0.6g, FT-IR (KBr): 3237, 2962, 2923, 1631, 1566, 1544, 1476, 1413, 1328, 1261, 1094, 860, 704. ^{1}H-NMR (DMSO) δ : 3.06(2H, t, *J* 6.50 Hz, 4-H), 3.26(2H, t, *J* 6.00 Hz, 5-H), 6.98-7.93(7H, m, 6-H, 7-H, 8-H, 9-H, 3'-H, 4'-H and 5'-H), 10.58 (1H, br s, N-H) ppm. (Found: C, 69.78; H, 4.27; N, 9.59%. Calc. for $C_{17}H_{12}N_2OS$ (292.71): C, 69.75; H, 4.25; N, 9.57%).

7-Methyl-3-thiophen-2-yl-4,5-dihydro-10*H*-2-oxa-1,10-diaza-cyclopenta[*a*] carbazole (4b)

M.p: 68-70°C, Yield: 0.6g, FT-IR (KBr): 3451, 3185, 2917, 2850, 1631, 1589, 1536, 1433, 1353, 1317, 1291, 1260, 1020. ^{1}H-NMR (DMSO) δ: 2.43 (3H, s, 7-H), 2.90(2H, t, *J* 6.00 Hz, 4-H), 3.15(2H, t, 5-H), 7.01-7.40(6H, m, 6-H, 8-H, 9-H, 9-H, 3'-H, 4'-H, 5'-H), 9.71(1H, br s, NH) ppm. (Found: C, 70.34; H, 4.94; N, 9.12%. Calc. for $C_{18}H_{14}N_2OS$ (307.38): C, 70.33; H, 4.91; N, 9.11%).

9-Methyl-3-thiophen-2-yl-4,5-dihydro-10*H*-2-oxa-1,10-diaza-cyclopenta[*a*] carbazole (4c)

M.p: 75-78°C, Yield: 0.7g, FT-IR (KBr): 3448, 3186, 2917, 2849, 1622, 1534, 1371, 1338, 1264, 1245, 1163, 1139, 954, 798. ^{1}H-NMR (DMSO) δ : 2.08 (3H, s, 9-H), 2.96(2H, t, *J* 6.00 Hz, 4-H), 3.24(2H, t, *J* 6.50 Hz, 5-H), 6.80-7.48(6H, m, 6-H, 7-H, 8-H, 3'-H, 4'-H and 5'-H), 9.93(1H, br s, NH) ppm. (Found: C, 70.34; H, 4.95; N, 9.13%. Calc. for $C_{18}H_{14}N_2OS$ (307.38): C, 70.33; H, 4.91; N, 9.11%).

7-Chloro-3-thiophen-2-yl-4,5-dihydro-10*H*-2-oxa-1,10-diaza-cyclopenta[*a*] carbazole (4d)

M.p.: 90-93°C, Yield: 0.8g, FT-IR (KBr): 3447, 3193, 2912, 2842, 1630, 1465, 1443, 1371, 1315, 1238, 1204, 983, 865, 746. ^{1}H-NMR (DMSO): 2.90(2H, t, *J* 6.00 Hz, 4-H), 3.15(2H, t, *J* 6.00 Hz, 5-H), 6.96-7.55(6H, m, 6-H, 8-H, 9-H, 3'-H, 4'-H and 5'-H), 9.86(1H, br s, NH) ppm. (Found: C, 62.35; H, 3.65; N, 8.57%. Calc. for $C_{17}H_{11}N_2OSCl$ (327.59): C, 62.33; H, 3.62; N, 8.55%).

7-Bromo-3-thiophen-2-yl-4,5-dihydro-10*H*-2-oxa-1,10-diaza-cyclopenta[*a*] carbazole (4e)

M.p.: 75-80°C, Yield: 0.8g, FT-IR (KBr): 3445, 3204, 2921, 2843, 1726, 1629, 1461, 1441, 1370, 1272, 1203, 1044, 981, 956, 856, 737. ^{1}H-NMR (DMSO): 2.86(2H, t, *J* 4.50 Hz, 4-H), 3.11(2H, t, *J* 6.00 Hz, 5-H), 7.01-7.69(6H, m, 6-H, 8-H, 9-H, 3'-H, 4'-H and 5'-H), 10.35 (1H, br s, NH) ppm. (Found: C, 54.90; H, 3.21; N, 7.54%. Calc. for $C_{17}H_{11}N_2OSBr$ (372.04): C, 54.88; H, 3.19; N, 7.52%).

Preparation of 3-Thiophen-2-yl-2,4,5,10-tetrahydro-1,2,10-triaza-cyclopenta[*a*]carbazoles (5a-e)

Respective 2-Thiophen-2-ylmethylene-2,3,4,9-tetrahydro-carbazol-1-one (**3**, 1 mmol) was dissolved in absolute ethanol (20 ml) and hydrazine hydrate (0.5 ml, 10 mmol) was added and this mixture was irradiated in a microwave oven for 5 min. Then the solvent was removed under reduced pressure. The crude reaction mixture was poured into ice cold water and the solid obtained was filtered off, washed with water, dried and purified over column chromatography with 1:2 petroleum ether: ethyl acetate mixture to get **5.**

3-Thiophen-2-yl-2,4,5,10-tetrahydro-1,2,10-triaza-cyclopenta[*a*]carbazole (5a)

M.p: 205-210°C, Yield: 0.7g, FT-IR (KBr): 3435, 3236, 2921, 1599, 1566, 1546, 1388, 1365, 1175, 1134, 759, 706. ^{1}H-NMR (DMSO): 3.07(2H, t, *J* 6.50 Hz, 4-H), 3.17(2H, t, *J* 5.50 Hz, 5-H), 7.05-7.90(7H, m, 6-H, 7-H, 8-H, 9-H, 3'-H, 4'-H and 5'-H), 7.98(1H, s, 2NH), 8.98(1H, br *s*, N-H) ppm. (Found: C, 69.32; H, 5.47; N, 14.24%. Calc. for $C_{17}H_{13}N_3S$ (294.46): C, 69.34; H, 5.49; N, 14.27%).

7-Methyl-3-thiophen-2-yl-2,4,5,10-tetrahydro-1,2,10-triaza-cyclopenta[*a*]carbazole (5b)

M.p: 195-199°C, Yield: 0.6g, FT-IR (KBr): 3241, 1631, 1567, 1545, 1487, 1385, 1259, 1222, 1167, 947, 801, 711. ^{1}H NMR (DMSO) δ: 2.38 (3H, s, 7-H), 3.08(2H, t, *J* 6.00, 4-H), 3.26(2H, t, *J* 5.00 Hz, 5-H), 7.15-7.84(6H, m, 6-H, 8-H, 9-H, 3'-H, 4'-H and 5'-H), 7.90 (1H, s, 2NH), 11.64(1H, br s, NH) ppm. (Found: C, 70.10; H, 5.92; N, 13.60%. Calc. for. $C_{18}H_{17}N_3S$ (308.63): C, 70.05; H, 5.94; N, 13.61%.

9-Methyl-3-thiophen-2-yl-2,4,5,10-tetrahydro-1,2,10-triaza-cyclopenta[*a*]carbazole (5c)

M.p: 180-185°C, Yield: 0.8g, FT-IR (KBr): 3232, 2922, 1631, 1565, 1541, 1477, 1439, 1412, 1385, 1342, 1246, 1178, 1050, 970, 857, 821. ^{1}H NMR ($CDCl_3$): 2.71(3H, s, 9-H), 3.05 (2H, t, *J* 6.50 Hz, 4-H), 3.15(2H, t, *J* 5.00 Hz, 5-H), 6.87-7.57(6H, m, 6-H, 7-H, 8-H, 3'-H, 4'-H and 5'-H), 8.00(1H, s, 2NH), 9.35(1H, br s, NH) ppm. (Found: C, 70.09; H, 5.93; N, 13.62%. Calc. for $C_{18}H_{17}N_3S$ (308.63): C, 70.05; H, 5.94; N, 13.61%).

7-Chloro-3-thiophen-2-yl-2,4,5,10-tetrahydro-1,2,10-triaza-cyclopenta[*a*]carbazole (5d)

M.p: 222-225°C, Yield: 0.6g, FT-IR (KBr): 3228, 2922, 2851, 1630, 1563, 1542, 1484, 1467, 1441, 1415, 1383, 1314, 1259, 1241, 1174, 1134, 974, 916, 869, 804, 760. ^{1}H NMR (DMSO): 3.10(2H, t, *J* 6.00 Hz, 4-H), 3.38(2H, t, *J* 5.00 Hz, 5-H), 7.06-7.66(6H, m, 6-H, 8-H, 9-H, 3'-H, 4'-H and 5'-H), 8.01(1-H, s, 2NH), 9.23(1H, br s, NH) ppm. (Found: C, 62.07; H, 4.08; N, 12.76%. Calc. for $C_{17}H_{14}N_3SCl$ (328.84): C, 62.09; H, 4.05; N, 12.78%).

7-Bromo-3-thiophen-2-yl-2,4,5,10-tetrahydro-1,2,10-triaza-cyclopenta[*a*]carbazole (5e)

M.p: 204-208°C, Yield: 0.7g, FT-IR (KBr): 3447, 3230, 2923, 2852, 1628, 1562, 1541, 1483, 1463, 1440, 1416, 1382, 1258, 1221, 1137, 1038, 971, 804, 760, 704. ^{1}H NMR (DMSO) δ: 3.13(2H, t, *J* 6.50 Hz, 4-H), 3.38(2H, t, *J* 4.50 Hz, 5-H), 7.06-7.83(6H, m, 6-H, 8-H, 9-H, 3'-H, 4'-H and 5'-H), 8.00(1H, s, 2NH), 9.02(1H, br s, NH) ppm. (Found: C, 54.67; H, 4.09; N, 11.12%. Calc. for $C_{17}H_{14}N_3SBr$ (373.29): C, 54.69; H, 4.05; N, 11.11%).

Acknowledgments

One of the authors M.S thanks to the University Grants Commission (UGC), New Delhi, for the award of Major Research Project. F.No. 32-281/2006 (SR) 28.03.2007. The authors also thank Indian Institute of Science, Bangalore for providing NMR data.

REFERENCES

1. V. Barbieri and M.G. Ferlin, *Tetrahedron Lett.,* 2006, **47**, 8289-8292.
2. R. Abramovitch and A. Bullman, *Synlett.,* 1992, 795-796.
3. V. Sridar, *Curr. Sci*., 1998, **74**, 446-450.
4. V. Sridar, *Indian J. Chem.*, 1996, **35B**, 737-738.
5. A. Dhakshinamoorthy and K. Pitchumani, *Appl. Catal.*, 2005, **292**, 305-311.
6. J.M. Kremsner and C.O. Kappe, *Eur. J. Org. Chem.,* 2005, 3672-3679.
7. T.M. Lipinska and S. Czarmocki, *J. Org. Lett*., 2006, **8**, 367-370.
8. M. Bleile, H.H. Otto and J. Mona, *Fur. Chemie*., 2005, **136**, 1799-1868.
9. A.G. Mustafin, L.N. Khalilov, R.R. Ismagilov, Z.M. Baimetov, L.V. Spirikhin, L.B. Abdrakhmanov and G.A. Tolstikov, *J. Russian Chem. Bull*., 1999, **48**, 2121-2123.
10. S.Yu. Kukushkin, P.Yu. Ivanov, L.M. Alekseeva, V.I. Levina, K.I. Kobrakov, N.B. Grigorev and V.G. Granika, *J. Russian Chem. Bull.,* 2005, **54**, 1887-1891.
11. J.R. Suresh, U.K. Syam Kumar, H. Ilap and H. Junjappa, *Tetrahedron,* 2001, **57**, 781-790.
12. C.H. Collins and P.M. Lyne, "Microbial Methods, University Park Press", Baltimore. 1970.
13. S.C. Singh Jadon, N. Gupta and R.V. Singh, *Indian. J. Chem.,* 1995, **34A**, 733-736.
14. N. Dharmaraj, P. Viswanathamurthy and K. Natarajan, *Trans. Met. Chem.*, 2001, **26**, 105.
15. P.G. Lawrence, P.L. Harold and O.G. Francis, *J. Antibiot. Chemother.,* 1980, **5**, 1597-1600.
16. M. Sekar, S. Vanitha and K.J. Rajendra Prasad, *Z. Naturforsch,* 1994, **49**, 687-689.
17. D. Sowmithran and K.J. Rajendra Prasad, *Heterocycles,* 1986, **24**, 711-717.
18. D. Sowmithran and K.J. Rajendra Prasad, *Heterocycles*, 1986, **24**, 2195-2200.
19. D. Sowmithran and K.J. Rajendra Prasad, *Indian J. Chem.,* 1987, **26B**, 277-278.
20. D. Sowmithran and K.J. Rajendra Prasad, *Indian J. Chem.*, 1986, **25B**, 1179-1181.
21. M. Sekar and K.J. Rajendra Prasad, *Indian J. Chem*., 1994, **33B**, 479-481.
22. M. Sekar and K.J. Rajendra Prasad, *Indian J. Chem*., 1995, **34B**, 731-733.